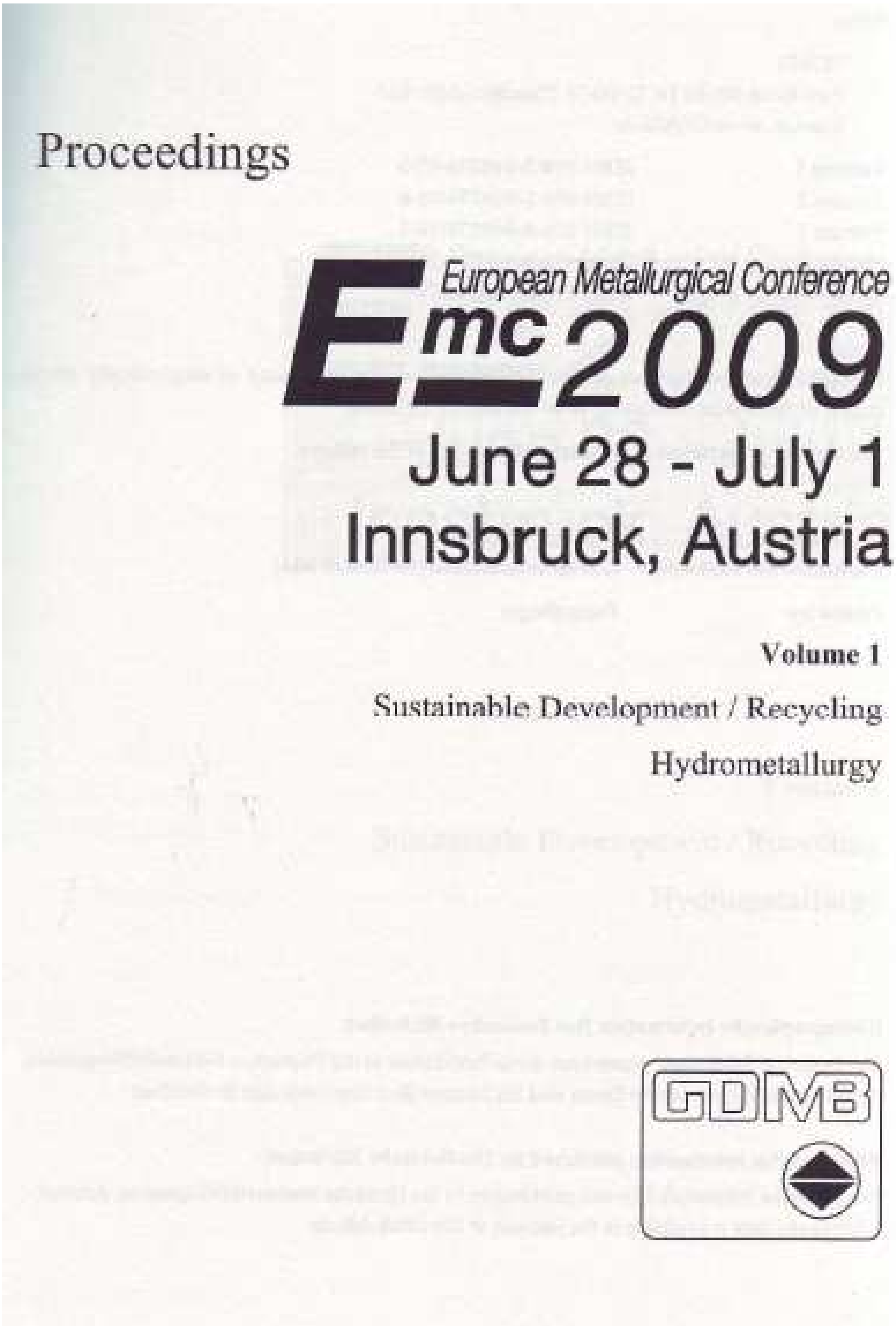
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Hydrometallurgical treatment of printed circuit boards from used computers after pyrolytic treatment

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Abstract

The hydrometallurgical route for tin and copper recovery from printed circuit boards (PCB) after pyrolytic treatment was studied in this work. The fractions of crushed PCB of -8 +0, -8 +3, -3 +0 mm were used for leaching experiments, before of which the samples were submitted to pyrolytic pretreatment at 300, 500, 700 and 900 °C for 15, 30, 60 minutes.

