

Hydrometallurgical treatment of used printed circuit boards after thermal treatment

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ABSTRACT

The hydrometallurgical route both of copper and tin extraction from printed circuit boards (PCBs) of used personal computers after thermal pretreatment is discussed in this work. The crushed and sorted PCBs into -8+0 mm, -8+3 mm, -3+0 mm fractions were used for experiments. The samples were thermally pretreated at temperatures 300 °C, 500 °C, 700 °C and 900 °C for 15, 30 and 60 minutes in the presence of air (combustion) before leaching.

Leaching solution of 1 M HCl and temperature of 80 °C were used during leaching. Both original as well as thermally pretreated samples were leached at these conditions.

Weight loss between 5 and 35 % was recorded during burning depending on temperature. The increase of burning temperature resulted in copper extraction into solution up to 98%, while copper extraction from non-burned samples after leaching was up to 6 %. On the contrary the highest extraction for tin was achieved after leaching of the original samples without burning. Increase of burning temperature resulted in decrease of copper extraction.

1. INTRODUCTION

At present the demand for electric and electronic equipment (EEE) still increases. These equipment, in comparison with other consumer products, have relatively short lifetime. The result is the production of big quantities of used EEE. Therefore, the logical consequence is the effort to establish and improve recycling of wastes from electric and electronic equipment (WEEE).

The reasons which necessitate treatment of WEEE are the quantities of these wastes (in the European Union 6.5-7.5 million metric tons are generated every year, representing 16 kg per inhabitant) as well as the content of valuable metals (0.1 % Au, 0.2 % Ag, 20 % Cu, 4 % Sn). In addition, WEEE also contain hazardous substances (heavy non ferrous metals, plastics) (Křištofová, 1998; Steinmann, 2000; EU-Richtlinie, 2001; Petraníková, 2007).

PCBs are typical basic construction components of EEE. They contain sufficient amounts of metals however their construction causes problems during metal recovery.

Electronic wastes can be principally treated by using several methods: pyrometallurgical, hydrometallurgical or combined. The most commonly used is the pyrometallurgical process involving combustion. Combustion is used for the removal of plastics and other organic materials and the subsequent concentration of metals. The crushed PCBs are burned in a furnace resulting in the production of a solid residue with elevated metal content. Plastics are burned out to generate either volatile compounds or slag containing refractory oxides. During this process some metals (i.e copper and lead) act as collectors for other metals. Thus, only alloys and not pure metals are obtained (Hornung et al., 2007).

Temperature is an important parameter during combustion. Combustion requires the presence of oxygen, mainly from the air, so that the temperature exceeds 1200°C. Most of plastics contain halogens and therefore degradation of hazardous gaseous emissions is ensured.

Antrekovitsch et al., (2006) compared pyrometallurgical, hydrometallurgical and elec-

trometallurgical processes for WEEE processing. From the point of view of pyrometallurgy they were focused on melting with its advantages and disadvantages, but not on combustion as a pretreatment step.

Tohka and Lehto (2005) studied the influence of mechanical WEEE treatment followed by a thermal processing step. This work, as in the previous case, was focused on high-temperature processes, whereby the formation of volatile combustion gases was discussed and useful compounds were recovered as melting products. By comparing pyrolysis and combustion authors proposed that the pyrolytic process should be applied before combustion and melting so that the hazardous volatile compounds were removed from the system. They also provided examples of hybrid industrial processes.

Hageluken (2005) presented an example of pyrometallurgical processing of WEEE applied in Umicore company.

Antonetti (2004) studied also the high-temperature recovery of metals from PCB composite materials using a fluidized furnace and oxygen as carrier gas. Several volatile compounds were identified and analyzed at specific temperatures and air flow rates.

However, it was found in the laboratory, that thermal treatment in the presence of oxygen caused problems due to imperfect combustion. That is why Huang Jianjun et al., (2004) applied plasma treatment to PCBs. The result of this process is the release of environmentally acceptable gaseous emissions and the production of a vitrified solid residue suitable for disposal.

