

ACIDIC LEACHING OF COPPER AND TIN FROM USED CONSUMER EQUIPMENT

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Abstract

This work is focused on studying thermal pretreatment and leaching of copper and tin from printed circuit boards (PCBs) from used consumer equipment. Thermal treatment experiments were realized with and without presence of oxygen at 300 °C, 500 °C, 700 °C and 900 °C for 30 minutes. Leaching experiments were performed at 80 °C in 2M HCl in two stages. The first stage consisted of classic leaching experiments of samples without and after thermal treatment. The second stage consisted of oxidative leaching experiments (blowing of air or oxygen) with the aim to intensify metals leaching. The results of thermal treatment experiments show that maximal mass loss after burning (combustion) was 53 % (700 °C) and after pyrolysis 47 % (900 °C). Oxidative leaching resulted in complete dissolution of copper and tin after 60 or 90 minutes of thermally treated samples. Pyrolysis and combustion have positive effects on metals dissolution in comparison with samples without thermal pretreatment. Moreover, the dissolution of metals is more effective and needs shorter leaching time.

Keywords: Recycling; Consumer equipment; Leaching; Thermal pretreatment; Copper; Tin.

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). Worldwide, the highest market share is represented by large household appliances (43 %), followed by IT and telecommunications equipment (40 %), consumer equipment (8 %, television sets, radio sets, video cameras, etc.), small household appliances (3 %) and electrical and electronic tools (3 %) [1].

In the European Union approximately 8 million metric tons of WEEE are generated every year with annual increases of 3 – 5 % [2]. In the whole world approximately 20 to 50 million metric tons of WEEE are generated annually. This amount of waste is considerable not only for its quantity, but also because of dangerous substances such as heavy metals and plastics. Nevertheless, 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 raw materials is 2 – 5 g.t⁻¹, which represents hundreds of times less than in EEE. It follows that WEEE should not be regarded as waste

but as a valuable secondary raw material [3].

At present, most scientific papers [4 – 21] focus on processing of printed circuit boards (PCBs) from used computers. The main reason is that these boards contain interesting quantities of metals and are regarded as a “high grade” secondary raw material. Printed circuit boards are not only present in personal computers but are now widespread in almost all devices such as televisions, monitors, radios and others (4th category of WEEE: “consumer equipment”).

The content of valuable metals in “consumer equipment”, considered as “low grade” secondary raw material [22], is not as high as in “high grade” material (Table 1). The result is that higher attention is paid to processing of PCBs from used computers. On the other hand, the content of metals in “low grade” material is still much higher than in primary raw material (ore), which clearly indicates the necessity for treatment of this secondary raw material.

WEEE is essentially a composite material consisting of a mixture of various metals, plastics, ceramics, etc.; therefore its processing is complex. In principle it can be processed by pyrometallurgical, hydrometallurgical or combined methods. Most of the WEEE is processed by the pyrometallurgical method in aggregates for copper smelting. Plastics contained

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in WEEE pose a problem because of their large amount and potential generation of hazardous volatile substances within the process. Nevertheless, thermal processing is one of the most effective ways of metal recovery and therefore new ways for improving this process are searched. In this regard, WEEE can be either thermally processed in the presence of air, alternatively oxygen (i.e. burning/combustion), or in absence of oxygen (i.e. pyrolysis).

Table 1. Average content of metals in ores, high grade material and low grade material [22 – 25]

	Content / mass-%		
	Ores	High grade material	Low grade material
Fe	30 – 55	4.5 – 20	23 – 62
Cu	0.5 – 1.0	7 – 20	3.4 – 21
Al	25 – 30	1 – 14	1 – 10
Pb	0.5 – 15	0.3 – 6	0.2 – 1
Sn	< 1	2.9 – 4.9	0.72 – 1.4
	Content / ppm		
	Ores	High grade material	Low grade material
Au	5 – 7	16 – 566	10 – 20
Ag	5 – 7	189 – 1380	115 – 280
Pd	3 – 5	3 – 210	4 – 10

This work is focused on the effect of thermal pretreatment on subsequent hydrometallurgical processing of copper and tin from printed circuit boards from consumer equipment by leaching in two stages. The first stage consists of the classical leaching; the second stage consists of oxidizing leaching. As oxidizing reagents air and oxygen were used. The reason is that these reagents were not used in scientific papers for printed circuit boards leaching up to the present.

2. Experimental part

2.1 Material

The input sample consisted of pieces of equipment (Figure 1), which were classified according the Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on waste electrical

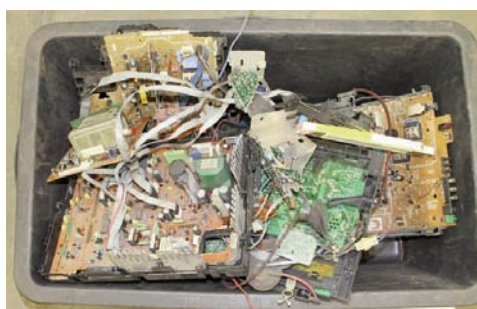


Figure 1. Input material for mechanical pretreatment experiments

and electronic equipment (WEEE) in the 4th category “consumer equipment”. After mechanical and physical pretreatment (Figure 2), sub-sampling was realized to obtain representative samples for chemical analysis. Chemical analysis of sample after mechanical and physical pretreatment was realized using atomic absorption spectrometry (AAS) the result of which is presented in Table 2.

