HYDROMETALURGICAL TREATMENT OF PRINTED CIRCUIT BOARDS IN HYDROCHLORIC ACID WITH OXIDANT

Dusan Orac[1)], Nikola Vrablova[1)], Miroslav Urban[1)], Tomas Havlik[1)]*
[1)] Technical University of Kosice, Faculty of Metallurgy, Department of Non-Ferrous Metals and Waste Treatment, Kosice, Slovakia

[*]Corresponding author: e-mail: dusan.orac@tuke.sk, Tel.: (+421) 055 / 602 24 12, Department of non-ferrous metals and waste treatment , Faculty of Metallurgy, Technical University of Košice, Letna 9, 042 00 Kosice, Slovakia

Abstract
This paper deals with the leaching of printed circuit boards (PCBs) from used personal computers for the purpose of investigating tin and copper extraction into solution with and without blowing of oxygen under different conditions. During the leaching process the influence of blowing of oxygen and granularity on tin and copper extraction was observed. The experiments were performed at 80 °C in the aqueous solution of HCl at concentration 2M. Three fractions (*–8 +0 mm, –1 +0 mm, –0.6 +0 mm*) were used for the experiments. From the experiments it results that copper is leached only with blowing of oxygen and at the end of experiments practically the same extractions for all three fractions were achieved. On the other hand, tin is leached also without blowing of oxygen, but the extractions were lower. The highest extraction of copper 85 % and tin 82 % was achieved at fraction *–8 +0 mm*.

Keywords: hydrometallurgy, leaching, PCBs, hydrochloric acid, tin, copper

1 Introduction

In the European Union about 8 million tons of waste from electrical and electronic equipment (WEEE) is generated annually, with the annual increase of 3 – 5 % [1]. From a global perspective it represents about 20 – 50 million tons [2].

Printed circuit boards (PCBs) represent a significant part of WEEE. In recent years, the average PCBs production has grown by about 8.7 % worldwide, whilst in China it has been as much as 14.4 %. PCBs represent approximately 6.5 % of the weight of a computer [3].

PCBs contain valuable metals such as gold, silver, copper and others. When considering all components of a personal computer, the highest amount of these metals is contained in PCBs. A very important fact is that the content of these metals in PCBs is much higher than in raw materials. In the case of gold and silver the content in PCBs is a hundred times higher and in the case of copper it is twenty times higher than in raw materials. The high content of these metals as well as their prices predetermine the use of PCBs as an important secondary raw material, as current amounts of primary raw materials for production of certain metals are critical.

The PCB processing methods can be generally divided into pyrometallurgical, hydrometallurgical and combined methods. These methods can be preceded by material pretreatment through physical or thermal processes. The aim of the pretreatment is mainly the reduction of input material volumes, release of required components and concentration of metals.

This work is dealing with leaching of PCBs, so in the Tab. 1 results from several authors dealing with hydrometallurgical processing of PCBs are presented.

This work focuses on the leaching of PCBs from used personal computers in the hydrochloric acid medium with and without blowing of oxygen with the aim to observe tin and copper passing into the solution under different conditions and to find out optimal conditions for their leaching.