The leaching experiments were realized in 1M solution of HCl at 80 °C. The samples with and without pyrolysis were introduced to leaching.

The sample mass losses after pyrolysis were from 10 to 30 % depending on temperature of pyrolysis. The increasing of pyrolysis temperature increases an extraction of copper and tin leaching. By leaching of sample without thermal treatment the highest extractions of copper 6 % and of tin 68 % were achieved, whereas by leaching of pyrolysed sample the extractions of copper 63 % and tin 98 % were achieved.

Keywords: WEEE, electronic waste, printed circuit boards, pyrolysis, leaching, HCl

Introduction

Electrical and electronic equipments (EEE) belong to daily life and at the end of their life cycle become a waste. This material contains lots of valuable components, so it should not be taken as a waste, but as a valuable secondary raw material. The reasons, which might play a role in processing of waste from electrical and electronic equipments (WEEE), are followed:

- the amount (in EU: 6.5 – 7.5 millions of tons are being generated annually)
- the metal content (0.1 % Au, 0.2 % Ag, 20 % Cu, 4 % Sn)

- the content of substances, which could have hazardous character like heavy non – ferrous metals and plastics

For instance, the gold content in the primary source vary within 2 – 5 g/t, what is hundred times less than in EEE [1 – 3].

Most of the EEE contains printed circuit boards (PCBs). Special attention is paid to these PCBs, because they contain the interesting content of metals. On other hand, their construction causes the problems in recycling processes.

Electronic waste could be principally processed by pyrometallurgical or hydrometallurgical method or by combination both of them. Pyrometallurgical processing in copper smelter plants is the mainly used method for processing of electronic waste. The plastics present in waste cause a problems, because of their big amount and for formation of hazardous substances during process. Even though, the thermal processing is one of the most effective method for metals recovery and therefore new ways, how to optimized and make this process effective, are studying and searching. The suitable methods for this purpose look processes of pyrolytic treatment.

The pyrolysis is a method for thermal degradation of organic materials without presence of gasifying media like oxygen, air, carbon dioxide and water vapor, etc. The advanced saturated hydrocarbons fission during pyrolysis and lower unsaturated products are created [4]. The nitrogen and argon are used for generation of inert atmosphere. Three fractions are resulting from the process:

- Solid phase, where the metals are concentrated;
- Tar liquid fraction;
- Gaseous phase, which could contain also the volatilized metal compounds.

The advantage of pyrolysis is also in possibility of usage of the liquid products in chemical or energetic industry. The metals after pyrolysis stay in their original form, as in the waste, because the oxidation is depressed.

Two recycling pyrolytic processes are used presently, namely Pyrocom and Haloclean. Pyrocom process operates at temperature around 700 °C, whereby two products are obtained. The first one contains HCl, HBr, H2O, CO, CO2, phenol and the second one ceramics, glass and metals. The gaseous fraction is showered by water; metal dust is separated in filter and it is treated in order to recover metals. Gaseous phase is cooled; advanced hydrocarbons are removed, so emissions mainly consist of polluted air [5].

The aim of Haloclean process is to obtain fuel without halogens and solid residue with metals. Authors [6] used in their experiments batch with content of gold 300 g/t and bromine 5 %. They achieved two times higher concentration of gold after pyrolysis in residue. The used time of whole process was from 1 – 4 hours and the results are three fractions: HBr, oil without bromine and solid phase with metals.

In the work [7], most of the plastics were removed pyrolytically, what represents 30 % of mass sample loss. They achieved suitable batch for copper converter with lower content of plastics. Creation of hazardous substances was eliminated.

