



Hydrometallurgical treatment of used printed circuit boards after thermal treatment

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ABSTRACT

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

The leaching solution of 1 M HCl and temperature of 80 °C was used for the leaching. The original as well as thermally pretreated samples were leached under these conditions.

The weight losses within the range from 5% to 35% were achieved by burning depending on the burning temperature. 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%. The opposite effect was observed in the case of the tin leaching, where the highest extraction was achieved when the original sample was leached. The increase of the burning temperature caused the lowering of the copper extraction.

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1. Introduction

The demand for electric and electronic equipment (EEE) still increases at present time. This equipment, in comparison with other consumer products, is rather often exchanged and became to be waste. It results in a great amount of used EEE. The logical consequence is the effort to find and improve recycling of waste from electric and electronic equipment (WEEE).

The reasons that give rise to the treatment of WEEE lie in amount of this waste (in the European Union 6.5–7.5 million metric tons are generated every year, which represents 16 kg per inhabitant) as well as in the interesting content of metals (0.1% Au, 0.2% Ag, 20% Cu, 4% Sn). However, WEEE also contains hazardous substances (heavy non-ferrous metals, plastics) (Kristofova, 1998; Steinmann, 2000; EU-Richtlinie, 2001; Petranikova, 2008).

The printed circuit boards (PCBs) are a characteristic construction component of EEE. They contain interesting volumes of metals, but on the other hand, their construction caused problems in metal recovery processes.

Electronic waste can be principally treated by several methods: pyrometallurgically, hydrometallurgically or by combined methods. Typically, the pyrometallurgy is used, while combustion occurs. The 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 the slag phase with refractory oxides. During this process some metals (copper and lead) can behave like collectors of other metals. Thus, only alloys with unexpected composition are obtained, not pure metals (Hornung et al., 2007).

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. Such solution is described by several authors, for example Hall and Williams (2008), Wang et al. (2010), Mitan et al. (2007), Blazso and Czegeny (2006); Shareefdeen et al. (2002).

Antrekowitsch et al. (2006) compared pyrometallurgical, hydrometallurgical and electrometallurgical methods of WEEE treatment. From the pyrometallurgical point of view they concentrated on melting with its advantages and disadvantages, and not on combustion being a pretreatment step.

Tohka and Lehto (2005) studied the influence of the mechanical WEEE treatment with the subsequent thermal treatment step. The work, similarly to the previous one, 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

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of this process the hazardous volatile compounds are removed from the system. They also mention examples of hybrid industrial processes.

Hageluken (2005) presents the example of the pyrometallurgical treatment of WEEE in Umicore Company.

Also Antonetti et al. (2004) discuss the high-temperature method of the metals 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.

As laboratory research found that the thermal treatment with the presence of oxygen caused problems with imperfect combustion, Jiajun et al. (2004) 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 (2007) studied the combustion of electronic waste using 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, which are connected with the formation of gaseous emissions after burning, in case they did not reach the sufficient temperature for the hazardous substances degradation.

It follows from the above that WEEE combustion processes, especially PCBs, in the presence of air are considered as processes present in pyrometallurgical processes used for the melting of these wastes. The combustion as a possible pretreatment for subsequent recycling processes of WEEE is not particularly mentioned. That is the reason why this work is focused on the study of combustion influence on the subsequent hydrometallurgical recovery of copper and tin from PCBs by leaching. Basically a combined pyro-hydrometallurgical method of the treatment of printed circuit boards from used computers is considered.

2. Experimental part

2.1. Material

Seventy-three kilograms of used PCBs were collected. 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 automatic sample divider. This sample was sieved into two fractions: $-8+3$ and $-3+0$ mm. The obtained products were analyzed by chemical analysis using atomic absorption spectrometry (AAS). The results of the analysis are presented in Table 1.

The differences between individual fractions in composition are caused due to anisotropy and heterogeneity of analyzed samples and errors in AAS as well.

2.2. Combustion

The thermal pretreatment experiments of the crushed PCBs with the 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 with presence of air at 300, 500, 700 and 900 °C for the period of 15, 30 and 60 min. The weight of each sample used in the burning process was 5 g. The sample was batched into a ceramic sample boat and fed into a quartz reactor. The air was blown into the reactor during the experiments by a laboratory compressor. The gaseous and liquid products created during the combustion were trapped in a condensation system which consisted of five washing flasks. Three of them were empty (for the safety reasons) and 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 the 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.

