

Leaching of copper and tin from used printed circuit boards after thermal treatment

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ABSTRACT

The hydrometallurgical route of copper and tin extraction from printed circuit boards (PCBs) of used personal computers after thermal pretreatment is discussed. The samples were thermally pretreated within temperature range of 300–900 °C during 15, 30 and 60 min. Two methods of the thermal pretreatment were studied: burning and pyrolysis. The leaching solution of 1 M HCl at 80 °C was used. The original as well as thermally pretreated samples were leached. The weight losses within the range from 5 to 35% were achieved. The increase of burning temperature causes the copper extraction into solution up to 98%, while copper extraction into solution from non-burned samples was up to 6%. In the case of the tin leaching the highest extraction was achieved when the original sample was leached. The increase of the burning temperature caused the lowering of the copper extraction. The increase of the pyrolysis temperature enhances copper and tin extraction.

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1. Introduction

The share of electric and electronic equipment (EEE) in the market is considerable and its amortization is relatively high, which results in its constant replacement. This replacement leads to the generation of a great amount of waste from electric and electronic equipment (WEEE). In the European Union approximately 8 million tonnes are generated every year with the annual increase of 3–5% [1]. In the whole world approximately 20–50 million tonnes of WEEE are generated [2]. This amount of waste is considerable not only for its quantity, but also because of dangerous substances such as heavy metals and plastics. On the other hand, this type of waste represents the source of valuable components, e.g. 0.1% Au, 0.2% Ag, 20% Cu and 4% Sn. For comparison, the gold content in primary materials is 2–5 g/t, which represents hundred times less than in EEE [3]. It follows that WEEE should not be regarded as waste but as a valuable secondary raw material.

WEEE is essentially a composite material consisting of a mixture of various metals, plastics, ceramics, etc.; therefore its processing is difficult. Most of the WEEE is processed by the pyrometallurgical method in aggregates for copper smelting. Plastics contained in WEEE pose a problem because of their large amount and potential generation of hazardous volatile substances. Nevertheless, the thermal processing is one of the most effective ways of metal recovery, and therefore new ways for improving this process are

sought. In this regard, WEEE can be either thermally processed in the presence of air, alternatively oxygen (i.e. burning), or in absence of oxygen (i.e. pyrolysis).

Combustion is a common pyrometallurgical process used to remove plastics and other organic materials with the aim of concentrating metals. Crushed PCBs are burned in a furnace and a solid residue with concentrated metals is generated. Plastics are burned out to create either volatile compounds or slag with refractory oxides. During this process only alloys are obtained [4].

Temperature is an important parameter of combustion. The combustion proceeds in the presence of oxygen, mainly from the air, so the temperature should be over 1200 °C. The major part of plastics present in WEEE contains halogens, and by this process the degradation of hazardous gaseous emissions is ensured.

Antrekowitsch et al. [5] in their review article compared different methods of WEEE treatment. From the pyrometallurgical point of view they discussed melting with its advantages and disadvantages, and they did not consider combustion being a pretreatment step.

Tohka and Lehto [4] compiled published works dealing with mechanical WEEE treatment with the subsequent thermal treatment step. This report, similarly is focused on high-temperature processes, while the formation of volatile combustion gases and the recovery of utilizable compounds as melting products are discussed. From the comparison of pyrolysis and combustion processes the authors incline to the opinion that the pyrolytic process should precede combustion and melting, because by means of this process the hazardous volatile compounds are removed from the system. They also mention examples of hybrid industrial processes.

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Also Antonetti et al. [6] discuss the high-temperature method of metal recovery from composite materials, which printed circuit boards are made of, using a fluidized furnace and oxygen as a carrier gas. They analyzed and identified several volatile compounds at specific temperature and air flow rate conditions. The thermobalance study showed that the degradation reaction begins at 288 °C and it is completed at 362 °C, with an 18–22% weight loss.

As laboratory research found that the thermal treatment with the presence of oxygen caused problems with imperfect combustion, Huang et al. [7] applied plasma treatment to printed circuit boards. This process results in environmentally acceptable gaseous emissions and vitrified solid residue, which is suitable for deposition.

Burkovic [8] studied three types of waste (connectors, crushed PCBs and connectors connected with polyethylene together with crushed wires). In the first case, waste was firstly burned and then the ash from combustion was melted together with borax and charcoal addition. After melting the products were milled and sieved. The slag was separated from the metal part. In the second case, after burning the slag was sieved and only a metal fraction was melted. A part of precious metals went to ash and also to slag. The authors did not mention possible risks connected with the formation of gaseous emissions after burning, in case they did not reach the sufficient temperature for the hazardous substances degradation.

Rabah et al. [9] burned the printed circuit boards at different temperatures. They found that the thermal processing at 300 °C has no significant effect on the weight loss, representing about 5%. The increase of temperature to 600 °C caused a weight loss of 60%. A further increase of temperature to 900 °C resulted in a weight loss up to 65%. Subsequently, the solid residue was leached in 4 M H₂SO₄ and 4 M HNO₃. The recovery of copper and tin in H₂SO₄ at the temperature of 100 °C and leaching time of 60 min reached 100% while the recovery of lead was only about 10%. Leaching in HNO₃ at 100 °C resulted in the complete extraction of copper after 40 min, tin after 50 min and lead after 60 min.

Hageluken [10] describes the pyrometallurgical treatment of WEEE in industrial conditions in Umicore Company, (Hoboken, Belgium).