Tab. 1 Results of PCBs leaching from several authors

Authors	Leaching reagents	Results
Kim et al. [4] (2011)	HCl + Cl_2	Cu (71 %), Zn (98 %), Sn (96 %), Pb (96 %)
Orac et al. [5] (2011)	HCl	Cu (0.5 %), Sn (100 %)
Ha et al. [6] (2010)	thiorea + $Fe_2(SO_4)_3$	Au (69.36 %), Ag (100 %), Cu (100 %)
	aqua regia	Au (100 %), Ag (88.51 %), Cu (100 %)
	NH_3 – $(NH_4)_2S_2O_8$	Au (12.76 %), Ag (100 %), Cu (88.87 %)
	H_2SO_4	Au (6.05 %), Ag (90.37%), Cu (100 %)
Havlik et al. [7] (2010)	HCl (leaching after thermal pretreatment)	Cu (98 %)
Pencak et al. [8] (2010)	HCl + O_3	Cu (99. 97 %)
Li a Huang [9] (2010)	$Na_2S_2O_3$ + $CuSO_4$ + NH_4OH	Au (92 %), Ag (90 %)
Park a Fray [10] (2009)	HCl + HNO_3	Ag (98 %), Pd (93 %), Au (97 %)
Xie et al. [11] (2009)	H_2SO_4 + ultrasound	Cu (97.83 %)
Castro a Martins [12] (2009)	H_2SO_4	Sn (< 0.01 %), Cu (< 0.01 %)
	H_2SO_4 + HCl	Sn (96.3 %), Cu (29.8 %)
	HCl	Sn (98.2 %), Cu (20 %)
	HCl + HNO_3	Sn (85.8 %), Cu (34.3 %)
Ping et al. [13] (2009)	H_2SO_4 + NaCl + $CuSO_4$ + air	Cu (100 %)
Bari et al. [14] (2007)	NH_3 + $(NH_4)_2S_2O_8$	Cu (99 %), Zn (60 %), Ni (9 %)
Oishi et al. [15] (2007)	$(NH_4)_2SO_4$ + Cu^{2+}	Cu (21 %), Sn (0 %), Pb (2.6 %)
	NH_4Cl + Cu^{2+}	Cu (12 %), Sn (0 %), Pb (9.1 %)
Sheng a Etsell [16] (2007)	HNO_3/HCl	Au
	Cu(II) – NH_3 – $(NH_4)_2SO_4$	Cu (90 %)
Madenoglu [17] (2005)	HNO_3/HCl	Au, Cu
Quinet et al. [18] (2005)	HCl/NaOH + HNO_3/H_2O_2	Pd (93 – 95 %)
	cyanide/thiorea	Au, Ag (> 95 %)
Oh et al. [19] (2003)	H_2SO_4/H_2O_2	Cu, Fe, Zn, Ni, Al (> 95 %)
	$CuSO_4$ – NH_4OH – $(NH_4)_2S_2O_3$	Au, Ag (> 95 %)
Veglio et al. [20] (2003)	H_2SO_4	Cu (94 – 99 %)
Mecucci a Scott [21] (2002)	HNO_3	Cu, Pb (> 95 %)

2 Experimental part

2.1 Material

73 kg of used printed circuit boards were collected before the leaching experiments. At first, hazardous parts such as batteries and condensers were manually removed from the PCBs. After that the PCBs were crushed on a hammer crusher. The representative sample of 2 kg was obtained from the crushed material by quartering. From that sample (fraction *–8 +0 mm,* Fig. 1a) next sample for chemical analysis was taken, Tab. 2. Remaining part was milled on Weber Bros. laboratory pulverizing mill into two fractions *–1 +0 mm* and *–0.6 +0 mm* (Fig. 1 b, c).