3. Results and discussion

3.1. Combustion

Fig. 3 shows the weight loss comparison of samples after combustion at different temperatures and time of the thermal treatment. At combustion temperature of 300 °C, less than 10% of sample weight was removed. It is caused by insufficient temperature for burning out the plastics which are present in PCBs. With increasing the temperature the weight loss of samples increased, and the highest loss was observed at 900 °C after 18 min of combustion. It is necessary to mention that the difference between 900 and 700 °C after 15 min was inconsiderable.

3.2. Leaching

3.2.1. Influence of combustion temperature on copper extraction

Fig. 4 shows copper leaching curves of several fractions of crushed PCBs. From the figure it follows that the copper leaching is not influenced only by the different content of copper in fractions, Table 1, but apparently also by the contact between the leaching reagent and the metal. In the crushed PCBs particles with the fraction size of $-3+0$ mm more amounts of copper are evidently uncovered, which can be leached easily.

Fig. 5 shows copper leaching curves of thermally pretreated PCB samples in 1 M HCl at different combustion temperatures in comparison with samples without thermal treatment. The copper extraction is comparable with the sample without thermal treatment at combustion temperature of 300 °C. It is conspicuously caused by the fact that at this temperature the plastics do not burn, and therefore the copper is not uncovered from PCBs. After combustion at 900 °C practically all present copper was leached out.

The leaching curves of copper of PCBs in 1 M HCl after 30 min of combustion at 700 °C are shown in Fig. 6. Two different grain size fractions were used for the leaching experiments, while the results of thermally treated and thermally untreated samples were compared. It turned out that the grain size with order of millimeters has no significant influence on extraction, although the difference at samples without thermal treatment is about 10%. The copper extraction was significantly influenced by the fact

Table 1
Chemical composition of PCBs.

Metal		Sn [%]	Cu [%]	Au [%]	Ag [%]
Fraction	$-8+0$ mm	5.94	21.3	0.007	0.01
	$-8+3$ mm	1.32	8.62	0.020	0.05
	$-3+0$ mm	4.0	14.41	0.032	0.07

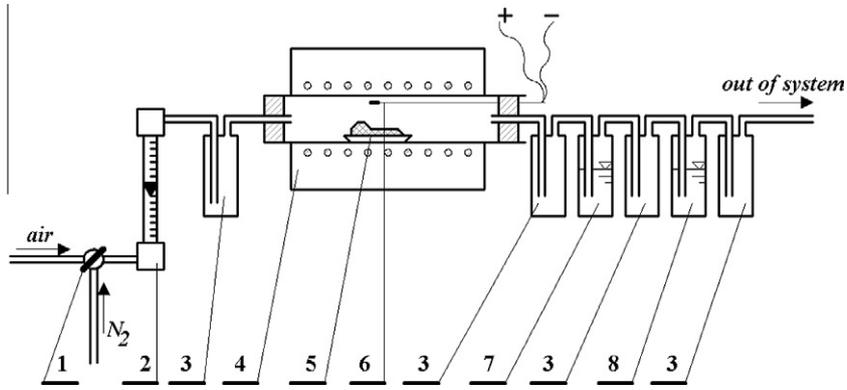


Fig. 1. Apparatus for thermal treatment 1-tap, 2-volumeter, 3-empty bubbler, 4-laboratory furnace, 5-ceramic sample boat, 6- thermocouple, 7-NaOH solution, 8-H₂SO₄ solution.

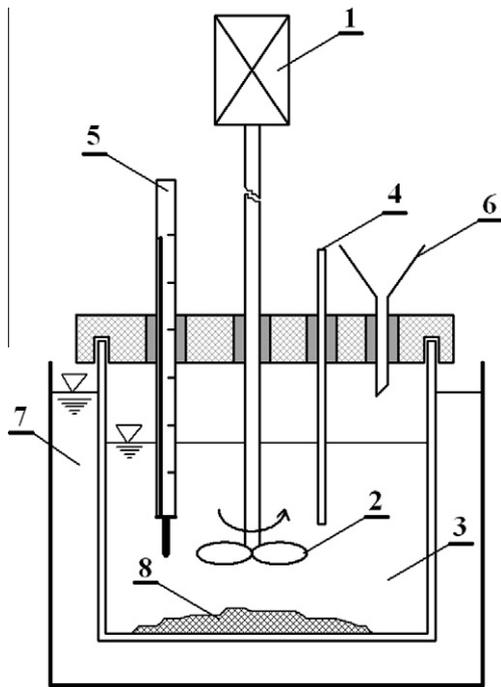


Fig. 2. The scheme of the leaching apparatus (Havlik, 2008). 1 – stirrer motor; 2 – propeller; 3 – leaching pulp; 4 – sampler; 5 – thermometer; 6 – feeder; 7 – water thermostat; 8 – crushed PCBs.