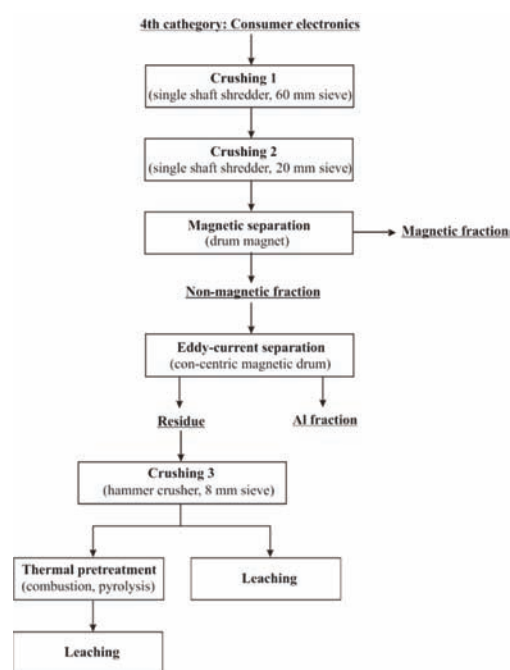


Figure 2. Overall scheme of realized experiments

Table 2. Chemical analysis of material after mechanical and physical pretreatment

Metal	Cu	Sn	Pb	Fe	Au	Ag	Al	Zn
Content [%]	26.37	3.12	1.57	0.21	0.002	0.01	3.85	1.3

2.2 Mechanical and physical pretreatment

Mechanical pretreatment the input material (Figure 2) of consisted crushing in two stages using a single shaft shredder with different discharge grates. These steps were carried out for initial liberation of materials from composites with a discharge grate of 60 mm and further comminution in preparation for sorting operations that require smaller particles sizes (discharge grate of 20 mm). Crushing was followed by magnetic separation, where the magnetic fraction was removed by a drum magnet. The non-magnetic fraction was further processed by electrodynamic separation using a con-centric eddy-current separator for which two fractions were obtained (Al fraction and residue) [25].

Because of their shape it is expected that wires that

largely contain copper and tin attachments from soldering connections and particles with similar shapes accumulate in the residue from eddy-current separation. These particles are neither removed during magnetic separation, as they are not magnetizable, nor during eddy-current separation, because they lack a minimum inductivity for sufficient separation forces to occur due to their small cross sectional area. Due to the presence of copper and tin the residue fraction presents a viable source, while these and other non-ferrous metals are naturally present in the non-ferrous fraction from eddy-current separation. Therefore, this fraction was used for thermal pretreatment and leaching experiments.

The residue fraction was transferred to a hammer crusher (8 mm discharge grate) to yield a fraction $-8 +0$ mm (Figure 3). The reduction of particle size is necessary in preparation for metallurgical treatment, as described in the following.

Figure 4 shows cumulative curves of material after Crushing 1, 2 and 3. From the graph the effect of particle size reduction can be clearly seen.

2.3 Thermal pretreatment

Thermal pretreatment experiments of material with and without presence of air were carried out in a



Figure 3. Input material used for experiments (20x zoom)

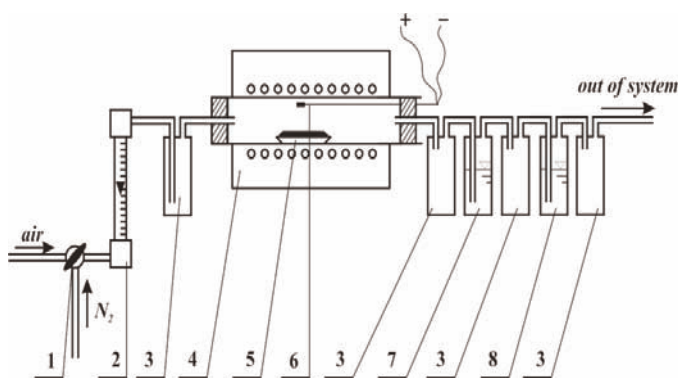


Figure 5. The scheme of the apparatus for thermal treatment: 1 – tap, 2 – volumeter, 3 – empty bubbler, 4 – laboratory furnace, 5 – ceramic sample boat, 6 – thermocouple, 7 – NaOH solution, 8 – H_2SO_4 solution

laboratory apparatus, the scheme of which is shown in Figure 5. The crushed material was thermally pretreated at 300 °C, 500 °C, 700 °C and 900 °C for a period 30 minutes. The sample was batched into a ceramic sample boat and fed into a quartz reactor. During the experiments either nitrogen ($100 \text{ dm}^3 \cdot \text{h}^{-1}$) from a pressure cylinder or air ($100 \text{ dm}^3 \cdot \text{h}^{-1}$) 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 5 washing flasks. The role of these solutions was to entrap the substances, contained in gaseous emissions.