Burkovic (2007) studied combustion of electronic waste using three types of wastes (connectors, crushed PCBs and connectors connected with polyethylene together with crushed wires). In the first case, the waste was first burned and then the resulting ash was melted with the addition of borax and charcoal. The products were then milled and sieved and the slag was separated from metals. In the second case, the slag was sieved after burning and only a metal fraction was melted. Part of precious metals went to ash and slag. The authors did not mention possible risks connected with the release of gaseous emissions after burning, since they did not reach the temperature required for hazardous substances degradation.

It is seen from the previous analysis that the

combustion of WEEE and especially PCBs can be achieved by using pyrometallurgical processes in the presence of air. Combustion as a possible pretreatment step for WEEE is not particularly mentioned. This work is focused on the study of the influence of combustion on the following hydrometallurgical step (leaching) aiming at recovery of copper and tin from thermally pretreated PCBs. Basically the present work studies a combined pyro - hydrometallurgical method for the treatment of PCBs present in used computers.

2. EXPERIMENTAL

2.1 Material

Seventy three kilograms of used PCBs were collected. The hazardous parts of PCBs were removed before crushing. Two kilograms of representative sample of crushed material was obtained by using an automatic sample divider. This sample was sieved into two fractions: -8+3 mm and -3 +0 mm. These products were chemically analyzed by AAS and the results are given in Table 1.

2.2 Combustion

Thermal pretreatment of crushed PCBs in the presence of air was carried out in the apparatus shown in Figure 1. PCBs were thermally pretreated at 300, 500, 700 and 900 °C for 15, 30 and 60 minutes. A 5 g sample was used for burning in each experiment. The sample was batched into a ceramic sample boat and fed into a quartz tube. Air was blown into the reactor by a laboratory pump. Gaseous and liquid products, generated during combustion, were trapped in a condensation system consisting of 5 washing flasks. Three of them were empty (safety reason) while the other two contained 0.5M solution of NaOH and 0.25M solution of H₂SO₄. The role of these solutions was to entrap the substances, which were part of gaseous emissions.

Table 1: Chemical composition of PCBs.

	Metal	Sn [%]	Cu [%]	Fe [%]
fraction [mm]	-8 +0	5.94	21.3	2.24
	-8 +3	1.32	8.62	0.19
	-3 +0	4.0	14.41	0.37

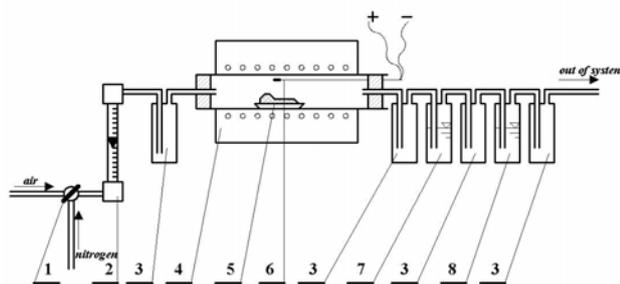


Figure 1: Thermal treatment apparatus. 1-tap, 2-volumeter, 3-empty bubbler, 4-laboratory furnace, 5-ceramic sample boat, 6- thermocouple, 7-NaOH solution, 8-H₂SO₄ solution.

2.3 Leaching

Leaching tests were carried out in the apparatus shown in Figure 2. Samples of 3 g without and after thermal treatment were leached in a glass reactor with constant stirring using 1 M solution of HCl at 80 °C for 180 minutes. The volume of the leaching reagent was 400 ml. Liquid samples were withdrawn at selected periods and analyzed by AAS to determine the content of copper and tin.