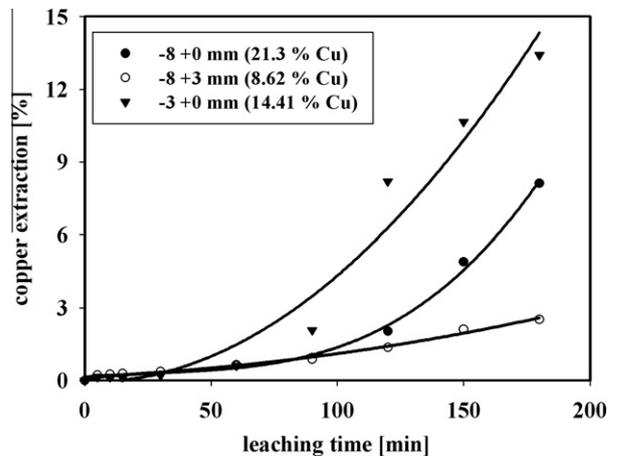


Fig. 4. Copper leaching curves of crushed PCBs at different grain size without thermal treatment.

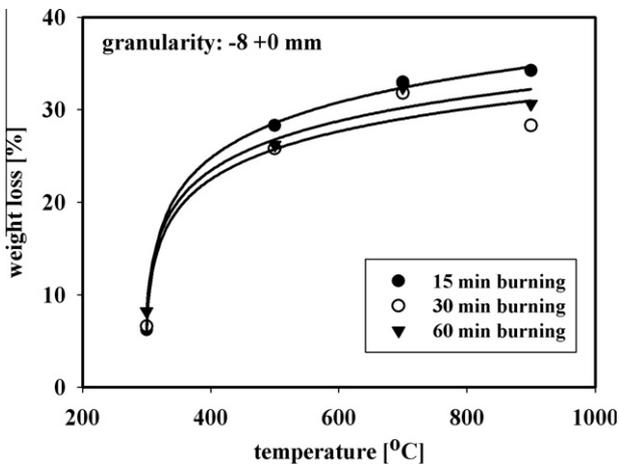


Fig. 3. The weight loss comparison of samples after combustion.

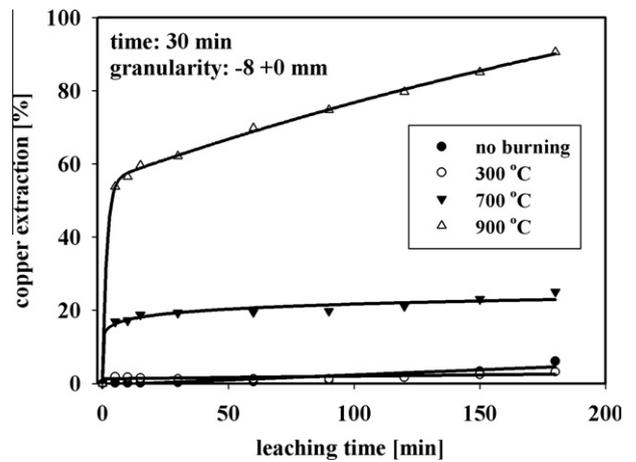


Fig. 5. Leaching curves of copper from PCBs after combustion at different temperatures.

whether samples were or were not burned. The overall extractions of the burned samples are about 80% and the difference between them is about 5%. The increase of the copper extraction for burned and unburned samples is significant, 70–80%.

Copper from the unburned samples is not leached markedly, which is logical, because HCl is a non-oxidizing acid and copper is leached significantly only in the oxidative environment. The

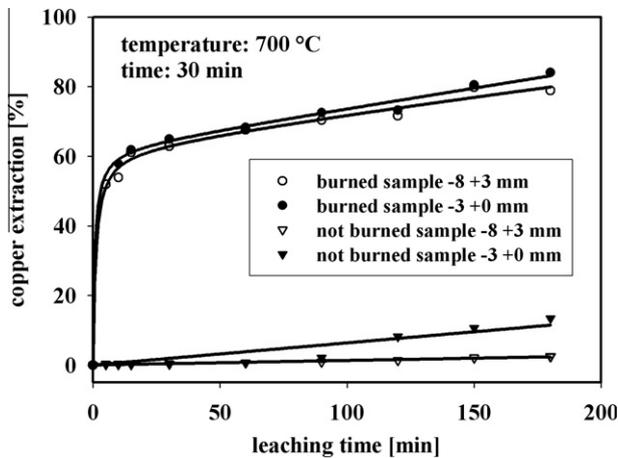


Fig. 6. The copper extraction at combustion temperature 700 °C for both grain size fractions.