2.4 Leaching

Leaching experiments were carried out in the apparatus shown in Figure 6. Experiments were realized in glass reactors with a volume of 800 ml immersed in a water bath at 80 °C using constant stirring. A water solution of hydrochloric acid with

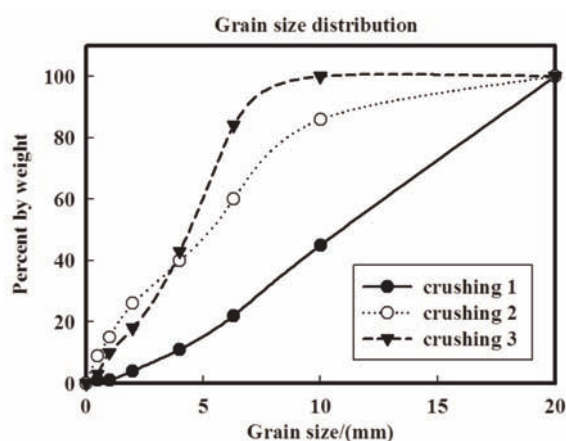


Figure 4. Cumulative curves of material after crushing

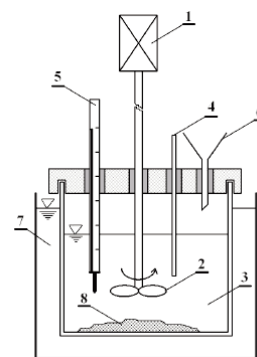


Figure 6. The scheme of the leaching apparatus [26]: 1 – stirrer engine; 2 – propeller; 3 – leaching pulp; 4 – sampler; 5 – thermometer; 6 – feeder; 7 – water thermostat; 8 – sample

2M concentration was used as leaching reagent. The volume of the leaching reagent was 400 ml and the weight of each sample was 10 g which results in liquid-to-solid ratio (L:S) of 40. The total duration of each experiment was 120 minutes. During experiments liquid samples (10 ml) were withdrawn after 5, 10, 15, 30, 60, 90 and 120 minutes, and were analyzed by atomic absorption spectrometry (Varian Spektrometer AA 20+) to determine the content of copper and tin. All results were corrected for volume change and evaporation.

Experiments were realized in two stages. In the first stage experiments without an oxidation reagent were carried out for:

- Samples without thermal pretreatment with grain size of $-8 +0 \text{ mm}$ and $-1 +0 \text{ mm}$
- Samples after thermal pretreatment (pyrolysis, combustion)

Subsequently, on the basis of obtained results from first stage experiments with an oxidation reagent (blowing of air and oxygen) were realized for:

- Samples without thermal pretreatment with grain sizes of $-8 +0 \text{ mm}$ and $-1 +0 \text{ mm}$
- Samples after thermal pretreatment at 700°C (pyrolysis, combustion)

3 Results and discussion

3.1 Thermal pretreatment

Figure 7 shows the weight loss comparison of samples after combustion as well as after pyrolysis at different temperatures of thermal treatment.

At a temperature of 300°C , less than 20 % of the sample weight was removed. This temperature is insufficient either for vaporization or for burning out the plastics which are present in the sample. This fact can be seen in Figure 8a and 9a. With the increase of temperature the weight loss of samples increased what caused gradual metals liberation from material (Figure 8a-d and 9a-d). The highest loss of about 53 % after combustion at 700°C and 47 % after pyrolysis at

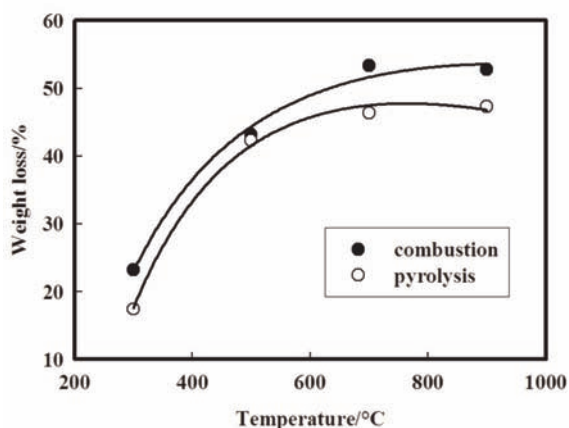


Figure 7. Temperature dependence of weight losses after burning and pyrolysis

900°C was observed. The difference between 700°C and 900°C for pyrolysis was only 1 %.

Using combustion, higher weight losses were achieved, the difference is around 7 %. During combustion the burning of plastics occurs and gaseous products are created, which apparently are released easier than volatile compounds released from plastics during pyrolysis. Moreover, weight loss after combustion can be higher due to formation of oxides which resulted in an increase of weight.

