Applied Mechanics and Materials
ISSN: 1662-7482, Vol. 832, pp 39-46
doi:10.4028/www.scientific.net/AMM.832.39

Submitted: 2015-09-16
Revised: 2015-11-24
Accepted: 2016-01-13
Online: 2016-04-01

Recovery of Copper and Tin from Used Printed Circuit Boards

Tomáš HAVLÍK[1,a *], Dušan ORÁČ[1,b], Ján JAŠČIŠÁK[1,c], Andrea MIŠKUFOVÁ[1,d] and Hedviga HORVÁTHOVÁ[1,e]

[1] Technical University of Kosice, Faculty of Metallurgy, Department of Non-ferrous Metals and Waste Treatment, Kosice, Slovakia

[a]tomas.havlik@tuke.sk, [b]dusan.orac@tuke.sk, [c]jan.jascisak@tuke.sk, [d]andrea.miskufova@tuke.sk, [e]horvathova.hedviga@tuke.sk

Keywords: WEEE, electronic waste, printed circuit board, burning, pyrolysis, leaching, HCl, hydrometallurgy

Abstract. This work focuses on possibilities to recover tin and copper by hydrometallurgical processes from printed circuit boards (PCBs) of discarded personal computers after thermal treatment. For experimental work crushed and sorted printed circuit boards with various granularity /-8 +0 mm, -8 +3 mm, -3 +0 mm/ were used. They were exposed to thermal treatment at temperatures 300 °C, 500 °C, 700 °C and 900 °C before leaching for 15, 30 and 60 minutes. The two thermal treatments were studied: in air flow, i.e. burning, and pyrolysis (without air flow). For leaching experiments 1M solution of HCl at 80 °C was used. Under the mentioned conditions both samples, the thermally treated sample of PCB as well as the original untreated printed circuit board, were leached with the aim to compare the experimental results. Weight losses during burning accounted for 5 to 35 %, while pyrolysis caused weight losses from 10 to 30 %, depending on the thermal treatment temperature. The higher the burning temperature, the higher the extraction of copper into the solution with up to 98%.However, extraction of copper from non-burned samples does not exceeded 6 %. An opposite effect has been observed during leaching of tin, where the highest extraction was reached using thermally untreated samples, and extraction decreased with an increasing burning temperature. With increasing pyrolysis temperature a higher extraction level was observed during leaching of copper and tin into the solution. The maximal extraction was reached with the leaching of thermally untreated samples, namely 6 % for copper and about 68 % for tin whereas the extraction of copper and tin achieved with thermally treated samples was 63 % and 98 %, respectively.

Introduction

The percentage of amortization of electrical and electronic devices is relatively high, which is what causes the production of large amount of WEEE (Waste of Electrical and Electronic Equipment). Worldwide approximately 20-50 million tons of WEEE are generated yearly, while the European Union accounts for 8 million metric tons of the WEEE production every year with an annual increment of 3-5% [1-2]. This waste is very notable for its quantity and content of various types of materials, such as hazardous elements, like mainly heavy metals (e.g. 20 % Cu and 4 % Sn) and plastics. However WEEE contains also quantity of valuable elements e.g. 0.1 % Au, 0.2 % Ag. Therefore, WEEE should not be considered waste; instead it should be valued as second raw material.

Due to the fact that WEEE is a composite material which contains a mixture of metal, plastic and ceramic materials etc., its treatment is a very challenging process. Generally, WEEE can be treated by pyrometallurgical, hydrometallurgical or combination processes. Electronic waste is very often treated pyrometallurgically in copper smelter aggregates. The plastic materials in WEEE are problematic due to their large volume, leading to a risk of volatilization of hazardous volatile substances in the process. In spite of these problems, thermal treatment is still one of the most effective methods for metals recovery. For the purpose of increasing effectiveness and optimizing the process, it is important to search for new ways of thermal treatment. WEEE can either be thermally treated in the presence of air (oxygen) i.e. burning, or in an environment free of oxygen i.e. pyrolysis.