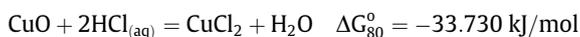
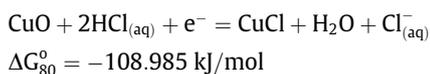
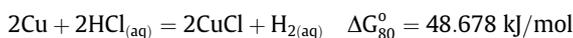
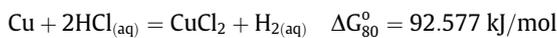
Table 2

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

T [°C]	$2\text{Cu} + \text{O}_{2(g)} = 2\text{CuO}$ ΔG° [kJ/mol]	$4\text{Cu} + \text{O}_{2(g)} = 2\text{Cu}_2\text{O}$ ΔG° [kJ/mol]
300	-103.062	-63.485
700	-68.504	-48.759
900	-51.822	-41.602

copper is oxidized to oxides during combustion; thermodynamically CuO is more preferable than Cu_2O . Table 2 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 the copper is leached out from burned samples, Figs. 5 and 6, while the ΔG° values for copper oxides leaching are negative.



3.2.2. Influence of combustion temperature on tin extraction

Fig. 7 shows leaching curves of the tin from individual fractions of crushed PCBs. The curves maintain the same trend as in the case of copper, Fig. 4; and this fact supports the considerations about the contact of leaching reagent to metallic tin. Obviously, as tin dissolves in HCl perfectly; and also reached extractions are much higher than in the case of copper.

Fig. 8 shows leaching curves of the tin from PCBs in 1 M HCl at different temperatures. Simultaneously, for the comparison the kinetic curve of the tin leaching from unburned PCBs is introduced. Contrary to the case of copper, the increase of combustion temperatures has a negative influence on the tin leaching. The tin extraction from the unburned samples is higher. Similar extraction was also achieved from the sample which was burned at 300 °C, which is given by the fact that at this temperature neither degradation of plastics nor their removing from the sample occurs.

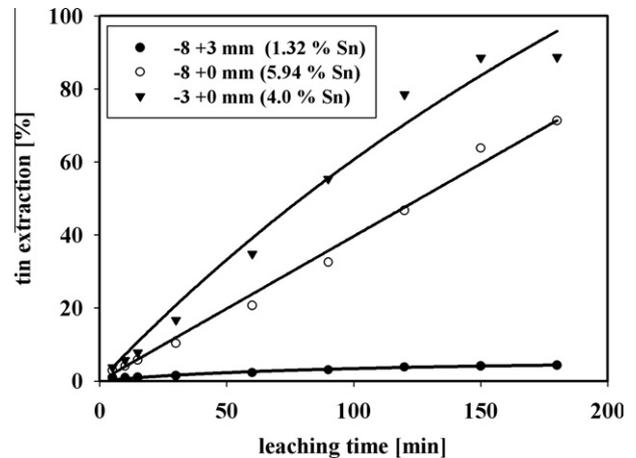


Fig. 7. Tin leaching curves of crushed PCBs at different grain size without thermal treatment.

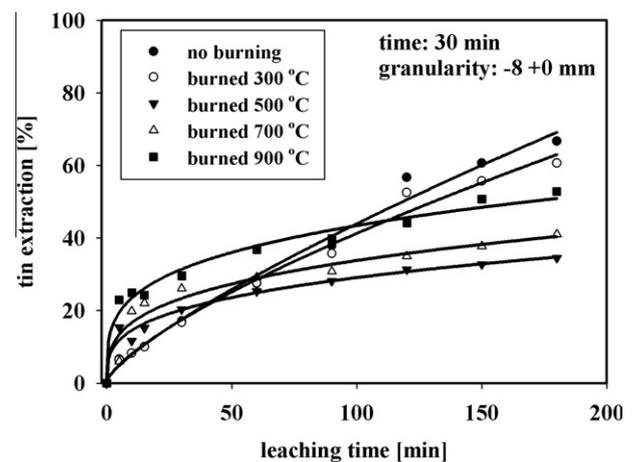


Fig. 8. Tin leaching curves from PCBs burning at different temperatures.