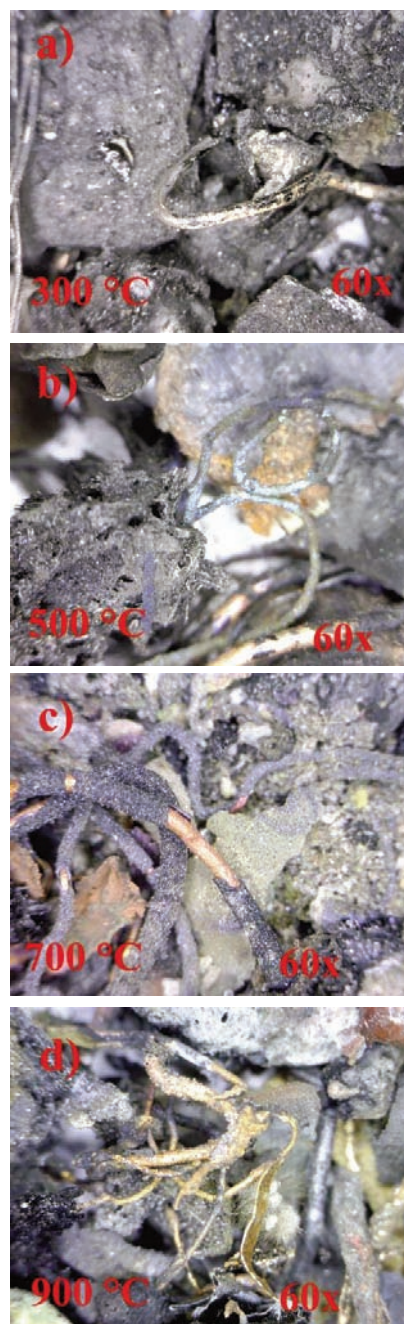


Figure 8. Samples after combustion at different temperatures (60x zoom)

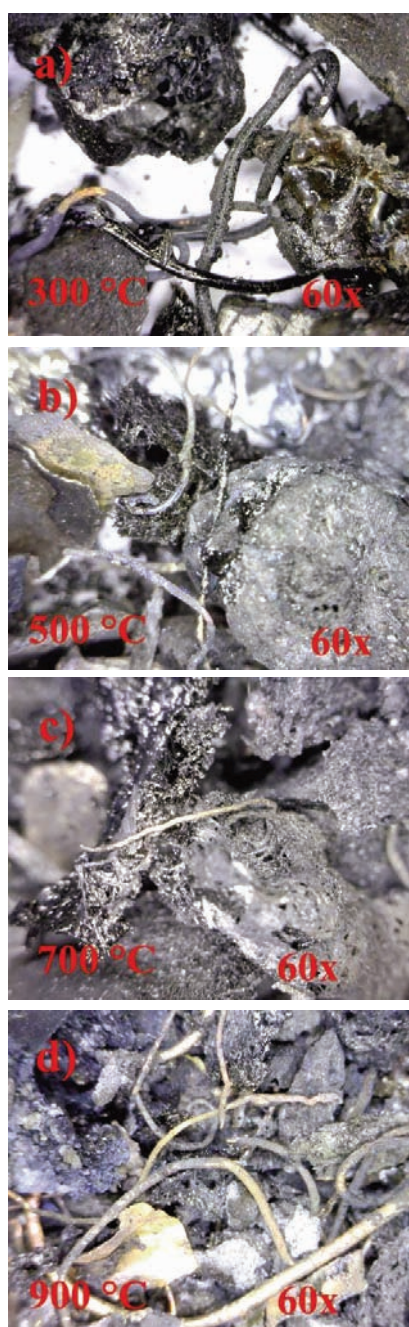


Figure 9. Samples after pyrolysis at different temperatures (60x zoom)

3.2 Leaching

Leaching experiments consisted of two stages. In the first stage, the behavior of metals (copper, tin) in the non-oxidative leaching conditions was studied. The aim of this stage was to determine the influence of thermal pretreatment on copper and tin lixiviation. Based on the results of the first stage conditions for oxidative leaching by air and oxygen were chosen, in

order to intensify metals dissolution.

Figure 10a,b shows tin lixiviation curves of thermally pretreated (pyrolysis, combustion) and thermally untreated samples (-8 +0 mm, -1 +0 mm). From the graphs follows, that the behavior of tin leaching is different for pyrolyzed and burned samples. Different tin extractions were also observed by leaching of thermally untreated samples. Tin extraction from the fraction -1 +0 mm was markedly higher (about 50 %) than from the fraction -8 +0 mm. This is caused by an enlargement of the reaction surface and thus better access of leaching reagent.