In the work [8], PCBs were crushed to -4.4 +0.7 mm and pyrolysed at temperature 200 °C and 500 °C. The metals stayed in solid residue and halogens from bromine flame retardants went in most to gaseous product. Gaseous product was cleaned in water, at which halogens were leached out, what allowed utilizing tar as a fuel.

Antimony is present in flame retardants as SbBr3. This compound vaporized during pyrolysis at temperatures 550 – 850 °C. It hydrolyzed after contact with water or CO2 to Sb2O3 and is caught on filter.

Printed circuit boards contains large amount of copper and tin. Hence, the aim of this work is to study the possibility of copper and tin leaching after pyrolytic treatment of PCBs.

2. Experimental

2.1 Material

Before experiments 73 kg of used printed circuit boards were collected. The hazardous parts were removed manually from PCBs and dressed PCBs were crushed by using of the hammer crusher. The representative sample of 2 kg was obtained by automatic sample divider. This sample was sieved to fractions -8 +3 and -3 +0 mm. The obtained products were chemically analyzed by AAS method, Tab 1.

Table 1: Chemical composition of PCBs

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

2.2 Pyrolysis

The pyrolysis was carried out in the laboratory apparatus the scheme of which is shown in Fig 1. The crushed printed circuit boards were pyrolysed at 300 °C, 500 °C, 700 °C and 900 °C for 15, 30 and 60 minutes. The weight of each sample was 5.2 g. The ceramic sample boat was charged with sample and put into reactor. The nitrogen gas for saving of inert atmosphere, which is needed for pyrolysis, was used. Gaseous and liquid products, created during process, were captured in the condensation system, consisting of five rinsing flasks. Three of them were empty (safety reason) and inside of other two the solutions of 0.5M NaOH and 0.25M H_2SO_4 were placed. These solutions absorbed the soluble substances from gaseous emissions.

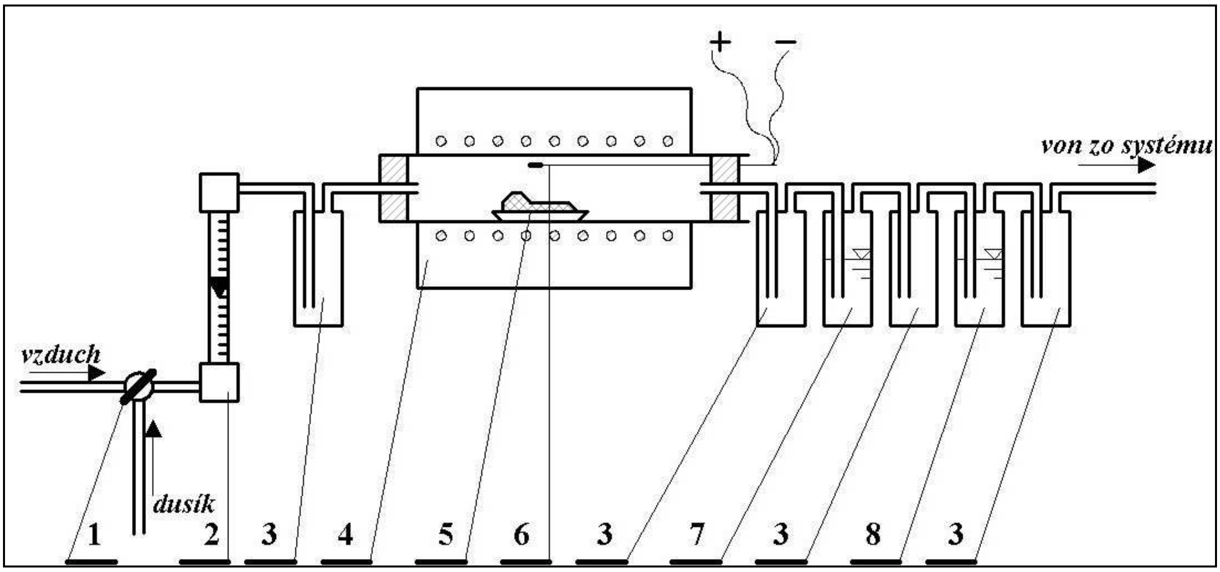

Figure 1: The scheme of the laboratory apparatus for thermal treatment

1-tap, 2-volumeter, 3-empty bubbler, 4-laboratory furnace, 5-ceramic boat, 6- thermocouple, 7-NaOH solution, 8-H_2SO_4 solution