Tab. 2 Chemical analysis of PCBs

Kovy	**Cu**	**Sn**	**Au**	**Ag**
Obsah [%]	19.14	5.94	0.007	0.01

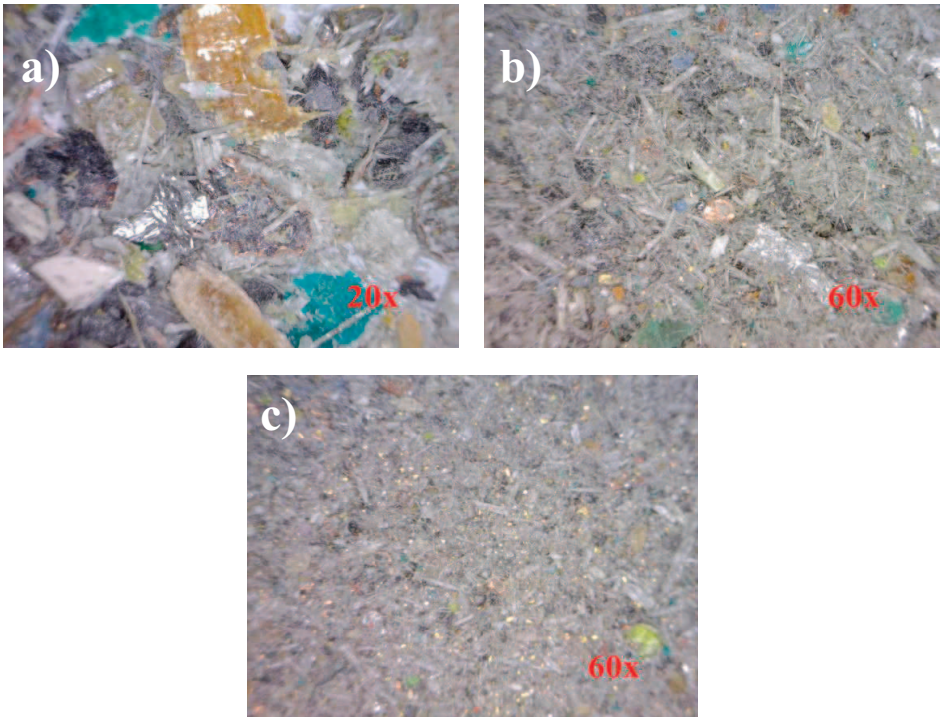

Fig. 1 Input samples of PCBs
a) fraction *–8 +0 mm*, b) fraction *–1 +0 mm*, c) fraction *–0.6 +0 mm*

2.2 Leaching

The leaching experiments of PCBs were performed in the apparatus, whose scheme is shown in Fig. 2. The experiments were carried out in glass reactors with the volume of 800 ml, dipped into water bath at the temperature 80 °C using constant stirring and blowing of oxygen. The aqueous solution of hydrochloric acid at concentration 2M was used as a leaching reagent. The volume of the leaching reagent was 400 ml. The sample weight 10 g was used for the leaching, which represents liquid to solid ratio L:S = 40. All samples for each experiment were obtained by manual quartering. Three granularities of the material were used for the experiments. The

first fraction consisted of the original PCB sample after crushing with the granularity of *–8 +0 mm*. Another two fractions (*–1 +0 mm, –0.6 +0 mm*) were obtained by milling. The total experiment time was 120 minutes. The time period for the withdrawal of liquid samples during the experiment was 5, 10, 15, 30, 60, 90 and 120 minutes. The withdrawn samples with the volume of 10 ml were analyzed for tin and copper content by the atomic absorption spectrometry (Varian Spectrometer AA 20+). All results were corrected due to sample volume changes caused by sampling and evaporation processes.

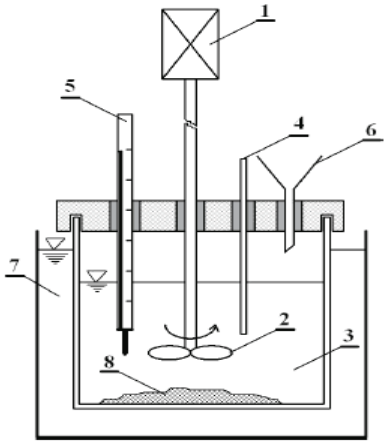

Fig. 2 The scheme of the leaching apparatus [22]
1 – mechanical stirrer; 2 – propeller; 3 – leaching pulp; 4 – sampler;
5 – thermometer; 6 – feeder; 7 – water thermostat; 8 – sample of PCBs

2.3 Thermodynamics of PCBs leaching

Tin and copper were present in the metallic form in the PCBs, and therefore only this form was considered during calculations.

From the thermodynamic calculations of tin and copper leaching for reactions (1) – (5) [23] it results that leaching of metallic tin can also take place under non-oxidizing conditions, unlike metallic copper. Tin leaching reactions in hydrochloric acid, (1) and (2), show a negative value of Gibbs free energy (ΔG^o)**,** which means that from the thermodynamic point of view they are likely to run in the direction of product creation.