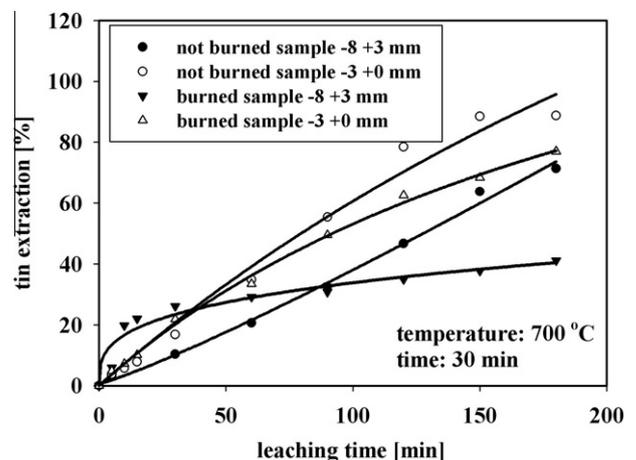


Fig. 9. The tin extraction at combustion temperature 700 °C of different fractions.

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

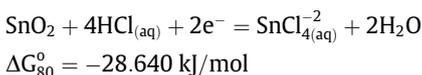
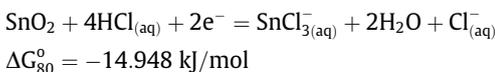
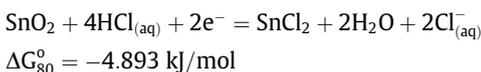
Table 3

The values of standard Gibbs free energy change, ΔG° , for tin oxidation at different temperatures.

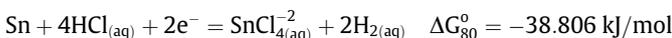
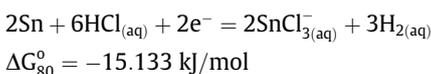
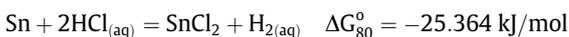
T [°C]	$2\text{Sn} + \text{O}_{2(\text{g})} = 2\text{SnO}$ ΔG° [kJ/mol]	$\text{Sn} + \text{O}_{2(\text{g})} = \text{SnO}_2$ ΔG° [kJ/mol]
300	–224.930	–463.279
700	–182.998	–379.289
900	–162.751	–338.464

However, at 700 °C organic substances are burned and removed from batch (Fig. 3). Thus it can not be supposed that these substances protect the tin from contact with the leaching reagent. Just opposite – it can be assumed that present metals are in better contact with the leaching reagent. It results that after burning there is a tin oxidation, from the thermodynamic point of view preferably to SnO_2 , as it is documented in Table 3.

The created oxide is nonvolatile and covers the metallic tin or the present tin alloy. However, this oxide is minimally leached in HCl, as it is proved by the low value of standard Gibbs free energy change ΔG° for the creation of stannic chloride. In this system also a creation of complex substances is possible, but their formation is probably followed by lower reaction kinetics.



The reaction of metallic tin with HCl is more expected than the reaction of tin dioxide, as it is shown by the following thermodynamic analysis.



The results of the tin leaching from burned and unburned samples, respectively, as well as with different granularity are the achieved values. Obviously, the kinetics of chemical reaction or leaching mechanisms also plays an important role.

4. Conclusion

At 700 and 900 °C the amount of removed plastics increases. The maximum plastics removal efficiency was 35% at 900 °C after 15 min while 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.

During the leaching of thermally untreated samples it was observed that copper is leached only in small amounts. It could be caused by the fact that HCl is a non-oxidizing acid and theoretically copper should not be leached. The outside atmosphere is always pulled down into the solution. The atmosphere contains oxygen, which works as an oxidizing agent. However, this effect was not studied in this work; this one is a challenge for future research. Moreover, copper is covered with plastics and they protect metallic copper from contact with the leaching reagent. This is the reason

why crushing has a positive effect on the copper extraction; to uncover the active surface, which becomes a part of the leaching process.

Tin is placed on the surface of PCBs and is in good contact with the leaching reagent. The burning process causes oxidization of the solder surface, and created SnO_2 is more difficult to be leached in HCl than metallic tin.

The higher copper extractions were achieved using burned samples. It is a consequence of the removal of plastics in order to enlarge the reaction surface and thus the reaction of metallic copper to oxide during burning. The copper oxide is leached in HCl relatively well, compared with metallic copper. On the contrary, the recovery of tin after PCBs burning seems less suitable, because during the burning process tin oxidizes, and tin oxides are more stable in HCl than the metallic tin. This work is a temporary part of project in framework of which the complex pyro–hydro processing of PCBs will be suggested.

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