2.3 Leaching

Leaching was realized in the apparatus, scheme of which is shown in Fig 2. Both samples, pyrolysed and without pyrolysis, were leached in 1M HCl for 180 minutes at 80 °C with constant stirring. The volume of 400 ml leaching solution and sample weight of 3g were used in each experiment. The liquid samples were taken according to given time schedule at 5, 10, 15, 30, 60, 90, 120, 150 and 180 minutes. The samples were analyzed by AAS method for copper and tin amount.

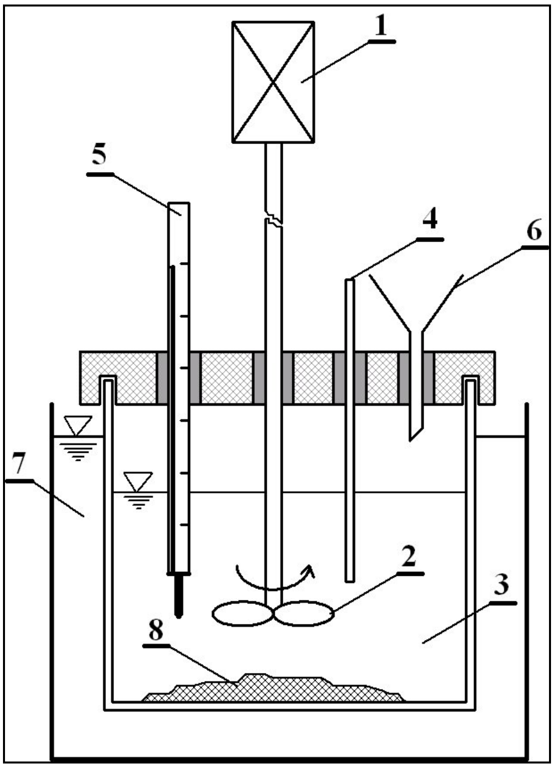

Figure 2: The scheme of the leaching apparatus (1 – stirrer engine; 2 – propeller; 3 – leaching pulp; 4 – sampler; 5 – thermometer; 6 – feeder; 7 – water thermostat; 8 – crushed PCBs)n

3.1 Pyrolysis

Fig. 3 shows the temperature dependences of sample weight losses after pyrolysis in various times. It follows from the picture, that process is relatively fast and duration of pyrolysis has particularly no influence to amount of vaporizing substances. The process is relatively slow at 300 °C because of the fact, that the plastics are mostly degraded above 300 °C. The efficiency of volatility increased with increasing of temperature. The highest efficiency is achieved around 30 %, but it is apparent, that temperatures around 500 °C and time around 15 minutes are sufficient for effective removal of volatile compounds of PCB, represented mostly by present plastics.