On the other hand, the reactions of metallic copper leaching, (3) and (4), show a positive value of ΔG^o, which means they will not run. The reactions of copper leaching in hydrochloric acid solutions at oxygen presence (5) show a negative value of ΔG^o, and therefore from the thermodynamical point of view it is probable that they will run, as opposed to copper leaching without the oxygen presence (reactions 3 and 4), where the values of ΔG^o were positive.

$Sn + 2HCl_{(a)} = SnCl_{2(a)} + H_{2(g)}$ $\Delta G°_{80} = -56.091$ kJ/mol (1)
$2Sn + 4HCl_{(a)} + O_{2(g)} = 2SnCl_{2(a)} + 2H_2O$ $\Delta G°_{80} = -568.804$ kJ/mol (2)

$Cu + 2HCl_{(aq)} = CuCl_2 + H_{2(g)}$ $\Delta G°_{80} = 92.577$ kJ/mol (3)
$2Cu + 2HCl_{(aq)} = 2CuCl_2 + H_{2(g)}$ $\Delta G°_{80} = 1.68$ kJ/mol (4)
$2Cu + 4HCl_{(aq)} + O_{2(g)} = 2CuCl_{2(aq)} + 2H_2O$ $\Delta G°_{80} = -341.751$ kJ/mol (5)

2.4 Results and discusion

2.4.1 Copper behavior in the leaching process

Influence of oxygen

Fig. 3 a – c show kinetics curves of copper leaching in 2M HCl with and without blowing of oxygen at 80 °C, for three fractions *(–8 +0 mm, –1 +0 mm, –0.6 +0 mm*) and L:S ratio = 40.

From the graphs it results that copper is leached only in the present of oxygen as it follows from the thermodynamic calculations of copper leaching.

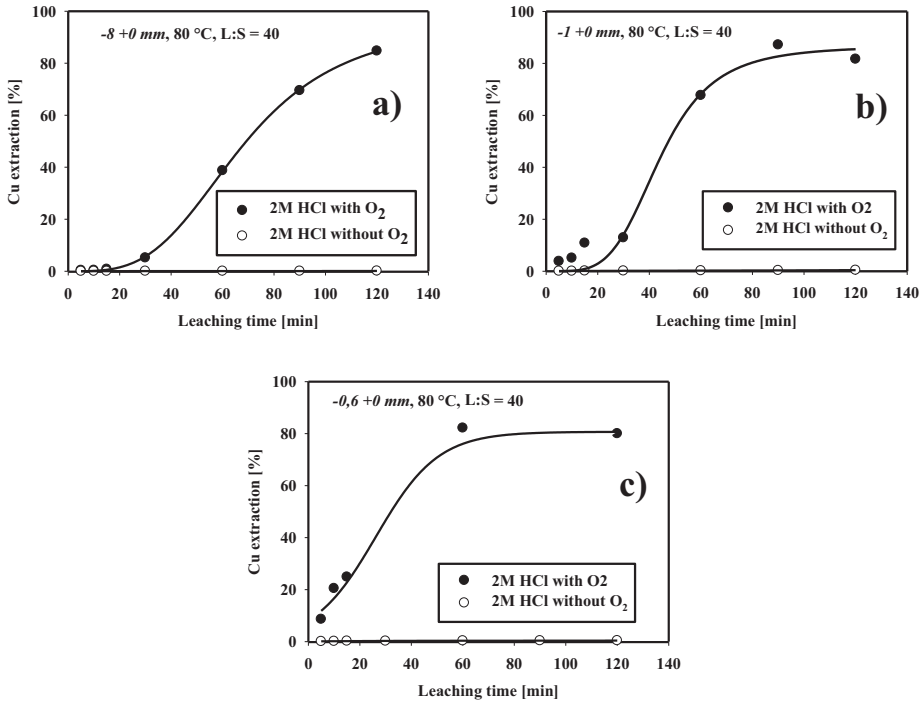

Fig. 3a – c Kinetic curves of copper leaching in 2M HCl with and without blowing of oxygen

Influence of granularity

Fig. 4 shows kinetics curves of the copper leaching for three grain fractions of PCBs at 80 °C in 2M HCl, for 120 minutes.