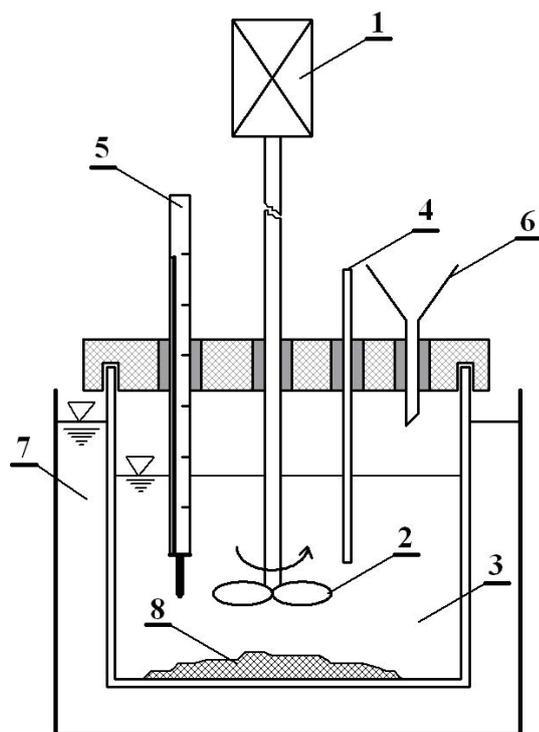


Figure 2: Leaching apparatus 1-stirrer engine; 2-propeller; 3-leaching pulp; 4-sampler; 5-thermometer; 6-feeder; 7-water thermostat; 8-crushed PCBs.

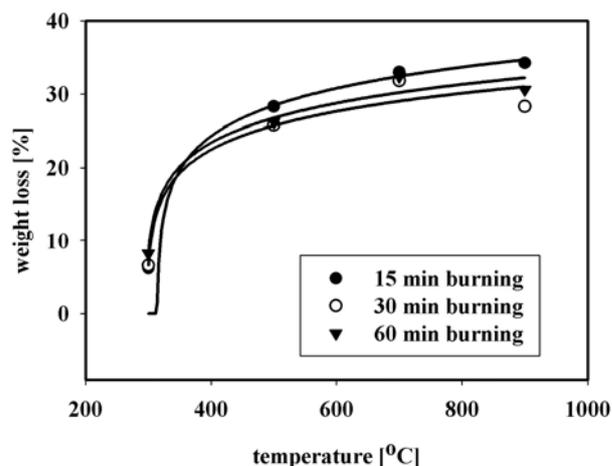


Figure 3: Weight loss of samples after combustion.

3. RESULTS

3.1 Combustion

Figure 3 shows the weight loss of samples after combustion at different temperatures and periods of thermal treatment. At combustion temperature of 300°C, less than 10 % of sample weight was lost; this is due to insufficient temperature for burning out plastics present in PCBs. With increasing temperature the weight loss increased and its highest value was observed at 900°C after 18 minutes of combustion. It should be mentioned that the difference between 900°C and 700°C after 15 minutes was negligible.

3.2 Leaching

3.2.1 Influence of combustion temperature on copper extraction

Figure 4 shows the kinetic curves of copper leaching for several fractions of crushed PCBs. It is seen from this figure that copper leaching is not only influenced by the different content of copper in the fractions (Table 1), but probably also by the contact area between leaching reagent and metal. In the crushed PCBs with a size fraction -3+0 mm more copper is evidently uncovered, which can be leached easily.

Figure 5 shows the kinetic curves of copper leaching of thermally pretreated PCBs in 1M HCl solution at different combustion temperatures in comparison with samples not subjected to thermal treatment. Copper extraction is comparable with that of the sample without thermal

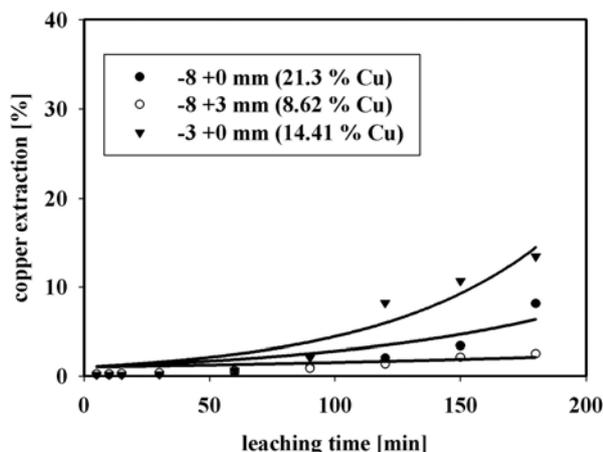


Figure 4: Kinetic curves of copper leaching from crushed PCBs for different grain sizes without thermal treatment.