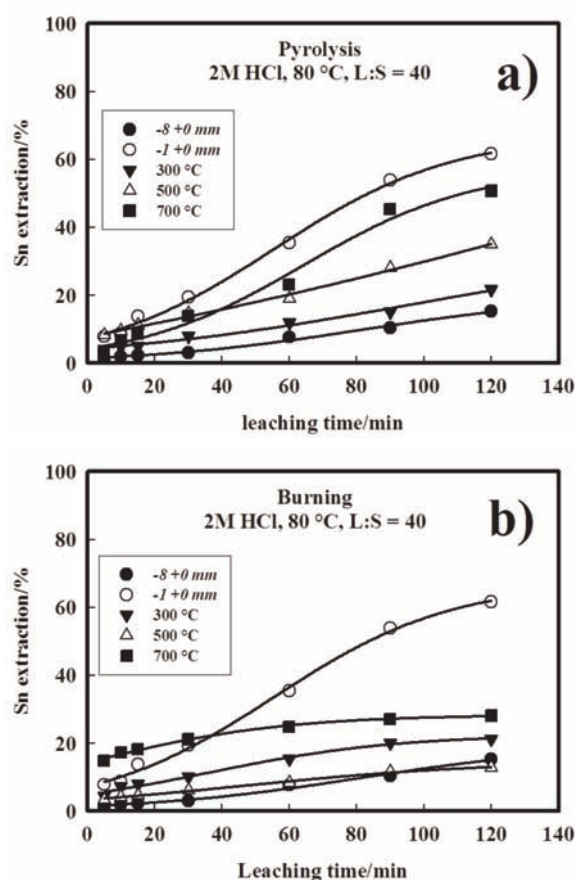
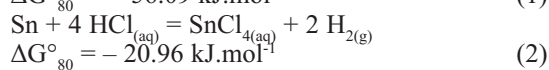
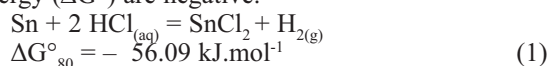


Figure 10. a, b Tin leaching curves a) pyrolyzed samples; b) burned samples

Experiments with pyrolyzed samples revealed, that pyrolysis has a positive effect on tin extraction. As tin remains in metallic form during pyrolysis, leaching can run according equations (1) and (2), because the values of change of standard Gibbs free energy (ΔG°) are negative.



Highest tin extraction (around 50 %) was achieved by leaching of a pyrolyzed sample at 700 °C in comparison with a thermally untreated sample (fraction -1 +0 mm) with highest extraction around 60 %. Furthermore, from the shape of the curves can be observed that the extension of leaching time would help to achieve higher tin extractions. From the leaching experiments of pyrolyzed samples clearly follows, that pyrolysis has an influence on tin liberation from samples. This is evident by the fact that by leaching of a thermally untreated sample within the fraction -8 +0 mm tin extraction of only 10 % was achieved, while leaching of a pyrolyzed sample achieved 50 %. To gain comparable results of tin extractions after pyrolysis it is necessary to mill the sample under 1 mm.

From the leaching experiments of burned samples follows, that combustion has no effect on tin leaching. This is due to the fact that during the combustion process tin oxides are formed (Table 3) in contrast to pyrolysis, which is under inert conditions.

From the thermodynamic calculations of ΔG° values (Table 3) follows, that the mechanism of tin oxide formation is the following: $\text{Sn} \rightarrow \text{SnO} \rightarrow \text{SnO}_2$. This means, that on the surface there is layer of SnO_2 present, below it is a layer of SnO and the bottom layer consists of metallic tin.

Table 3. The values of change of standard Gibbs free energy (ΔG°) for tin oxidation at different temperatures [27]

	$2 \text{ Sn}_{(s)} + \text{O}_{2(g)} = 2 \text{ SnO}_{(s)}$	$2 \text{ SnO}_{(s)} + \text{O}_{2(g)} = 2 \text{ SnO}_{2(s)}$	$\text{Sn}_{(s)} + \text{O}_{2(g)} = \text{SnO}_{2(s)}$
T [°C]	$\Delta G^\circ / \text{kJ.mol}^{-1}$	$\Delta G^\circ / \text{kJ.mol}^{-1}$	$\Delta G^\circ / \text{kJ.mol}^{-1}$
300	-224.93	-238.35	-463.28
500	-203.72	-217.14	-420.86
700	-182.98	-196.29	-379.29
900	-162.75	-175.71	-338.46

Oxide SnO_2 is not leached in HCl, as follows from the positive value of ΔG° for the reaction (3). From the description of Figure 10b resulted, that tin is also leached from burned samples, but in smaller amounts. This is due to the fact that part of tin was not oxidized and/or part of tin was oxidized only to oxide SnO . Leaching of SnO is probable from the thermodynamic point of view, because ΔG° values are negative for the equation (4). Moreover, cracks in the surface of material can occur during cooling of samples, causing better access of the leaching reagent to SnO and Sn layers.