Pyrolysis is a thermal decomposition of organic materials without the access of oxygen, air, carbon dioxide, water vapor, etc. Higher saturated hydrocarbons are cleaved during the pyrolysis, and lower unsaturated hydrocarbons are created [11]. Gases like nitrogen or argon can be used to create an inert atmosphere. This process usually results in three fractions:

- solid, where metals are concentrated;
- liquid tar fraction;
- gaseous, containing also volatile metal compounds.

The advantage of pyrolysis is also the possibility to use a liquid product for chemical or power industry. After pyrolysis metals remain in their original form, in which they occurred in waste because they do not oxidize.

Antrekowitsch et al. [12] pyrolyzed printed circuit boards. This procedure eliminated most plastics represented by approximately 30% weight loss of charge. Thus they gained an advantageous charge for copper converters with a low content of plastics, whilst generation of hazardous substances was precluded.

Chiang et al. [13] pyrolysed crushed printed circuit boards at 200 and 500 °C. Metals remained in the solid residue and halogens from brominated flame retardants mostly passed into gas products. A gas product was purified by water whereby halogens were leached allowing the use of tar as a fuel.

Vasile et al. [14] pyrolysed different kinds of materials, including also printed circuit boards. About 70% of solid residue, 22% of liquid product and approximately 8% of gases were obtained after

pyrolysis. Antimony from flame retardants is present in the form of SbBr₃, which evaporates at the temperature of 550–850 °C. In contact with water or CO₂ it is hydrolysed to Sb₂O₃ and collected on the filter [15].

Hall and Williams [16] dealt with pyrolysis of printed circuit boards from three different devices (computers, television sets and cell phones). In the first step the PCBs were crushed into pieces with the size of 1.5–2 cm². Samples with the weight of 20 g were for the experiments. The temperature of pyrolysis was 800 °C, and the time was 135 min. After pyrolysis the solid residue from computers represented 68.9%, from televisions 60% and from cell phones 82.2%.

In the paper [17] de Marco et al. pyrolysed polyethylene cables, telephones, cell phones and printed circuit boards. The experiments were carried out in an autoclave at the temperature of 500 °C for 30 min. The sample weight was 100 g. After the pyrolysis the solid residue from polyethylene cables was 32.9%, from telephones 34.4%, from cell phones 30.3% and from printed circuit boards 76.5%.

Jie et al. [18] dealt with the pyrolysis of printed circuit boards. The pyrolysis was carried out at 300–700 °C for 30 min. The sample weight was 50 g. The solid residue after pyrolysis was from 75 to 80%. Above 500 °C no significant impact of the temperature on the weight loss was observed.

The combination of pyrolysis and gasification in a laboratory scale is represented by the process called Pyromat [19] with the capacity of 5 kg/h. In the first stage of the thermal processing the pyrolysis is applied resulting in the solid residue and gas. The formed gas is then led into the gasifier operating at 900–1400 °C. The tests of this equipment for the electronic waste were carried out at the temperature of 550 °C for 15 min. The temperature in the gasification process was 1230 °C, which was achieved by adding a certain amount of oxygen and methane. The final gas after the wet cleaning was composed of CO, H₂, CO₂ and H₂O.

Two recycling pyrolytic processes are used presently, namely Pyrocom [20] and Haloclean [21]. The Pyrocom process operates at around 700 °C, whereby two products are obtained. The first one contains HCl, HBr, H₂O, CO, CO₂ and phenol, and the second one ceramics, glass and metals. The gaseous fraction is showered by water; metal dust is separated in the filter and is treated in order to recover metals. The gaseous phase is cooled; advanced hydrocarbons are removed, so the emissions consist mainly of polluted air.

The aim of the Haloclean process is to obtain fuel without halogens and solid residue with metals. Hornung et al. [21] used a batch with the content of gold 300 g/t and bromine 5% in their experiments. After pyrolysis they achieved a two times higher concentration of gold in the residue. The whole process took from 1 to 4 h, and it resulted in three fractions: HBr, oil without bromine and solid phase with metals.

The printed circuit boards (PCBs) are found in most EEE, and they are paid increasing attention because of interesting metal contents (Cu, Sn, precious metals) as well as complications during the metals recovery due to the PCB construction.

This work is focused on studying the impact of the thermal treatment on the subsequent hydrometallurgical recovery of copper and tin from PCB by leaching.

2. Experimental

2.1. Material

Seventy-three kilograms of used PCBs was collected before experiments. The hazardous parts of PCBs were manually removed before crushing in a hammer crusher. The representative sample of 2 kg was obtained from the crushed material by dividing in the

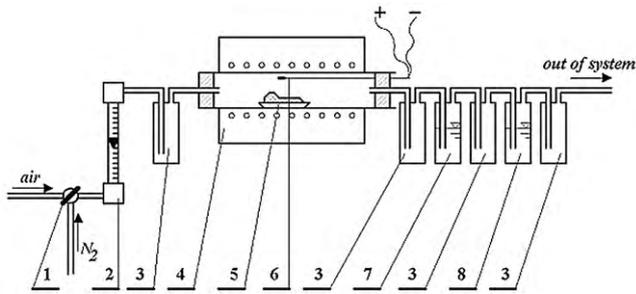


Fig. 1. The scheme of the apparatus for thermal treatment. (1) Tap, (2) flowmeter, (3) empty bubbler, (4) laboratory furnace, (5) ceramic sample boat, (6) thermocouple, (7) NaOH solution, (8) H₂SO₄ solution.

automatic sample divider. This sample was sieved into three fractions: $-8 +0$, $-8 +3$ and $-3 +0$ mm. The obtained products were analysed by chemical analysis using the AAS method. The results of the analysis are: 5.94% Sn, 21.3% Cu, 3.2% Pb and 2.24% Fe.

