

ORA 2  
KNA SO

# METALL

Fachzeitschrift für Metallurgie

Technik · Wissenschaft · Wirtschaft

**Klar,** Sie könnten  
ohne Kupfer leben

Allerdings benötigt man

**200 km**

unseres Kupferdrahts pro Windkraftanlage:  
Ohne Kupfer kein Ökostrom.

[www.aurubis.com](http://www.aurubis.com)

**Aurubis**  
Our Copper for your Life

## Special: Kupfer, Recycling

Kupfer zapft die Sonne an

Bauteile aus Kupferpulver

Laserschweißen von Kupfer

Abfallende von Schrotten

WEEE-Recycling

[www.metall-web.de](http://www.metall-web.de)

Einzel-Verkaufspreis: 21,00 €

65. Jahrgang · Mai 2011

Fachzeitschrift für Metallurgie

Technik · Wissenschaft · Wirtschaft

 Giesel Verlag GmbH

Giesel Verlag GmbH  
Postfach 5420 · D-30054 Hannover  
PVST · Dt. Post AG · Entgelt bezahlt

5



# Leaching of Tin and Copper from used print circuit boards in Hydrochloric acid

Orac D., Havlik T., Kukurugya F., Miskufova A., Takacova Z. (1)

**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 under different conditions. During the leaching process the influence of the temperature, leaching agent concentration and leaching time on tin and copper extraction was observed. The experiments were performed at the temperatures of 20, 40, 60 and 80 °C in the aqueous solution of HCl at concentrations of 0.25M, 0.5M, 1M and 2M. Three fractions were used for the experiments. From the experiments it results that the increase of temperature, HCl concentration and leaching time causes the increase of tin extraction in contrast to copper, where the selected conditions did not have any significant influence on the copper extraction into the solution. In the case of all three fractions, the complete tin extraction into the solution was achieved under the selected conditions (2M HCl, 80 °C, 360 min.). However, only in the -8 +0 mm fraction the selective leaching of tin (without copper passing into the solution) was reached. In the leaching of two other fractions (-8 +3 mm, -3 +0 mm) around 5 % of copper passed into the solution.**

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

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. The chemical composition of PCBs is very variable, and the content of certain metals is mostly given in a range of values. The published contents of copper [4 – 9] in PCBs vary from 3.7 to 25 %, tin 2 – 4 %, silver 0.0003 – 0.2 %, gold 0.00025 – 0.1 %, lead 1.5 – 3 %, zinc 0.4 – 1.6 %, aluminium 2 – 28 % and nickel 0.31 – 2 %. The metal content range depends on the PCB type, producer and year of manufacture. 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. For instance, the amount of primary raw materials for tin production at the current ore mining rate of 333 000 t/y is estimated for 17 years only, and according to optimistic estimations for 33 years. Moreover, 52 % of tin produced worldwide are used in solder production, where tin represents practically an irreplaceable component [10].

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

Oh et al. [11] describe the leaching of PCBs using sulphuric acid ( $\text{H}_2\text{SO}_4$ ) with the addition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as an oxidizing agent. When using 2M  $\text{H}_2\text{SO}_4$  with the addition of 0.2M  $\text{H}_2\text{O}_2$  at the temperature of 85 °C, the extraction of zinc and copper reached 100 % after 8 hours, while the extraction of iron and nickel reached 95 % and the tin extraction was 20 % after 12 hours. After leaching in  $\text{H}_2\text{SO}_4$ , the leaching in  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $\text{CuSO}_4$  and  $\text{NH}_4\text{OH}$  followed, with the aim to leach out gold and silver. Silver was leached out entirely after 24 hours and the gold extraction reached 95 % after 48 hours. Consequently, the solid residue was leached in NaCl solution with the aim to leach lead. The lead extraction of 95 % was achieved after 2 hours in the NaCl solution.