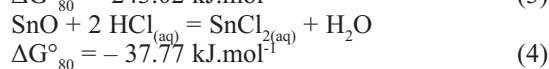
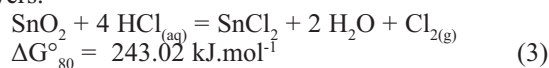


Figure 11a,b shows copper lixiviation curves of

thermally pretreated (pyrolysis, burning) and thermally untreated samples (-8 +0 mm, -1 +0 mm). It is observed from the graphs that the leaching process of pyrolyzed and burned samples is different. Highest copper extractions from pyrolyzed samples ranged around 2 %, while the highest copper extractions from burned samples reached 15 % at 700 °C. The difference in copper extractions is due to the fact, that during the combustion copper oxides are formed.

Copper is leached significantly only in oxidative

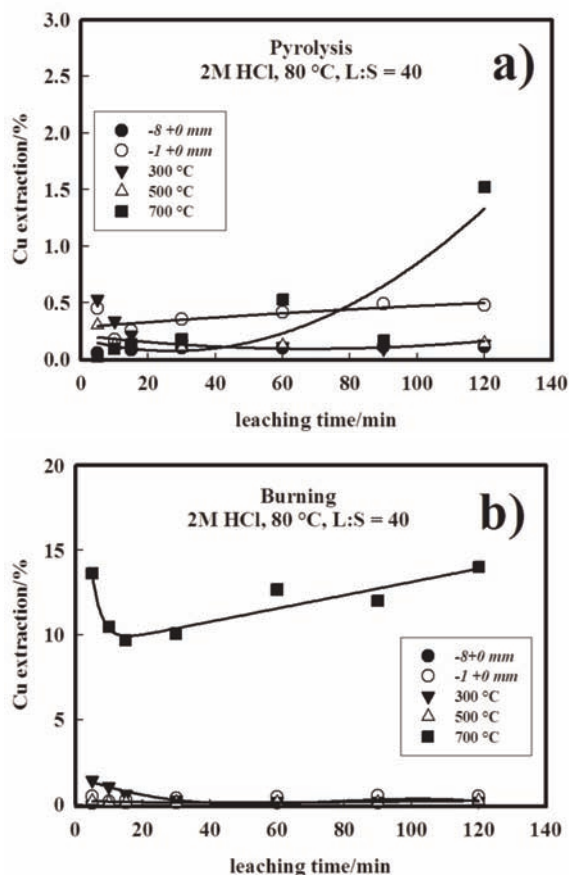
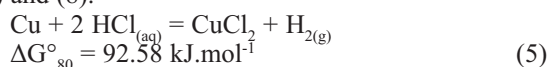
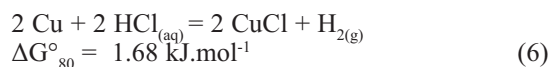


Figure 11. a, b Copper leaching curves a) pyrolyzed samples; b) burned samples

environments, but HCl is a non-oxidizing acid. For this reason, copper is not leached as follows from positive values of ΔG° for reactions (5) and (6). However, copper extractions around 2 % from pyrolyzed samples were observed. These small amounts of copper in the solution are caused by leaching of copper oxides which naturally covers the copper particles. From the thermodynamic point of view, the leaching of copper oxides is probable, as follows from the negative values of ΔG° for reactions (7) and (8).

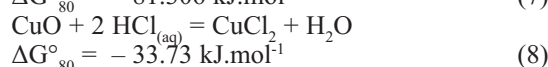
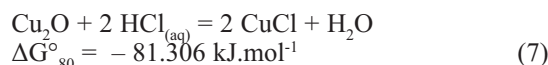




On the other hand, copper oxides during combustion are formed. From thermodynamic calculations (Table 4) follows, that the formation of copper oxides is: $\text{Cu} \rightarrow \text{Cu}_2\text{O} \rightarrow \text{CuO}$. Copper oxides are leached in HCl, as follows from the negative values of ΔG° for reactions (7) and (8). The reason why higher copper extractions were not reached is that copper consists of coarse particles, mostly from wires. For this reason, copper was partly oxidized on the surface and thus copper extraction of only around 15 % was achieved.

Table 4. The values of changed of standard Gibbs free energy (ΔG°) for copper oxidation at different temperatures [27]

	$4 \text{Cu}_{(\text{s})} + \text{O}_{2(\text{g})} = 2 \text{Cu}_2\text{O}_{(\text{s})} + \text{O}_{2(\text{g})} = 2 \text{Cu}_{(\text{s})} + \text{O}_{2(\text{g})} = 2 \text{CuO}_{(\text{s})}$	$2 \text{Cu}_2\text{O}_{(\text{s})} + \text{O}_{2(\text{g})} = 4 \text{CuO}_{(\text{s})}$	$2 \text{Cu}_{(\text{s})} + \text{O}_{2(\text{g})} = 2 \text{CuO}_{(\text{s})}$
T [°C]	$\Delta G^{\circ} / \text{kJ.mol}^{-1}$	$\Delta G^{\circ} / \text{kJ.mol}^{-1}$	$\Delta G^{\circ} / \text{kJ.mol}^{-1}$
300	-63.49	-79.15	-103.06
500	-56.05	-59.01	-85.56
700	-48.76	-39.49	-68.50
900	-41.60	-20.44	-51.82



From the leaching curve (copper extraction 15 %) is seen that it is a sectional process. First, there is rapid leaching of copper oxides from the surface (as described above), then the copper extraction decreases and again increases. The decrease of copper extraction is due to partial cementation. As almost all metals are less noble than copper in the sample (except gold and silver), cementation could be caused by one or more of these metals. The content of these metals in the sample is relatively low, compared to the amount of copper in the solution; the decrease was around 5 %. Consequently, copper leaching continued by the presence of oxygen from the environment or even by CuCl_2 (equation 17, 18, 19), which was created during the leaching of copper oxides in the first phase.