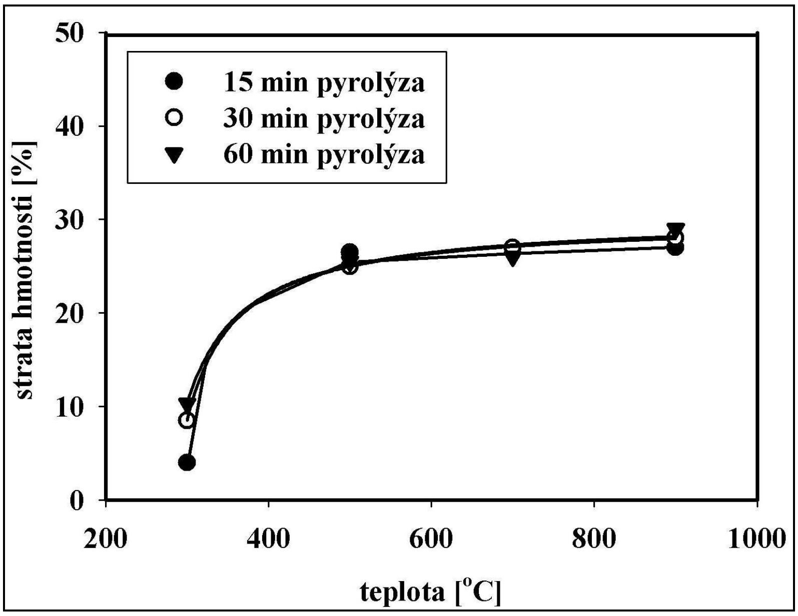

Figure 3: The temperature dependence of weight losses after pyrolysis

3.2 Leaching

3.2.1 The copper extraction influenced by pyrolysis

Fig 4 shows the kinetic curves of copper leaching from residue after pyrolysis of printed circuit boards in 1M HCl at different temperatures of pyrolysis comparing to original sample without thermal treatment. It follows from the graph, that pyrolysis at 300 °C has no significant influence to increasing of copper dissolution by leaching in compare with sample without thermal treatment. The increasing of pyrolysis temperature increases the extraction of copper into solution. The highest extraction was achieved at temperature of pyrolysis 900 °C.

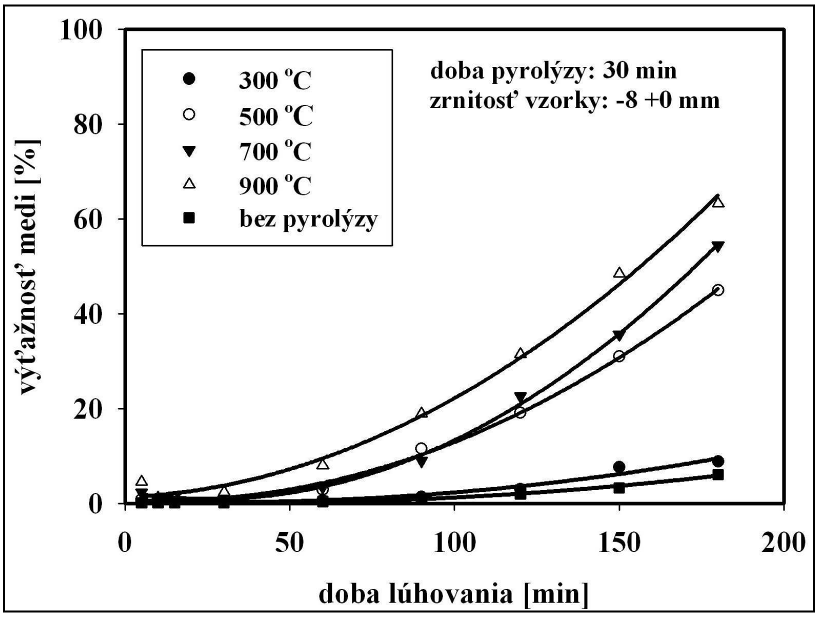

Figure 4: Copper extraction at different pyrolysis temperatures in compare with sample without thermal treatment

Fig 5 shows the kinetic curves of copper leaching after pyrolysis of two fractions (*-8 +3 mm, -3 +0 mm*) PCBs at 700 °C. It is evident, that pyrolysis has positive effect on transfer of copper into solution for both granular fractions. At the same time, the influence of specific surface was apparent – the smaller granularity represents bigger surface and that is why also more copper was transferred into solution at the same time.