The combustion is a standard pyrometallurgical process where plastic materials and other organic materials are removed and metals are concentrated. After burning crushed PCBs, metals are concentrated in furnace. Burned plastics are formed into volatilized products or create a slag phase. During this process some of the metals e.g. copper or lead, behave as collectors for other metals. This method allows the recovery of alloys or metal oxides, however, not pure metals.

An important parameter which affects burning is temperature. The majority of plastics contain halogens and thus the degradation of hazardous gas emission has to be assured. This is possible when the burning process is run under flowing oxygen, usually from the air and the temperature of burning is kept over 1200°C.

Based on the published literature, and by comparing the results from burning and pyrolysis processes, authors incline to the opinion, that to burning and melting processes should precede the pyrolytical process by which hazardous volatile components are removed from the system [3-6]. Metals stay in the same forms after pyrolysis as in the initial waste, because they do not convert to oxides. Almost any WEEE contains printed circuit boards, which are interesting due to their metals content (Cu, Sn, noble metals).They are also given higher attention by elaborators and researchers as a result of the complications that may arise during metals recycling (PCBs construction).

Burning processes which use air as an oxidizing reagent for WEEE are always regarded as a part of pyrometallurgical treatment. Authors often do not consider burning as part of the pre-treatment of WEEE followed by other recycling steps. Therefore, this work is focuses on studying the effect of thermal treatment following hydrometallurgical recovery of copper and tin from PCBs by leaching. By comparing results from leaching of thermally untreated samples of PCBs with samples treated with pyrolysis and burning, processes of pre-treatment for the next hydrometallurgical treatment of this type of WEEE were optimized.

Experimental work

Material. Crushed PCBs were quartering to a representative sample weighing 2 kg, and this sample was sieved into tree fractions: -8 +0 mm, -8 +3 mm, -3 +0 mm. Obtained products were analyzed by chemical analysis with the AAS method. Samples contained 5.94 % Sn, 21.3 % Cu, 3.2 % Pb and 2.24 % Fe.

Burning and pyrolysis. Thermal decomposition experiments of the crushed PCBs with or without air flowing were conducted using the equipment shown in Fig.1. Crushed PCBs were thermally treated at 300 °C, 500 °C, 700 °C a 900 °C for 15, 30 and 60 minutes. Input material was inserted into ceramic combustion vessel and this was again inserted into the silica grass tube. The nitrogen from the pressure cylinder or air from the compressor was blown into the tube during running experiments. Gasses and liquid products generated during the process were collected by condensation systems, which consisted of 5 glass washing bottles. Second and fourth washing bottles in the line were filled up with solutions 0.5M NaOH and 0.25M H_2SO_4, respectively. Three other bottles were empty and held safety function. The role of the bottles with solutions was to collect all soluble substances which were part of the gas emissions.

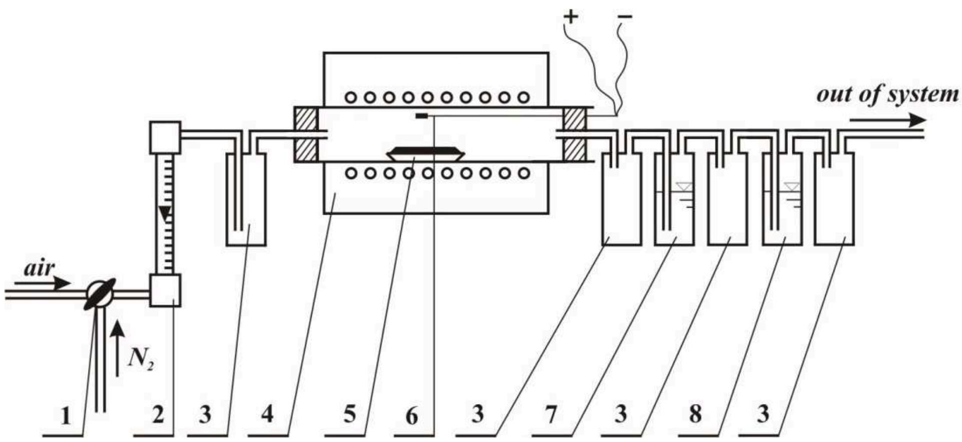


Figure 1 Experimental apparatus scheme for thermal treatment
1-tap, 2- air flow meter, 3-empty safety gas washing bottles, 4-laboratory furnace, 5-ceramic boat, 6-thermojunction, 7- solution NaOH, 8- solution H_2SO_4