treatment at combustion temperature 300 °C. This is due to the fact that at this temperature plastics do not burn and therefore copper is not uncovered from PCBs. After combustion at 900 °C practically all available copper was leached out.

The kinetic curves of copper leaching from PCBs in 1M HCl after 30 min of combustion at 700 °C are shown in Figure 6. Two fractions with different grain sizes were used in the leaching experiments, whereby the results of thermally treated and untreated samples can be compared. It is seen that grain size in the order of millimeters has no significant influence on extraction, although the difference between samples not subjected to thermal treatment is around 10 %. Copper extraction is significantly influenced when samples were burned. The overall extraction of burned samples is around 80 % and the difference between them is around 5 %. The increase of copper extraction for burned and unburned samples is significant, 70-

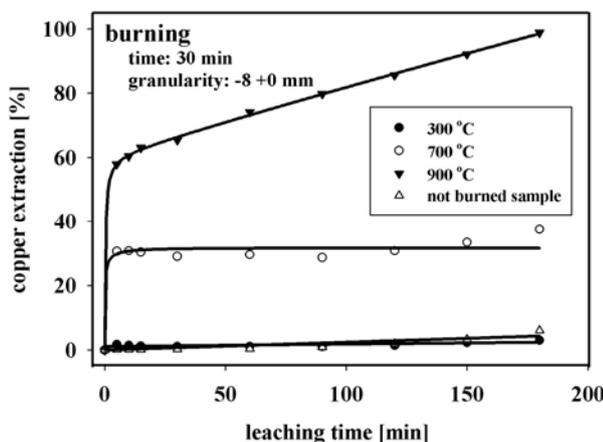


Figure 5: Kinetic curves of copper leaching from PCBs after combustion at different temperatures.

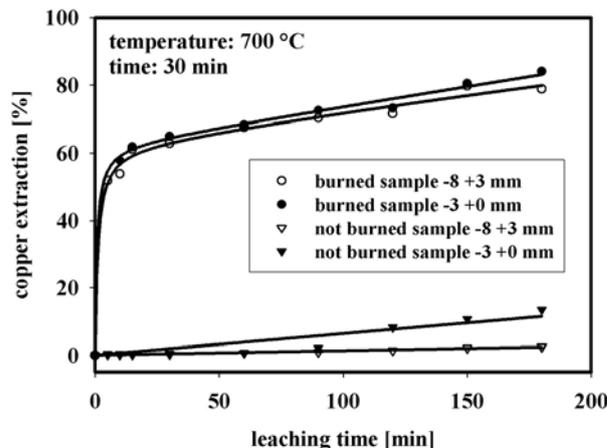


Figure 6: Copper extraction at combustion temperature 700 °C for both grain size fractions.

80 %.

Copper from unburned samples is not leached markedly, because HCl is a non-oxidizing acid and copper is leached significantly only in oxidative environments. Copper is oxidized to oxides during combustion; CuO is thermodynamically preferable than Cu₂O. Copper oxides in contrary to metallic copper are well leached in hydrochloric acid and this is a reason why copper is leached from burned samples (Figs. 5 and 6).

3.2.2 Influence of combustion temperature on tin extraction

Figure 7 shows the kinetic curves of tin leaching from individual fractions of crushed PCBs. The curves keep up the same trend as in the case of copper (Fig. 4), and this supports the statement regarding contact area between leaching reagent and metallic tin. Obviously, it seems that tin dissolves in HCl perfectly; also reached extractions are much higher as in the case of copper.