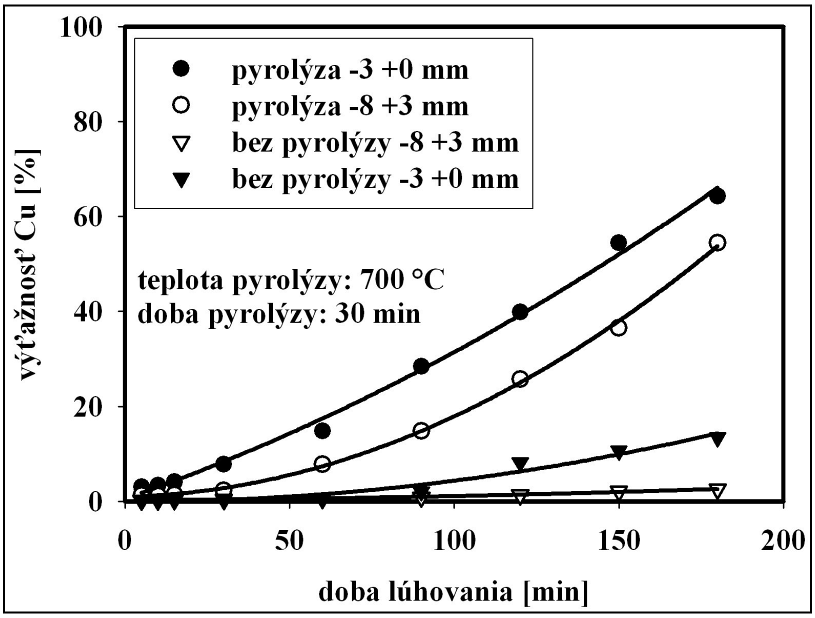

Figure 5: Kinetic curves of copper leaching from PCBs

3.2.2 The tin extraction influenced by pyrolysis

Fig 6 shows the kinetic curves of tin leaching from PCBs residue after pyrolysis in 1M HCl at different temperatures of pyrolysis in compare with sample without thermal treatment. Analogous to copper, the extraction of tin into solution of thermal treated sample at 300 °C was comparable with extraction of sample without thermal treatment. The increasing of pyrolysis temperature increases the extraction of tin into solution. The optimum tin extraction was achieved at the pyrolysis temperature of 500 °C and further increasing of pyrolysis temperature was not effective

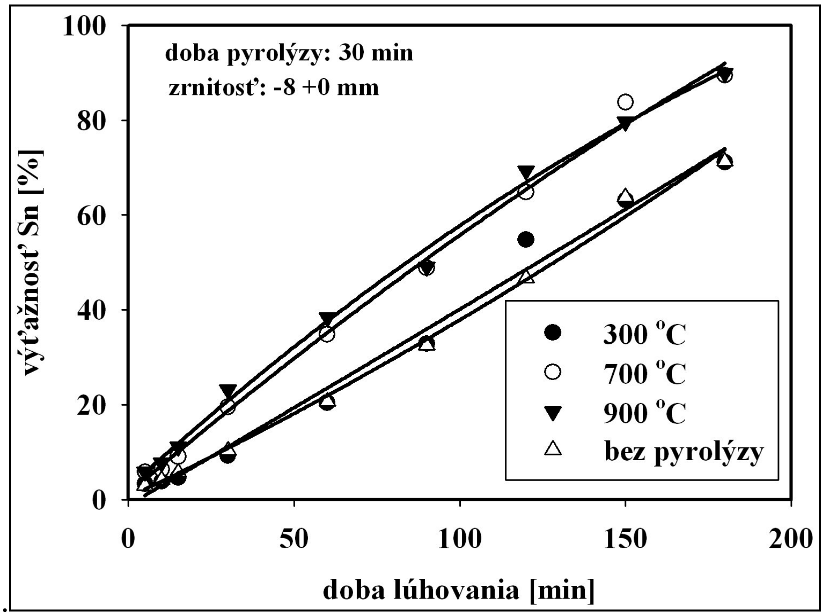

Figure 6: Tin extraction at different pyrolysis temperatures in compare with sample without thermal treatment

Fig. 7 shows kinetic curves of tin leaching in 1M HCl of two different granularity samples, *-8 +3 mm* and *-3 +0 mm*, after pyrolysis and without pyrolysis. It follows from the graph, in contrary to copper extraction, that pyrolysis has essentially no influence for tin dissolution. The similar tin extraction is achieved by leaching of samples without thermal treatment.