From the comparison of curves follows that extraction of copper into the solution is more intensive with decreasing of grain size. The copper extraction for fraction *–0.6 +0 mm* in the 30th minute was around 40 %, whereby the copper extraction for other two fraction 10 %. However, at the end of the experiments, practically the same extractions (around 85 %) for all fractions were achieved.

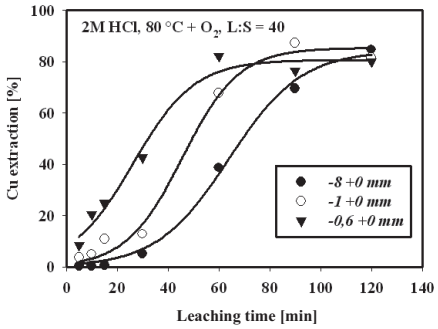

Fig. 4 Kinetic curves of copper leaching with blowing of oxygen for different fractions

2.4.2 Tin behavior in the leaching process

Influence of oxygen

Fig. 5 a – c show kinetics curves of tin leaching in 2M HCl with and without blowing of oxygen at 80 °C, for three fractions *(–8 +0 mm, –1 +0 mm, –0.6 +0 mm*) and L:S ratio = 40.

From the graphs it results that tin is leached also without present of oxygen. This fact suggested the thermodynamic calculations for reaction of tin leaching without oxygen for reaction (1). Without blowing of oxygen, the maximal tin extraction 65 % for fraction *–0.6 +0 mm* after 120 minutes was achieved.

On the other hand, the leaching of tin with blowing of oxygen was more intensive and in comparison with non-oxidative leaching higher extractions were achieved. The maximal tin extraction was 82 % for fraction *–8 +0 mm*.

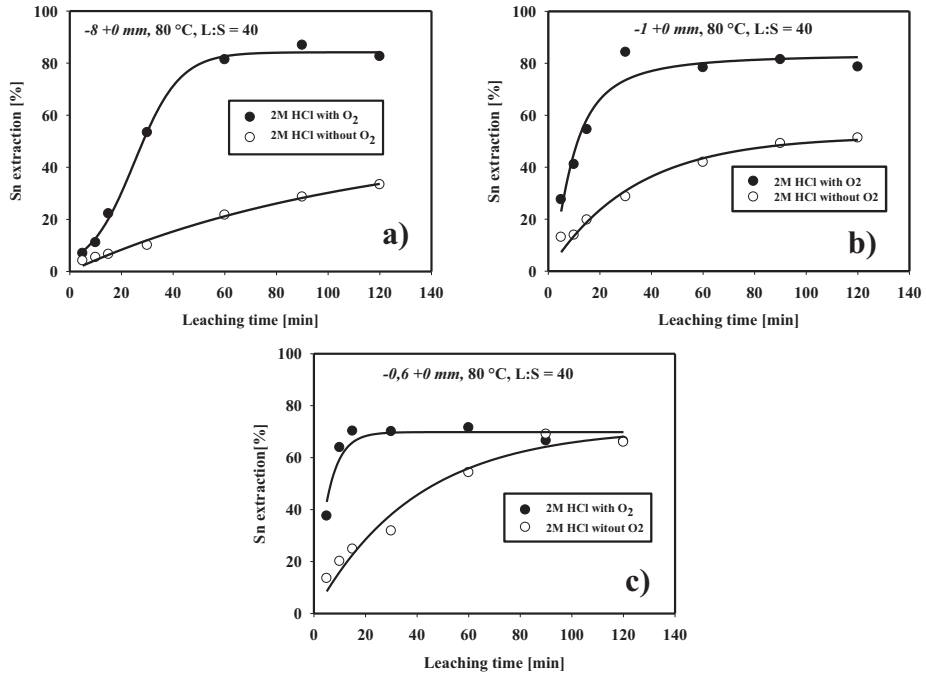

Fig. 5 a – c Kinetic curves of tin leaching in 2M HCl with and without blowing of oxygen

Influence of granularity

Fig. 6 shows kinetics curves of the tin leaching for three grain fractions of PCBs at 80 °C in 2M HCl, for 120 minutes.