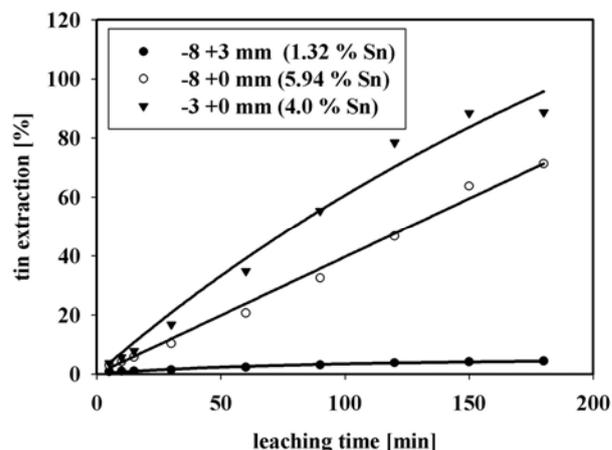


Figure 7: Kinetic curves of tin leaching from crushed PCBs at different grain sizes without thermal treatment.

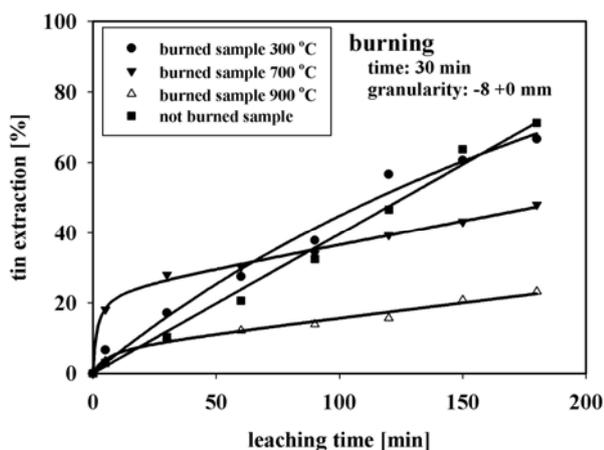


Figure 8: Kinetic curves of tin leaching from PCBs burned at different temperatures.

Figure 8 shows the kinetic curves of tin extraction from PCBs in 1 M HCl at different temperatures. For comparison, the kinetic curve of tin leaching from unburned PCBs is seen. Contrary to the case of copper, the increase of combustion temperature has a negative influence on tin leaching. Tin extraction of unburned samples is higher. Similar extraction was also achieved from a sample burned at 300 °C; this indicates that at this temperature there is no degradation and removal of plastics from the sample.

Figure 9 shows the kinetic curves of tin leaching in 1 M HCl from grain fractions -8+3 mm and -3+0 mm of burned and unburned PCBs. It is clear from this figure that contrary to copper, combustion has a negative impact on tin leaching, i.e. tin extraction decreased compared to unburned samples.

Because at 700 °C the organic substances are burned and removed from the charge (Fig. 3), it can not be deduced that these substances protect tin from the contact with the leaching reagent.

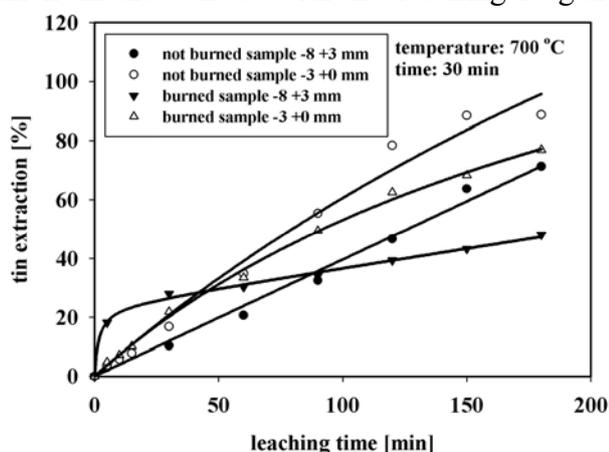


Figure 9: Tin extraction at combustion temperature 700°C for different fractions.