2.2. Burning and pyrolysis

The thermal pretreatment experiments of the crushed PCBs with and without presence of air were carried out in the apparatus, the scheme of which is shown in Fig. 1. The crushed printed circuit boards were thermally pretreated at 300, 500, 700 and 900 °C for the period 15, 30 and 60 min. The weight of each sample used in the burning process was around 5 g. The sample was batched into a ceramic sample boat and fed into a quartz reactor. During the experiments either nitrogen from a pressure cylinder or air using a laboratory compressor were blown in. The gaseous and liquid products created during the experiments were trapped in a condensation system which consisted of five washing flasks. Three of them (position 3) were empty to avoid penetration of liquid into furnace in case of emergency. The rest two contained 0.5 M solution of NaOH and 0.25 M solution of H₂SO₄. The role of these solutions was to entrap the substances, which were a part of gaseous emissions.

2.3. Leaching

The leaching was carried out in the apparatus shown in Fig. 2. The samples without and after the thermal treatment were leached in 1 M solution of HCl at 80 °C for 180 min using constant stirring in a glass reactor. The volume of leaching reagent was 400 ml and the weight of each sample was 3 g. During experiments the liquid samples were withdrawn after 5, 10, 15, 30, 60, 90, 120, 150 and 180 min, and were analyzed by atomic absorption spectrometry to determine the content of copper and tin.

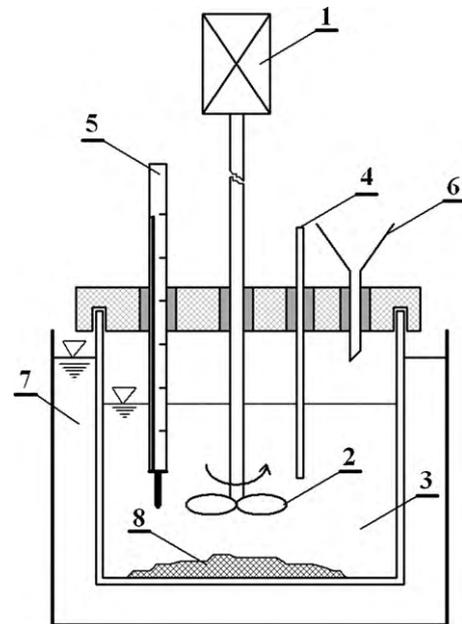


Fig. 2. The scheme of the leaching apparatus. (1) Mechanical stirrer, (2) propeller, (3) leaching pulp, (4) sampler, (5) thermometer, (6) feeder, (7) water thermostat, (8) crushed PCBs

3. Results

3.1. Thermal pretreatment

Fig. 3a and b shows the weight loss comparison of samples after burning as well as after pyrolysis at different temperatures and time of the thermal treatment.

The graph above shows that in both cases the process is relatively fast, and the duration of the thermal treatment has no particular influence on the amount of vaporizing substances. Only at 300 °C it can be observed that the process is slow, and at the least duration a relatively less sample was released than at a higher temperature.

At the temperature of 300 °C, less than 10% of the sample weight was removed. It is caused by the temperature insufficient either for vaporization or for burning out the plastics which are present in PCBs. With the increase of temperature the weight loss of samples increased, and the highest loss of about 30% was observed at 900 °C. However, it is apparent that temperatures about 500 °C and duration about 15 min are sufficient for the effective removal of volatile compounds of PCB, represented mostly by plastics. It is necessary to mention that the difference between 900 and 700 °C after 15 min was insignificant.

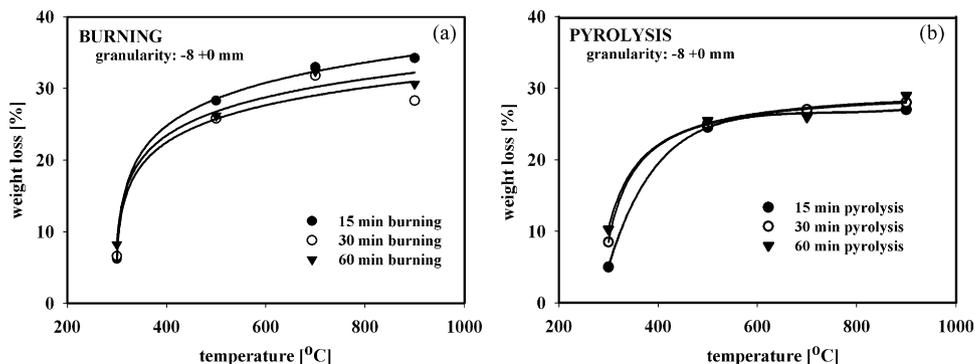


Fig. 3. The temperature dependence of weight losses after (a) burning, (b) pyrolysis.

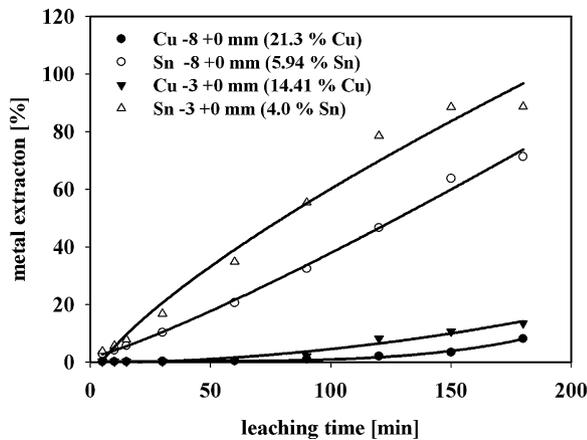


Fig. 4. Kinetic curves of copper and tin leaching from crushed PCBs of different grain size without thermal treatment.