Leaching. Leaching tests were realized in apparatus shown below (Fig.2). Original thermally untreated samples and thermally treated samples of PCB were leached in solution of HCl with a concentration of 1M for 180 minutes at 80°C with continual stirring in a glass reactor. The volume of leaching reagent was 400 ml and the volume of the test portion was 3 g. Liquid samples were collected after 5, 10, 15, 30, 60, 90, 120, 150 and 180 minutes and analyzed by atomic absorption spectrometry for contents of copper and tin.

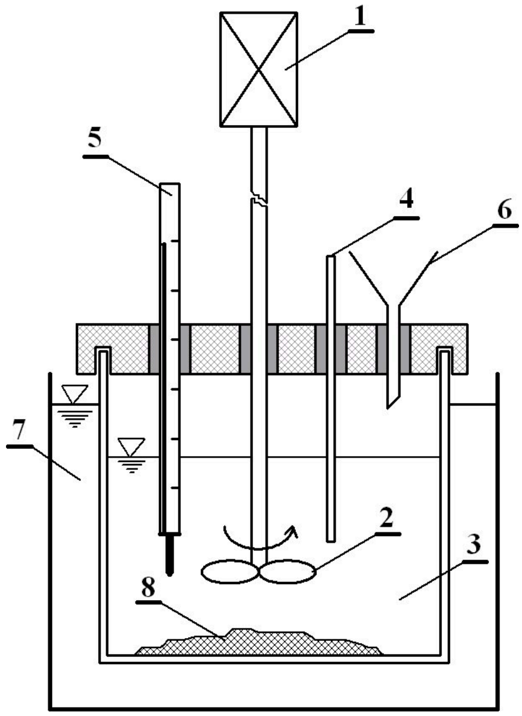
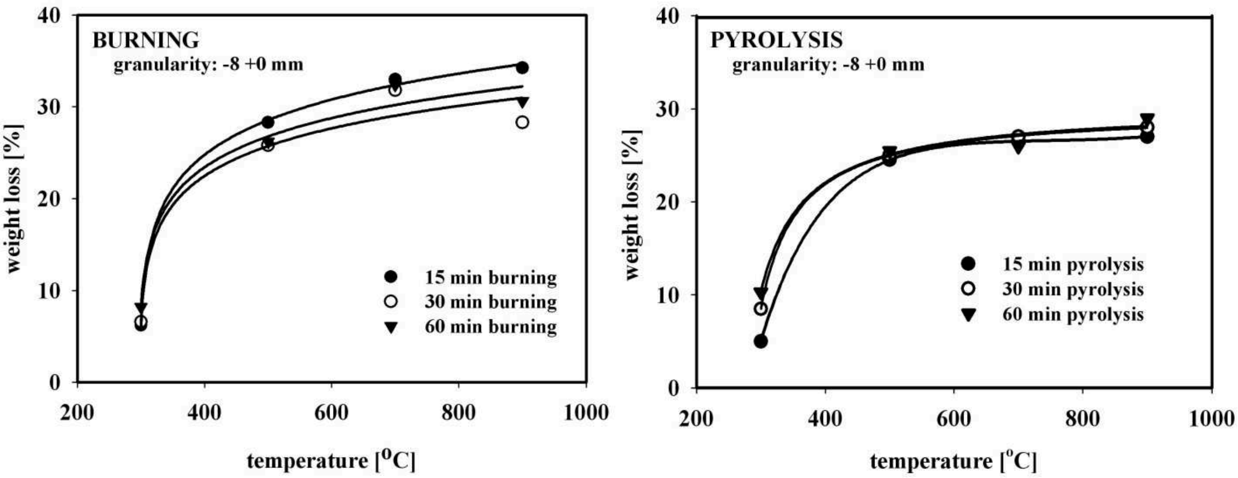