As mentioned above, the aim of leaching in the second stage was to intensify copper and tin transfer into solution by oxidative leaching (blowing of air or oxygen). Because the best results in the first stage were achieved with a sample that was thermally pretreated at 700 °C (pyrolysis, combustion), in the second stage experiments were carried out only with these samples. Moreover, for comparison also thermally untreated samples (-8 +0 mm, -1 +0 mm) were used.

In Figure 12a,b curves of tin leaching with

blowing air and oxygen are shown. From the graphs clearly follows, that blowing of air and oxygen has a positive effect on copper and tin dissolution. During the process, tin is leached from its metallic form (pyrolyzed samples) and also from oxides (burned samples). Equations (9) – (12) describe the process of oxidative leaching of metallic tin and tin oxides, whereby the values of ΔG° are significantly more negative in comparison with the non-oxidizing leaching.

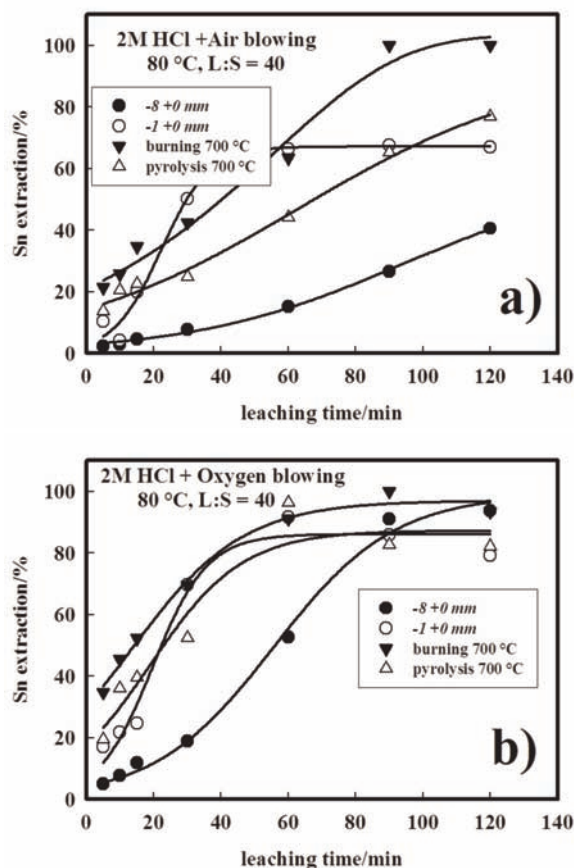
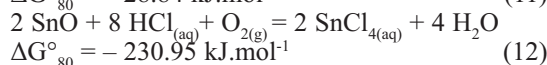
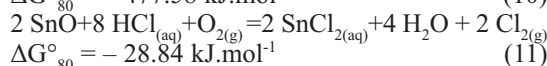
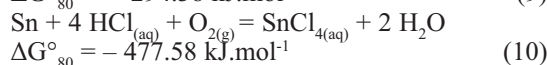
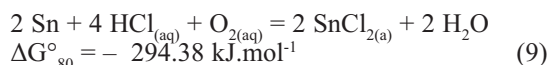


Figure 12. a, b Tin leaching curves in 2M HCl with blowing air and oxygen



The blowing of air and oxygen caused tin to be completely leached out. Whereas oxygen is a stronger oxidant than air, higher extractions were achieved. Moreover, complete tin dissolution was achieved

already after 90 minutes, while conventional leaching in the first stage would require an extension of leaching time.

In Figure 13a,b curves of copper leaching with blowing of air and oxygen are shown. As mentioned above, the transfer of copper into solution requires oxidative conditions. This fact was observed during copper leaching, when air and oxygen were blown into the solution. The equations (13) – (16) describe the process of oxidative leaching of metallic copper and copper oxides. From the shape of curves the influence of changing surface area on the transfer of copper into solution becomes apparent. From the leaching curves clearly follow the effect of thermal pretreatment on copper dissolution. Copper was completely dissolved from thermally treated samples using oxygen after 60 minutes, while copper extraction from thermally untreated samples achieved only 60 %.