The higher weight loss was achieved by burning than by pyrolysis, although the differences are not major. During the combustion the burning of plastics occurs and gaseous products are created, which apparently are released easier than volatile compounds released from plastics during the pyrolysis.

3.2. Leaching

3.2.1. Influence of thermal treatment on metal extraction

The metallic copper layers are overlaid by the laminate layers in the PCBs. This construction causes problems in the processing because the laminate inhibits the contact between a reaction medium and copper, which makes copper recovery complicated. Therefore, it is necessary in first step to liberate the components as far as possible. This is usually done by mechanical treatment – crushing.

Fig. 4 shows kinetics curves of copper and tin leaching from crushed PCBs of different grain size without thermal treatment in 1 M HCl at 80 °C.

Copper from the original sample leached in the solution of HCl significantly less than tin, which is caused by the fact that copper is covered with laminate while tin used in PCBs as a solder is located on the surface. The extractions of both metals increase with the decreasing grain size of the leached material, which is understandable, as the reaction interface surface between the solid and liquid phase is increasing [22].

Fig. 5a and b shows kinetics curves of copper leaching and Fig. 6a and b shows kinetics curves of tin leaching in 1 M HCl for 30 min at 80 °C from PCBs after the thermal treatment at different temperatures.

The extractions of copper and tin into the solution from a sample after the thermal treatment were comparable with the extractions from a sample without the thermal treatment. It is caused by the fact that at this temperature the plastics included in PCBs neither burn nor evaporate, thereby the original PCBs are changed only little. The increase of a thermal treatment temperature increases the extraction of copper into the solution. Pyrolysis itself significantly influences the extraction of copper into the solution. The extractions of copper are higher than after pyrolysis.

In the case of tin, the situation is different. In case of burning with the increasing temperature the extraction is reduced, but in case of pyrolysis it increases with the increasing temperature. The lower grain size of samples has a positive influence on the extraction in both cases.

4. Discussion

The obtained results indicate a different mechanism of behaviour of copper and tin in hydrochloric acid leaching after

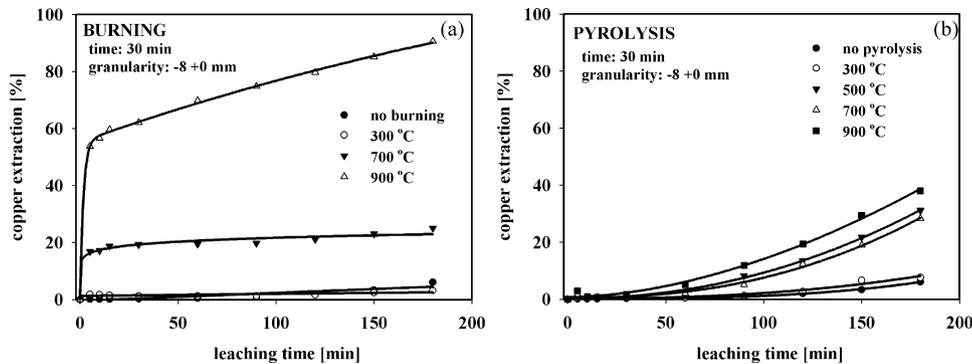


Fig. 5. Kinetic curves of copper leaching from PCBs after (a) burning and (b) pyrolysis at different temperatures.

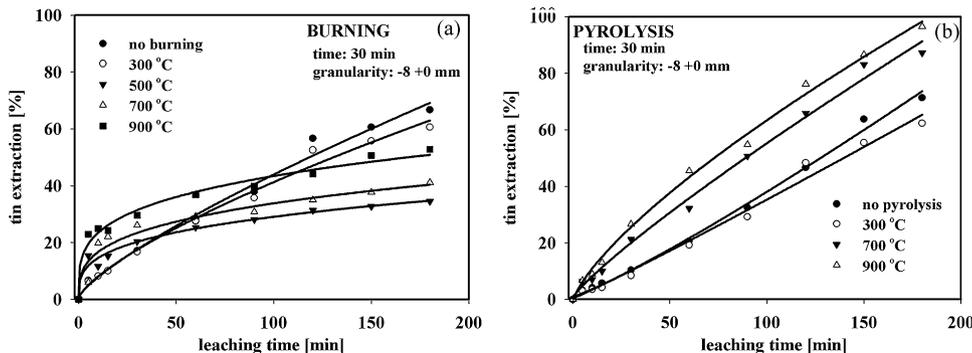


Fig. 6. Kinetic curves of tin leaching from PCBs after (a) burning and (b) pyrolysis at different temperatures.

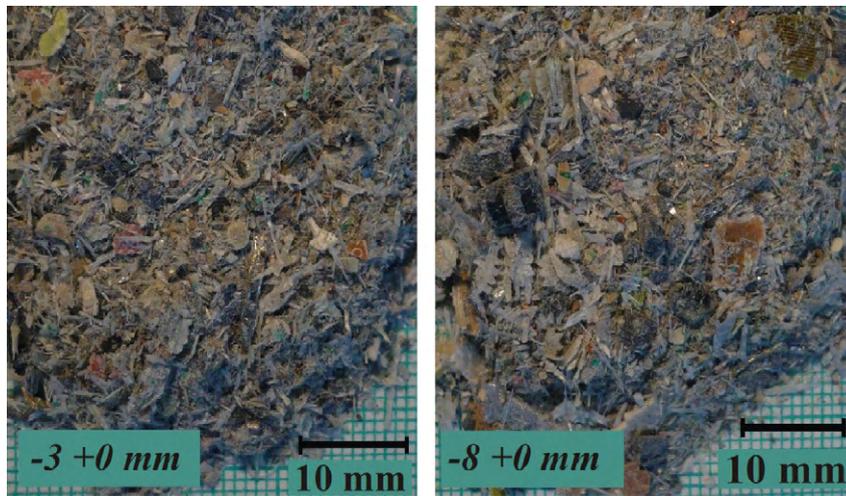


Fig. 7. Photographs of crushed PCBs.

burning or pyrolysis. Fig. 7a and b shows the samples of crushed PCBs used in the experimental study.