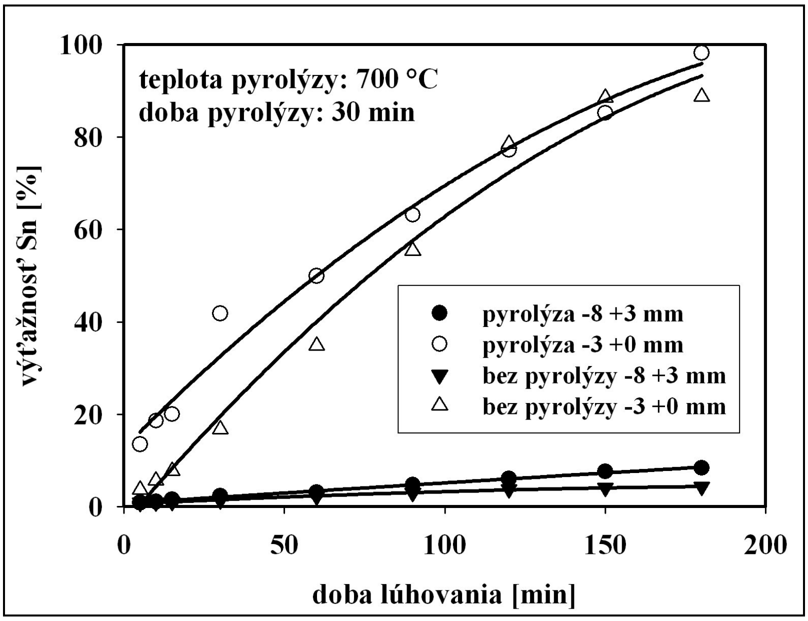

Figure 7: Tin extraction of different fractions at pyrolysis temperature 700 °C

4. Conclusion

In this work the possibility of thermal pretreatment of printed circuit boards from used computers by pyrolysis before hydrometallurgical treatment was studied.

Printed circuit boards are basically composite material, where copper and other components are mainly covered with plastics, which are mostly insoluble in inorganic acids. That is why the possibility of plastics removal from required components by pyrolysis, i.e. to volatilized them at elevated temperature without present of air was studied.

Pyrolysis at 300 °C has no effect to material behavior during leaching, because lots of plastics changed above this temperature. The higher temperatures of pyrolysis caused increasing amount of plastics removal.

The leaching of samples without thermal treatment confirmed difficult connection between plastics and copper, because its extraction into solution was around 6 % in compare with tin, where the extractions achieved 70 %. Tin is a part of solders and they are applied at the surface of PCBs. This fact ensures higher probability, that tin will come to contact with leaching reagent.

During leaching experiments of PCBs with aim to recover copper was find out, that pyrolysis has positive effect to copper extraction. At temperature 300 °C extractions were similar with samples without thermal treatment, what confirms the fact, that pyrolysis at this temperature has no influence to plastics removal. The increasing of pyrolysis temperature increases the copper extraction, whereby in dependence on temperature of pyrolytic pretreatment were achieved extractions of copper into solution from 40 to 80 %. The granularity has also effect on leaching; at smaller grain size (i.e. larger surface) higher extraction were achieved.

Temperature of pyrolysis 300 °C has, similarly as in copper case, no influence to tin leaching into solution. The increasing of pyrolysis temperature increased also tin extraction. At temperatures above 500 °C, the increasing of pyrolysis temperature has small effect to recovery of tin into solution. After 3 hours of leaching were achieved tin extractions into solution around 90 % and the tendency is of curves is progressive. It means that prolongation of leaching time would result in all dissolution of tin into solution.

The leaching of different granular fractions after thermal treatment and without thermal treatment of PCBs did not find out significant effect of pyrolysis process to tin extraction into solution, what confirm the fact, that practically all tin contained in sample will be in contact with leaching reagent.

Acknowledgement
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