Figure 2 Scheme of the leaching apparatus
(1) Mechanical stirrer, (2) propeller, (3) leaching pulp, (4) sampler, (5) thermometer, (6) feeder, (7) water thermostat, (8) crushed PCBs

Results

Thermal pre-treatment. Fig. 3 a,b compares the weight losses for samples after burning or pyrolysis at different temperatures and time periods of thermal effect.



a b

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

From experimental results (Fig. 3) it is clear, that thermal decomposition is relatively fast and that the time of thermal treatment does not have strong effect on the produced amount of released substances. Only at 300°C it is possible to observe that the process is slow and the amount of released sample is less that at higher temperatures.

At 300°C weight loss was less than 10 % of the original sample. This was probably caused due to insufficient temperature for volatilization and burning plastics contained in PCBs. With increasing temperature, weight losses increased as well. The highest reached efficiency was 30 % at 900°C. It is obvious that a temperature of 500°C and a duration of 15 minutes are adequate for effective removal of volatilized substances from PCBs consisting mainly of plastics. The difference in weight losses at 900°C and 700°C beyond 15 minutes are negligible.

The percentage of weight losses was higher after burning treatment than after pyrolysis, although differences in weight losses are not high. This could be caused by substances that are more readily released from volatilized in the process of burning than in pyrolysis.

The influence of thermal pre-treatment on metals leaching into the solution. PCBs contain layers of copper overlaid by laminates. These layers cause problems during treatment, because laminates avert contact between a liquid medium and cooper, negatively affecting copper extraction. For this reason it is necessary in the first step to liberate those two materials which is possible by mechanical treatment, namely crushing.

Fig. 4 displays kinetics curves of copper and tin leaching in 1M HCl at 80°C for thermally untreated samples.

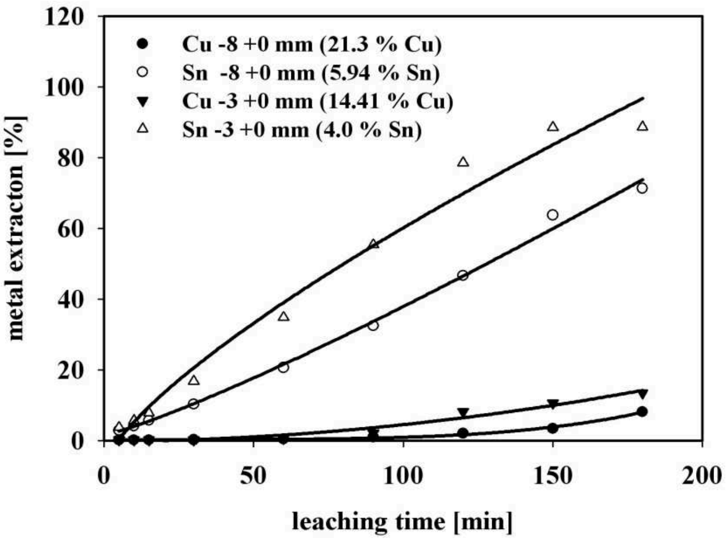


Figure 4 Kinetic curves of copper and tin leaching from non-thermal treated PCBs with various grain sizes

In the process of acidic leaching in HCl solution the amount of leached copper is lower of tin. The leaching of copper is inhibited by laminates which overlaid copper whilst tin is located on the reaction surface. The reduction of PCB grain size results in an increase of the reaction surface between liquid and solid phase, which has a positive influence on the extraction of metals into the solution [7].

Fig. 5 a,b shows the kinetic curves of copper leaching and Fig. 6a,b illustrates the kinetic curves of tin in 1M HCl during 30 minutes at 80°C from thermally treated samples at various temperatures.