Fig. 8a and b shows the sample of crushed PCBs after the thermal treatment at 900 °C; Fig. 9a and b shows the same samples after leaching.

As it is apparent from visual observation, the samples after pyrolysis and burning differ from each other. A part of plastics burns out during the combustion and the rest creates slag. The copper particles are either covered with oxides or completely oxidized. Tin or solder oxidized and it was not visually observable.

The sample partly carbonised due to the pyrolysis, and it differs from the sample exposed to the burning by its dark colour. The particles of copper remain non-oxidized and within the sample little non-oxidized spheres of tin or solder occur. In addition, in the sample also larger clumps of metal were observed. Tin creates alloy with copper already at low temperatures, which were exceeded in the thermal treatment. Tin solder contains up to 40% Pb, however at the temperature at which the thermal treatment took place, the alloy formation takes place as well. Fig. 10a shows the binary Sn–Cu system, and Fig. 10b

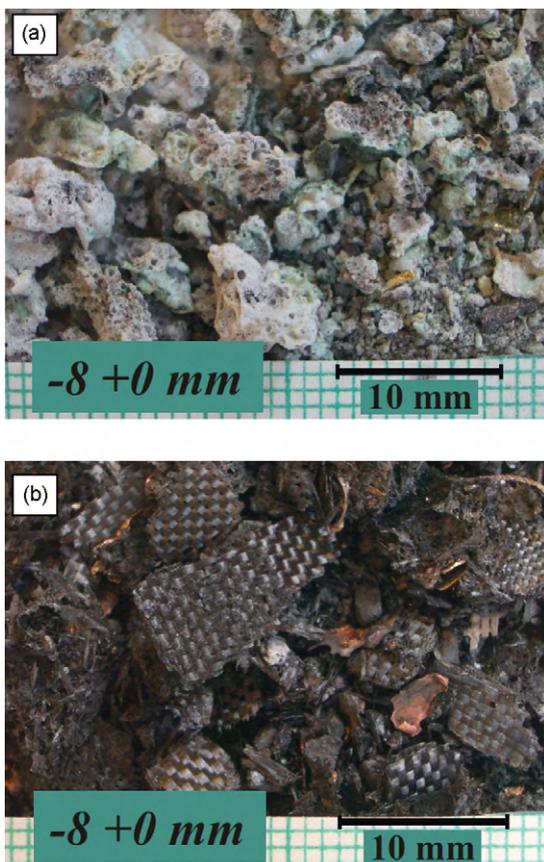


Fig. 8. Photographs of (a) burned and (b) pyrolysed PCBs.

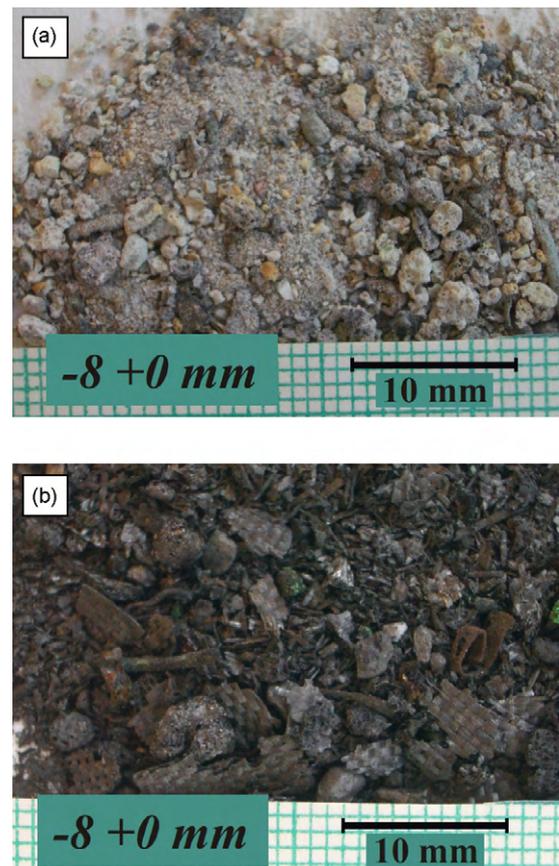


Fig. 9. Photographs of leached of (a) burned and (b) pyrolysed PCBs (a).