From the curves follows that blowing of oxygen increase the rate of tin extraction into solution. The tin extraction is more intensive in the first minutes of leaching for fine fractions. However, at the end of experiments the extractions are very similar. The highest extraction of tin (82 %) was observed at fraction *–8 +0 mm*.

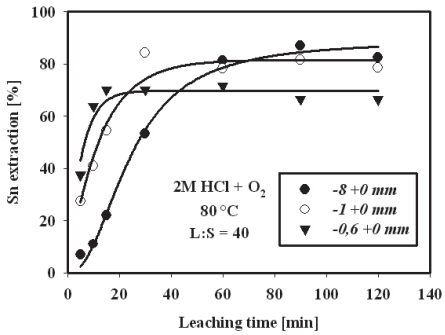

Fig. 6 Kinetic curves of tin leaching with blowing of oxygen for different fractions

2.4.3 Comparison of copper and tin leaching

Fig. 7 shows kinetics curves of the copper and tin leaching at 80 °C in 2M HCl, for 120 minutes.

From the comparison of both metals extraction follows that copper and tin are leached in different way. In the first phases of leaching, firstly the tin is leached and after 30 minutes copper starts to leach out. This fact could be caused by different ways. The tin is placed at the particles surface so is leached firstly. Consequently, after part of tin is leached out, the copper starts to leach out.

The copper leaching could not run only directly with oxygen, but also by leaching with $CuCl_2$. At first, $CuCl_2$ is formed in the process according to the reaction (5). After the formation of the sufficient amount of $CuCl_2$ in the solution, $CuCl_2$ participates in copper leaching according to the reaction (6). In addition, after part of tin is leached out, an additional surface area of copper was uncovered and reactive area grown larger, whereby the trend of curves in Fig. 7 can be explained.

$$Cu + CuCl_{2(aq)} = 2CuCl \qquad \Delta G°_{80} = -68.239 \text{ kJ/mol} \qquad (6)$$

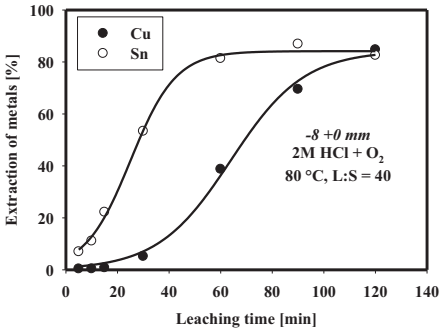

Fig. 7 Kinetic curves of copper and tin leaching in 2M HCl

3 Conclusion

From the experiments of printed circuit boars leaching in 2M HCl with and without blowing of oxygen follows that copper is leached only in the present of oxygen. The highest copper extraction around 85 % at three fractions *(–8 +0 mm, –1 +0 mm, –0.6 +0 mm*) after 120 minutes was achieved. The leaching process of each fraction was different. Copper was leached more intensive in the first phases with decreasing of grain size. However, at the end of experiments, practically the same extractions were achieved. This fact is important due to over-all treatment process, because no additional milling is important.

The behavior of tin during the leaching was rather different. The tin is leached also without present of oxygen, but it requires longer leaching time. On the other hand, tin leaching is more intensive with oxygen and the leaching rate is increasing. The highest tin extraction without oxygen was achieved 65 %, whereby with oxygen 82 % at fraction *–8 +0 mm*.

From the comparison of copper and tin leaching was found that tin is leached at first and after 30 minutes copper starts to leach. This phenomenon could be caused from the fact that tin is at the particle surface. Whereby, the copper leaching with $CuCl_2$ could be also possible.

This work continues on the results of another work (*Orac et al.* [5], 2011), where the authors presented the possibility of selective tin leaching from circuit printed board witout leaching of copper. This work shows the possibility of copper leaching from PCBs. Therefore, the leaching of copper with blowing of oxygen could be potential second step of printed circuit boards' treatment.

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