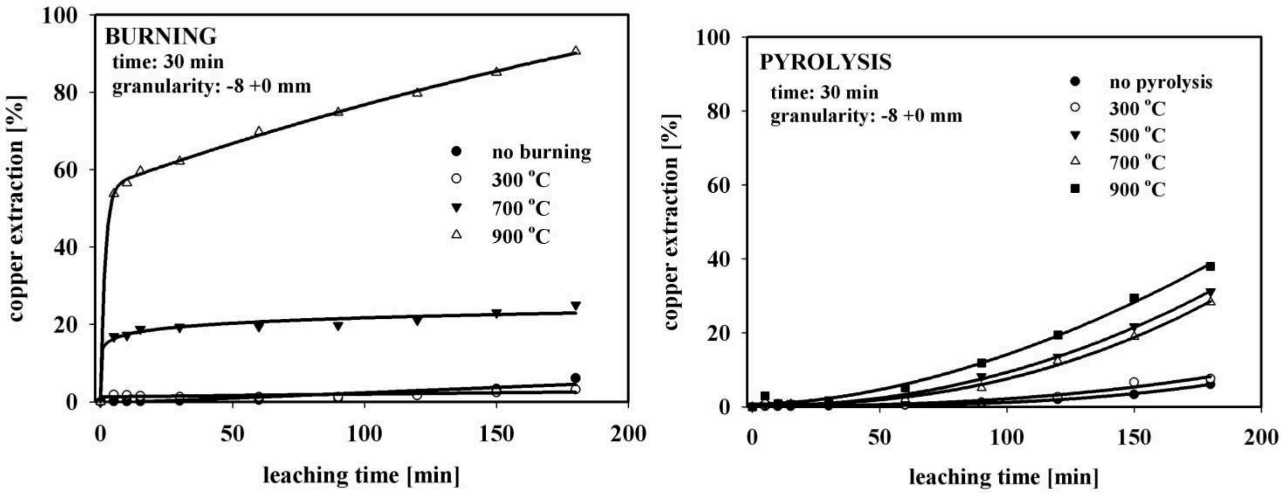
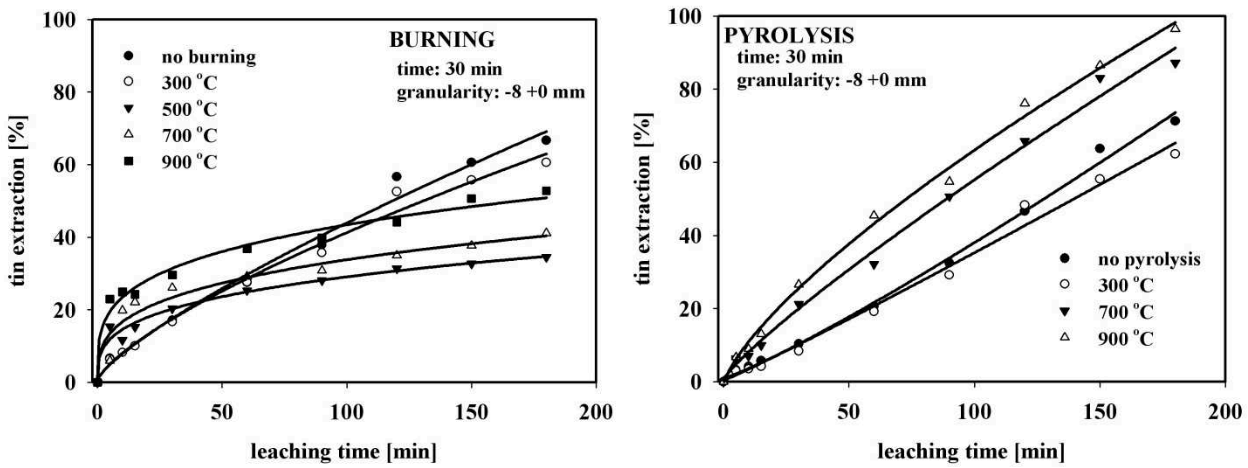