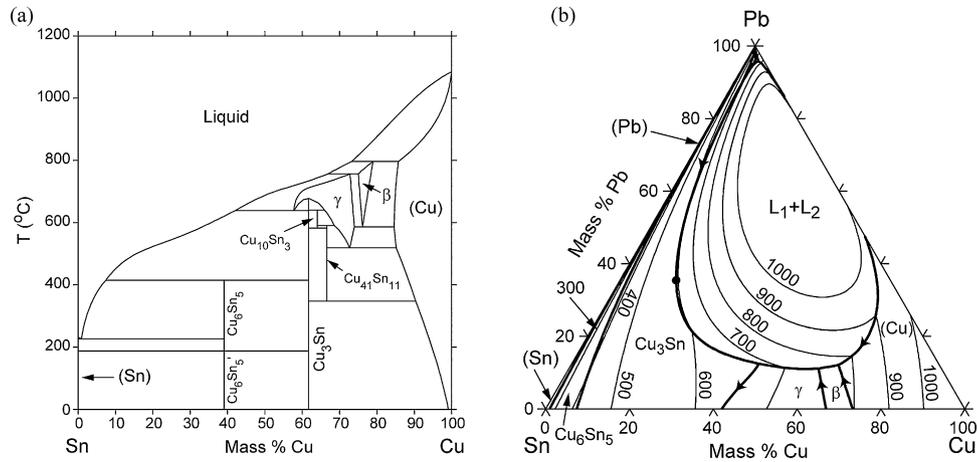
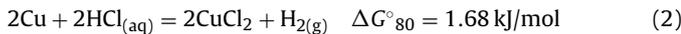


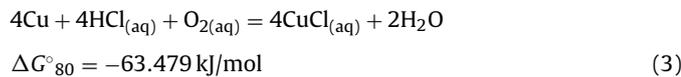
Fig. 10. Phase diagram of the (a) binary Sn–Cu and (b) ternary Cu–Sn–Pb system [22,23].

shows the ternary Cu–Sn–Pb system which results in the alloy formation.

The amount of copper leached from the original samples is substantially lower than in case of tin. The leaching of copper is inhibited by laminate while tin is located on the reaction surface. In addition, the surface of PCB is covered by a varnish. The reduction of PCB grain size results in the increase of the reaction surface, which has a positive influence on the extraction of metals into the solution. The behaviour of copper and tin during the different types of thermal treatment has a significant influence on their extraction. Copper is leached significantly only in the oxidative environment, however HCl is a non-oxidizing acid, and hence there should be no significant reactions between Cu and HCl [24].



During the leaching the oxygen from the surrounding atmosphere gets into the solution, which acts as an oxidizing agent according to:

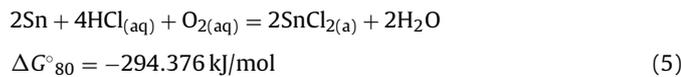


which may result in a partial transfer of copper into the solution, Fig. 5.

Unlike copper, tin is leached in HCl according to:



or in the presence of oxygen



and passes into the solution. Assuming the presence of oxygen in the solution tin reacts primarily, which corresponds to the measured values in Fig. 4.

Copper is oxidized to oxides during the combustion; thermodynamically CuO is more preferable than Cu₂O. Table 1 presents the calculated values of standard Gibbs free energy change, ΔG° , for copper oxidation at different temperatures.

The copper oxides, as opposed to metallic copper, are well leached in the hydrochloric acid, and this is the reason why copper

is leached out from burned samples.

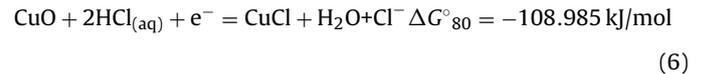


Fig. 5a represents the mechanism, where in the first five minutes most of copper leached from the oxides passes into the solution and then copper is leached more moderately, similarly to the samples after the thermal treatment.

Copper should not be oxidized during pyrolysis but it should remain in its elemental form. However, it results from Fig. 5b that copper from the pyrolysed samples after leaching also passes into the solution in a higher volume than in case of the original samples. One of the reasons is that after pyrolysis the reaction interface is increased due to the evaporation of plastics, which increases the amount of copper to be leached into the solution.

Analogous to copper oxidation, the tin surface is oxidized, too. From the thermodynamic point of view SnO₂ is preferred to SnO. Table 2 presents the calculated values of standard Gibbs free energy change, ΔG° , for tin oxidation at different temperatures.

Table 1

The values of changed of standard Gibbs free energy, ΔG° , for copper oxidation at different temperatures [25].

T [°C]	2Cu + O _{2(g)} = 2CuO ΔG° [kJ/mol]	4Cu + O _{2(g)} = 2Cu ₂ O ΔG° [kJ/mol]
300	-103.062	-63.485
700	-68.504	-48.759
900	-51.822	-41.602

Table 2

The values of changed of standard Gibbs free energy, ΔG° , for tin oxidation at different temperatures [25].

T [°C]	2Sn + O _{2(g)} = 2SnO ΔG° [kJ/mol]	Sn + O _{2(g)} = SnO ₂ ΔG° [kJ/mol]
300	-224.93	-463.279
700	-182.98	-379.289
900	-162.51	-338.464