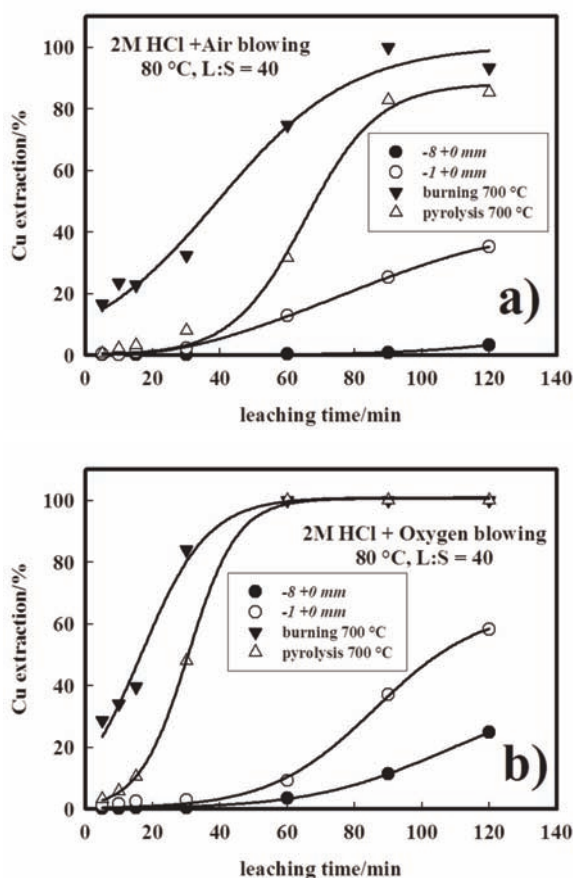
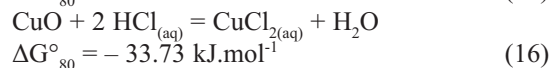
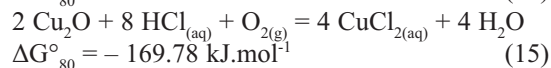
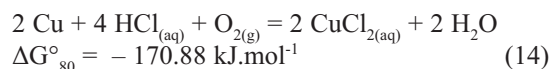
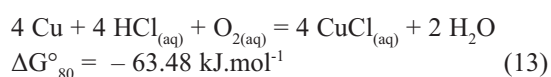
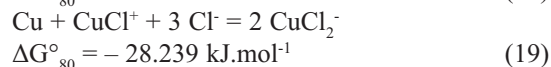
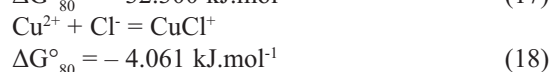
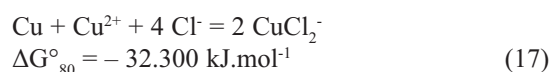


Figure 13. a, b Copper leaching curves in 2M HCl with blowing air and oxygen



Leaching of copper may not only run directly using oxygen or air, as described by equation (14), but can also run by leaching with CuCl_2 . This means that in the leaching process CuCl_2 is firstly created according to reaction (14) by oxygen. When a sufficient amount of Cu^{2+} in a solution is created, then Cu^{2+} is involved in copper leaching according to reaction (17) and/or reactions (18) and (19).



In the first stage, the highest copper extraction from pyrolyzed samples was around 2 %. In oxidative leaching experiments, 90 % of copper was leached out with air blowing and complete dissolution was achieved with oxygen blowing after 60 minutes. Similar results and again complete dissolution of copper were observed. On the other hand, copper extractions of thermally untreated samples increased significantly compared to the first stage, but extraction of only 60 % was achieved.

The comparison of copper extraction from thermally treated and untreated samples reveals the clear proof of the effect of thermal pretreatment. During thermal pretreatment, the organic phase is removed and copper is liberated, which causes better access for a leaching reagent. The result is a complete dissolution of copper and also significant shortening of leaching time.

4 Conclusions

Thermal pretreatment of material had no significant effect on plastics removal at 300 °C, because most plastics thermally decompose above this temperature. With increasing temperature the amount of removed plastics increased. Maximal weight losses represented 53 % at 700 °C for combustion and 47 % for pyrolysis, but the difference between 700 °C and 900 °C was only 1 %, which is negligible.

The behavior of tin in classical leaching (without blowing of air or oxygen) was different for pyrolysis and combustion. The experiments showed, that pyrolysis had a positive effect on tin leaching, while

combustion has a negative effect. Leaching of burned samples achieved lower extractions, which is due to oxidation, and thus formation of tin oxides, which are more difficult to leach. Highest tin extraction from pyrolyzed samples reached 50 % which is 40 % more than from the same sample without thermal pretreatment.

The behavior of copper in classical leaching was also different for pyrolysis and combustion. Highest copper extraction was around 15 % for burned samples compared to 2 % for pyrolyzed samples. During the combustion process copper oxides are formed which are leachable unlike metallic copper.

From the oxidative leaching experiments it follows that complete copper and tin dissolution from thermally pretreated samples was achieved. Oxidizing leaching of thermally untreated samples did not result in complete dissolution of metals after 120 minutes and the process would require a significant extension of leaching time. The experiments clearly reveal, that thermal pretreatment has positive effects by increasing the efficiency of leaching processes and significantly reducing leaching time.

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