Just opposite, these metals are in better contact with the leaching reagent. It is seen from the previous analysis that after burning tin is oxidized preferentially to SnO₂. The resulting tin oxide is non volatile and covers the metallic tin or the present tin alloy respectively. This oxide is only slightly leached in HCl, as indicated by the low value of standard Gibbs free energy ΔG^0 of tin chloride. It is also possible that complex substances are produced in this system, but their formation is probably governed by lower reaction kinetics.

The results of tin leaching from burned and unburned samples of different granularity indicate that the kinetics of individual chemical reactions and the leaching mechanism play the most important role.

4. CONCLUSION

Thermal treatment at 300°C does not have any marked influence on the separation of plastics from PCBs, since most of them are thermally degradable at higher temperature. The maximum efficiency regarding plastics removal was 35 % at 900 °C after 15 minutes.

During leaching of thermally untreated samples it was observed that only some copper was leached; this is due to the fact that HCl is a non-oxidizing acid and theoretically copper can not be leached. The atmosphere contains oxygen which is an oxidizing agent. Moreover, copper is covered with plastics which prevent contact between metallic copper and the leaching reagent. This is the reason why crushing that uncovers the active surface has a positive effect on copper extraction.

Tin is located on the surface of PCBs and is in good contact with the leaching reagent. Burning oxidizes the surface and causes the formation of SnO₂ which is more difficult than metallic tin to leach in HCl solutions.

Higher copper extraction was achieved using burned samples. This is because plastics were removed, the reaction surface was enlarged and therefore metallic copper was transformed to oxide. Copper oxide is leached in HCl relatively good in comparison to metallic copper. Otherwise, the recovery of tin after PCBs burning seems less suitable, because during burning tin is oxidized and tin oxides are more stable than metallic tin in HCl solutions.

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REFERENCES

- Krištofová, D., 1998. Selected Hydrometallurgical Technologies for Recycling of Electronic Waste, *Acta Metallurgica Slovaca*, 4, 1/1998, 132- 133
- Steinmann, H., 2000. Stopp der E-Schrott-Flut, *Umweltschutz*, 2000, 12.
- EU-Richtlinie, 2001. Kampf den Müllbergen A3 Umwelt, 14, 1/2, .66-67
- Petraníková, M., 2007. Spracovanie vyradených osobných počítačov, DP, TUKE, Košice.
- Hornung, A., W. Koch and H. Seifer, 2007. Haloclean and Pydra-a dual stage pyrolysis plant for recycling WEEE, Dostupné na internete: <<http://www.bsef-japan.com/index/files/W.%20Koch%20%20%20%20HALOCLEAN%20&%20PYDRA.pdf>>[cit.2007/11/11
- Antrekowitsch, H., M. Potesser, W. Spruzina and F. Prior, 2006. Metallurgical recycling of electronic scrap, EPD Congress 2006, (Howard S.M. et al. eds.) TMS 2006, 899-908.
- Tohka, A. and H. Lehto, 2005. Mechanical and Thermal Recycling of Waste from Electric and Electrical Equipment, Energy Engineering and Environmental Protection Publications Espoo, TKK-ENY-25.
- Hageluken, Ch., 2005. Recycling of electronic scrap at Umicore's integrated metals smelter and refinery, Proceedings EMC 2005, GDMB, 1-16.
- Antonetti, P., 2004. Degradation products of the process of thermal recovery of copper from lamina scraps in lab-scale fluidized bed reactor, *Journal of Hazardous Materials B108*, 199-206.
- Huang Jianjun et al., 2004. DC Arc Plasma Disposal of Printed Circuit Board, *Plasma Science & Technology*, 6, 4, 2004, 2424-2426.
- Burkovič, R., 2007. Poznatky z pyrometalurgickej úpravy vybraných druhov odpadov z elektrotechnického a elektronického priemyslu, *Recyklace odpadu XI*.