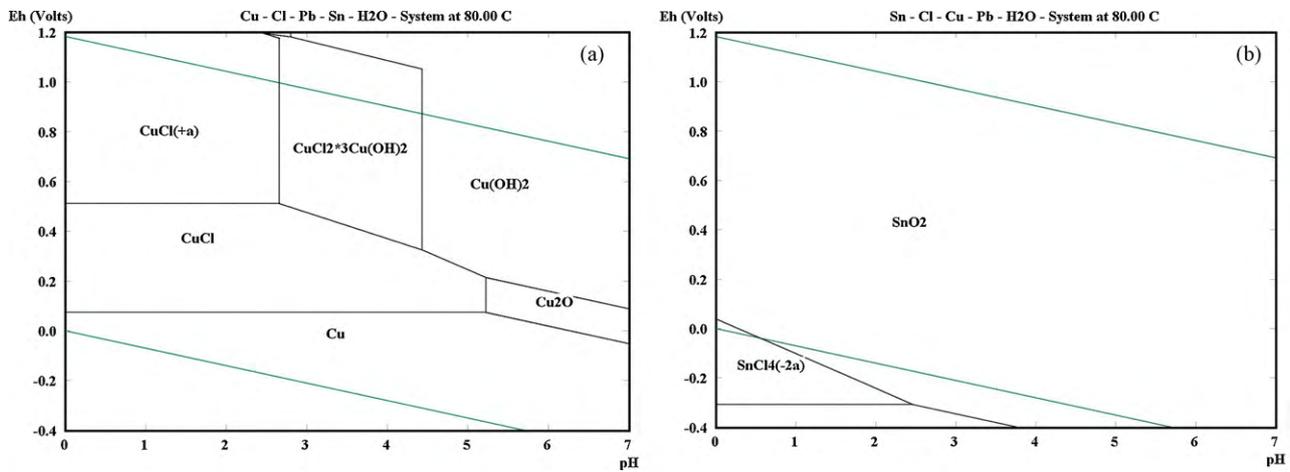


Fig. 11. E-pH diagram for Cu-Sn-Pb-Cl-H₂O system at 80 °C.

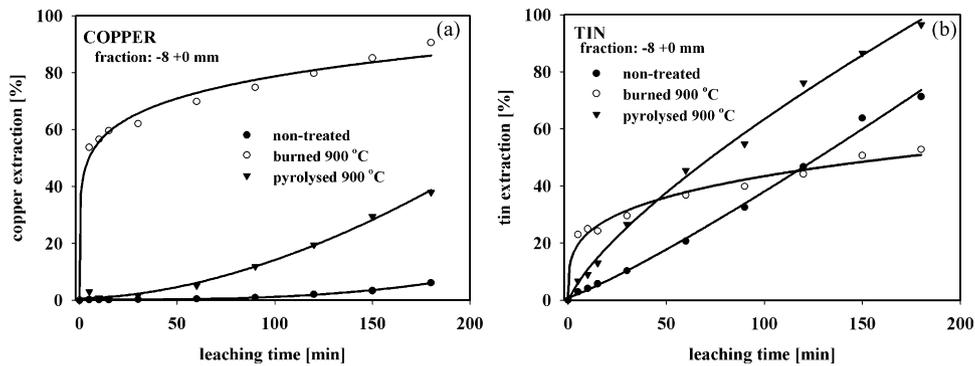
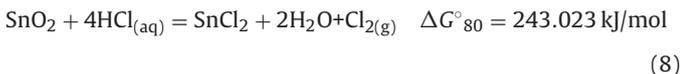


Fig. 12. Leaching kinetic curves for (a) copper and (b) tin from non-treated, burned and pyrolysed PCBs.

Tin oxides are not leached in HCl as it is indicated by the value of change ΔG° of SnO₂ creation according to:



The results of leaching show that the part of tin remained in the metallic form after combustion and was leached consequently; or that the part of tin oxidized to SnO, which is easily possible, because the burning of organic components could cause the creation of the reducing atmosphere near the reaction surface.



Fig. 11 shows E-pH diagram of the Cu-Sn-Pb-Cl-H₂O system at 80 °C with stability zones of species with the copper content and species with the tin content [25].

These diagrams describe the situation from thermodynamical i.e. equilibrium point of view. However, the kinetics and process mechanism play a significant role in the real process.

The behaviour of copper and tin in this system is described by Fig. 12.

According to the figure above, copper from the thermally untreated samples is leached only a little. This amount of copper passes into the solution by the leaching of the surface oxidized layer which was created on the surface by oxidation with air. The contact with a leaching agent is inhibited by the laminate, top varnish and a limited amount of oxidant – the oxygen from air. The varnish is removed during the pyrolysis and metallic copper covered by laminate is released. The reaction interface surface is increased and the kinetics of the copper leaching increases as well. During the

combustion copper oxidizes to CuO, which is leached in HCl. Copper oxidizes during the combustion to CuO, which is leachable in HCl. It is leached within the first minutes and then metallic copper is leached, but, of course, from a larger surface. It can be assumed that the surface of copper remains highly attacked after burning and this fact significantly supports the leaching kinetics.

Metallic tin is leached in HCl very well, as it results from Fig. 12b. The metals are not chemically changed during the pyrolysis, but the reaction surface is significantly increased. The question arises if an alloy of tin and copper is created during the pyrolysis; if so, this alloy is probably leached more intensively than the simple mixture of tin and copper. There are some clues from the viewpoint of metallic copper leaching, Fig. 12a. Most of tin or solder is oxidized after burning. Initially, the rest of the metal with the tin content is leached and the created oxide is leached considerably less than pure metal.

5. Conclusion

Pyrolysis as well as burning as possible pretreatment of PCBs before leaching was studied.

The thermal treatment at the temperature of 300 °C does not have any marked influence on the release of plastics from PCBs, because most of plastics are thermally degradable above this temperature. At higher temperatures the amount of removed plastics increases. The maximum plastics removal efficiency was 35% at 900 °C after 15 min.

During the leaching of thermally untreated samples tin is leached very well while copper is leached only in small amounts. It was confirmed that the particle size reduction results in the

increase of the metal extraction, which is caused by the increase of the reaction surface.

The burning results in the improvement of the copper extraction, whereby the burning temperature has a positive effect on this process. The highest extractions of copper were achieved at the pyrolysis temperature of 900 °C. During the burning, copper is released from the composite and is oxidized. The copper oxides, in contrast to pure copper, are leached relatively well in the non-oxidizing environment of hydrochloric acid. The copper extraction from the pyrolysed samples during the leaching increased, but it is probably caused by the release of copper from the composite and the increase of the reaction interface area as well as by the presence of the atmospheric oxygen.