Figure 5 Kinetic curves of copper leaching from PCBs after (a) burning and (b) pyrolysis at various temperatures.



a b

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

The extractions of copper and tin into the solution from a sample after thermal treatment at 300°C were comparable with the extractions from a sample without the thermal treatment. This temperature does not cause burning or volatilizing of plastics from PCBs, which causes only a few changes in original PCBs. Higher temperatures increase the extraction of copper into the solution. Pyrolysis itself significantly influences the extraction of copper into the solution. However, the extraction of copper after burning is higher than after pyrolysis.

In the case of tin extraction, the situation is different. When burning a sample, higher temperatures reduce the extraction, but in case of pyrolysis they increase extraction. Lower grain sizes of samples have a positive influence on the extraction in both cases.

Discussion. The amount of extracted copper from the original sample is significantly lower than the extraction of tin. The extraction of copper is inhibited by laminates whilst tin is presents at the reaction surface. Additionally, the surface of PCBs is covered by varnish. The smaller the grain sizes of PCBs are the higher reaction surface becomes, which positively affects the extraction of metals into the solution. The extraction is also significantly influenced by different behaviours of copper and tin during different types of thermal treatment. Copper is effectively leached only in an oxidizing medium, even though hydrochloric acid is a non-oxidizing acid and it could not lead to a significant chemical reaction between Cu and HCl [7].

The obtained results indicate a different mechanism of copper and tin in hydrochloric acid leaching after burning or pyrolysis.

Tin is extracted in HCl into the solution in contrast to copper. The presence of oxygen in the solution causes tin to react in preference which corresponds with measured data. Burning causes the oxidation of copper at the surface. In contrast to metallic copper, copper oxides are leached well in HCl. For this fact, copper is leached from burned samples.

Fig. 5a represents this mechanism; in the first 5 minutes most copper is extracted and further extraction of copper is moderate, similar to the extraction of non-thermally treated samples.

Generally, pyrolysis shall not oxidize copper and change its elemental form. Nevertheless, Fig. 5b shows that extraction of copper is higher in a leaching process from pyrolyzed samples than from original samples. One of the most probable reasons is that plastics are volatilized after pyrolysis followed by creating higher reaction interface and increasing the amount of extracted copper into the solution.

Tin leaching (Fig. 6) shows that after burning tin partially stayed in metallic form and consequently was extracted during leaching.

The behaviour of copper and tin in the studied system is illustrated in Fig. 7.