The tin behaviour is contrary to the copper. Metallic tin or solder, which is an alloy of tin and lead, is chemically leached in the hydrochloric acid without the presence of an oxidant. During the pyrolysis the PCB varnish is removed from the surface and reaction interface is increased, which increases the amount of tin extracted into the solution. During the burning an oxidation occurs to oxides which are difficult to be leached in the given environment. The result is that the amounts of tin extracted into the solution are lower than those gained from metallic tin.

The issue of possible creation of a copper and tin alloy during the thermal treatment, especially during the pyrolysis and the behaviour of this alloy in the leaching process has not been explored.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jhazmat.2010.07.107.

References

- [1] Ch. Drechse, Mechanical processes for recycling waste electric and electronic equipment with the rotorshredder and rotor impact mill, *Aufbereitungs Tech.* 47 (2006).

- [2] M. Petranikova, Treatment of End of Life Computers, Diploma Work, Technical University of Kosice, Kosice, Slovakia, 2008.
- [3] D. Orac, F. Kukurugya, T. Havlik, Treatment possibilities of waste from electric and electronic equipments, in: *Modern Trends in Secondary Raw Materials Treatment of Non-ferrous Metals*, Herliany, Slovakia, 2008, pp. 92–95, ISBN 978-80-8073-966-9.
- [4] A. Tohka, H. Lehto, Mechanical and Thermal Recycling of Waste from Electric and Electrical Equipment, Energy Engineering and Environmental Protection Publications, Espoo, 2005, TKK-ENY-25.
- [5] H. Antrekowitsch, M. Potesser, W. Spruzina, F. Prior, Metallurgical Recycling of Electronic Scrap, EPD Congress, 2006, pp. 899–908.
- [6] P. Antonetti, et al., Degradation products of the process of thermal recovery of copper from lamina scraps in lab-scale fluidized bed reactor, *J. Hazard. Mater.* B108 (2004) 199–206.
- [7] J. Huang, et al., DC arc plasma disposal of printed circuit board, *Plasma Sci. Technol.* 6 (2004) 2424–2426.
- [8] R. Burkovic, The knowledge from pyrometallurgical pretreatment of selected kinds of waste from electrotechnic and electronic industry, in: *Waste Recycling XI*, 2007.
- [9] M. Rabah, M. Mosa, G. Aly, Recovery of metals values from useless printed circuit boards, *Eurasian Chem J.* 9 (2007) 129–137.
- [10] Ch. Hagelucken, Recycling of electronic scrap at Umicore's integrated metals smelter and refinery, in: *Proceedings EMC 2005, GDMB*, pp. 1–16.
- [11] L. Starkbaumova, Z. Belohlav, P. Zamostny, The reactivity of cyclic and acyclic hydrocarbons at pyrolysis, Website, 2007. <http://www.chemicke-listy.cz>.
- [12] H. Antrekowitsch, M. Potesser, W. Spruzina, F. Prior, Metallurgical recycling of electronic scrap, Website, 2007. <http://www.unileoben.ac.at>.
- [13] H. Chiang, K. Lin, M. Lai, T. Chen, S. Ma, Pyrolysis characteristics of integrated circuit boards at various particles size and temperatures, *J. Hazard. Mater.* 149 (2007) 151–159.
- [14] H.-Ch. Zhang, F. Ling, A decision-making model for materials management of end-of-life products in the Pantex plant, Website, 2008. www.uraweb.org.
- [15] C. Vasile, et al., Feedstock recycling from plastic and thermoset fractions of used computers (I): pyrolysis, *J. Mater. Cycles Waste Manage.* 8 (2006) 99–108.
- [16] Proposal 500PC0347 for a Directive of the European Parliament and of the Council on the restriction of the use of certain hazardous substances in electrical and electronic equipment, Website, 2008. <http://www.trprint.com>.
- [17] W. Hall, P. Williams, Processing waste printed circuit boards for material recovery, *Circuit World* 33 (2007) 43–50.
- [18] I. de Marco, Pyrolysis of electrical and electronic wastes, *J. Anal. Appl. Pyrol.* 82 (2008) 179–183.
- [19] G. Jie, L. Ying-Shun, L. Mai-Xi, Product characterization of waste printed circuit board by pyrolysis, *J. Anal. Appl. Pyrol.* 83 (2008) 185–189.
- [20] H. Lehto, A. Tohka, L. Saeed, R. Zevenhoven, K. Heiskanen, Minimising environmental impact and improving synergism between mechanical and thermal processing of waste from electrical and electronic equipment, Website, 2006. <http://www.tkk.fi>.
- [21] A. Hornung, W. Koch, H. Seifer, Haloclean and Pydra – a dual stage pyrolysis plant for recycling weee, Website, 2007. <http://www.bsfe-japan.com>.
- [22] Available on Internet: <http://www.metallurgy.nist.gov/phase/solder/cusnw.jpg>.
- [23] Available on Internet: <http://www.metallurgy.nist.gov/phase/solder/cupbsn-1.jpg>.
- [24] T. Havlik, Hydrometallurgy – Principles and Applications, Woodhead Publ. Ltd., Cambridge, 2008, p. 536, ISBN 978-1-84569-407-4.
- [25] A. Roine, Chemical Reaction and Equilibrium Software HSC Chemistry®, ver. 6.0-software Outotec Research Oy.