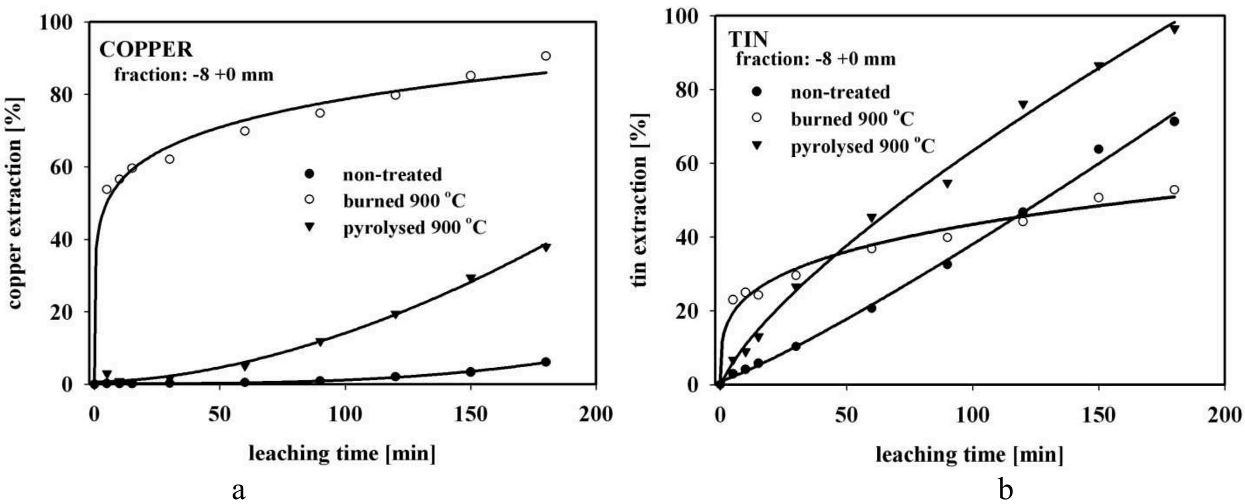


Figure 7 Leaching kinetic curves for (a) copper and (b) tin from untreated, burned and pyrolysed PCBs.

According to the figure above, copper is leached from the thermally untreated samples only a little. This amount of copper passes into the solution by the leaching of the oxidized surface layer which was created by oxidation with air.

Contact with a leaching agent is inhibited by the laminate, top varnish and a limited amount of oxidant namely oxygen from air. The varnish is removed during pyrolysis and metallic copper covered by laminate is released. The reaction interface and the kinetics of copper leaching are increased. During combustion, copper oxidizes to CuO, which is leached in HCl. It is leached within the first minutes and is followed by leaching metallic copper but from a larger surface. Simultaneously, it can be assumed that the surface of copper remains highly attacked after burning and this fact highly supports the kinetics of leaching. Metallic tin is leached in HCl very well, as seen in Fig. 7. Metals are not chemically changed during pyrolysis, but reaction surface is significantly increased.

Conclusion

Thermal treatment (pyrolysis and/or burning) of WEEE and especially PCBs is generally considered for re-melting these wastes. It is not specially considered for pre-treatment for recycling processes of WEEE. This work was focused on studying thermal treatment effects followed by hydrometallurgically acquiring copper and tin from PCBs of discarded personal computers.

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

During leaching of thermally untreated samples, tin is leached very well whilst copper is leached only in small amounts. It was confirmed that particle size reduction results in increased metal extraction, which is caused by increasing reaction surface.

Burning results in an improvement of copper extraction, where the burning temperature has a positive effect on this process. The highest extractions of copper were achieved at the burning temperature of 900 °C. During burning, copper is released from the composite and is oxidized at the same time. Copper oxides, in contrast to pure copper, are leached relatively well in the non-oxidizing environment of hydrochloric acid.

Copper extraction from pyrolysed samples during leaching increased. It could probably be due to copper released from the composite and the increase of the reaction interface as well as the presence of atmospheric oxygen.

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

Acknowlegement

This work was supported by Ministry of Education of the Slovak Republic under grant MŠ SR 1/0293/14. This paper is the result of the Project implementation: University Science Park TECHNICOM for Innovation Applications Supported by Knowledge Technology, ITMS: 26220220182, supported by the Research & Development Operational Programme funded by the ERDF. This work was supported by the Slovak Research and Development Agency under the contract No. APVV-14-0591.

References

[1] EU-Richtlinie, Kampf den Müllbergen A3 Umwelt, 14, 1/2, 2001, 66-67

[2] M. Petrániková, Treatment of used personal computers (in Slovak), Diploma thesis, TUKE, Košice, 2007.

[3] H. Antrekowitsch, M. Potesser, W. Spruzina, F. Prior, Metallurgical recycling of electronic scrap, EPD Congress 2006, (Howard S.M. et al. eds.) TMS 2006, 899-908

[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. Sruzina, F. Prior, Metallurgical recycling of electronic scrap, [online], Available at:
<http://www.unileoben.ac.at/~nem/dexkverpar/download/Papers/Metallurgical%20recycling%20of%20electronic%20scrap.pdf >

[6] W. Hall, P. Williams, Processing waste printed circuit boards for material recovery, Circuit World, Volume 33, Number 4, 2007, 43–50

[7] T. Havlik, Hydrometallurgy – Principles and applications, Woodhead Publ.Ltd., Cambridge, ISBN 978-1-84569-407-4, 2008, pp.536