Rabah et al. [12] studied leaching of copper, tin and lead from PCBs by means of 2M  $\text{HNO}_3$ , at the leaching temperatures of 20, 50, 75 and 100 °C. The leaching time was 60 minutes. The extraction of copper, tin and lead increased with the increase of temperature, and complete lixiviation of these metals was reached at 100 °C. In the paper also leaching (4M  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ) of the residue after the thermal treatment was studied. The extraction of copper and tin in  $\text{H}_2\text{SO}_4$  reached 100 % at the temperature of 100 °C after 60 min., whilst the lead extraction reached only 10 %. The complete lixiviation of copper from the residue in  $\text{HNO}_3$  at 100 °C was achieved after 40 minutes; in case of tin after 50 minutes and lead after 60 minutes.

Mecucci and Scott [13] leached crushed PCBs in 1 to 6 M  $\text{HNO}_3$  at two temperatures of 23 and 80 °C. The sample weight was 100 g and the volume of the leaching solution was 300 ml. Lead was leached out entirely after 360 minutes at all concentrations of  $\text{HNO}_3$ ; as for copper, only when using 6M  $\text{HNO}_3$ . The increase of the  $\text{HNO}_3$  concentration and temperature caused the increase of the copper extraction. The highest tin extraction, around 70 %, was achieved in 2 M  $\text{HNO}_3$ . The results of these experiments indicated the need for crushing the sample before leaching to ensure

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

Tab. 1: The chemical composition of PCBs



better access of the leaching solution to the desired metals.

Orac et al. [14] leached crushed PCBs for the purpose of leaching copper and tin in HCl solutions. In that paper the effect of acid concentration, temperature and liquid to solid ratio was investigated. The highest tin extraction, around 90 %, was achieved by using 2M HCl, at the temperature of 80 °C. The results of the experiments showed that with the increase of temperature and acid concentration the tin extraction increases as well. The copper extraction was always under 1 %, and the increase of temperature and acid concentration did not have any effect on the copper extraction into the solution.

In another paper Orac et al. [15] went on with the study of the tin and copper extrac-

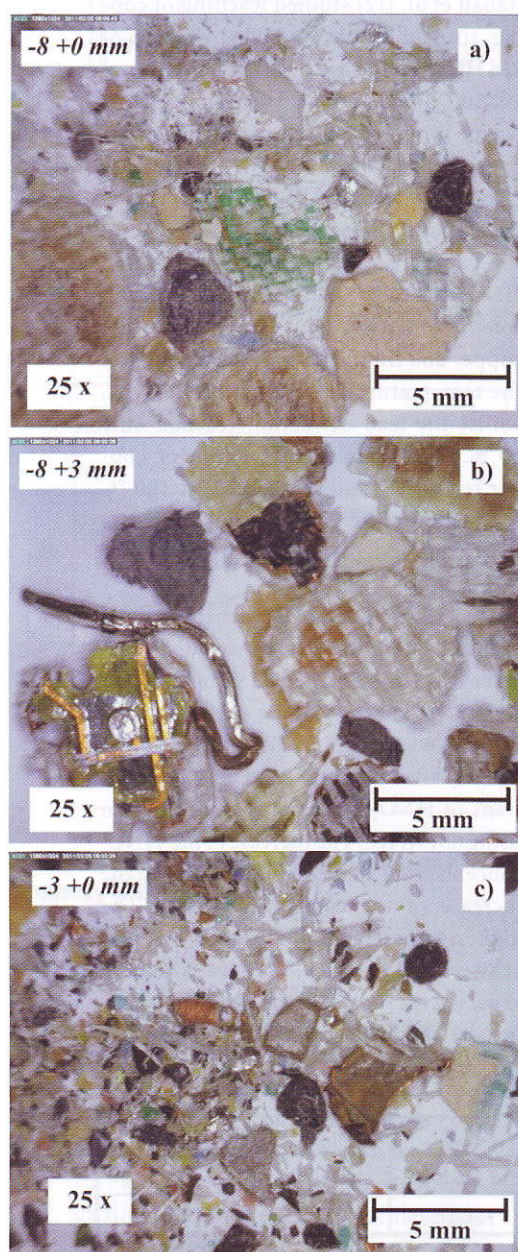


Fig. 1 a – c: Photographs of crushed PCBs

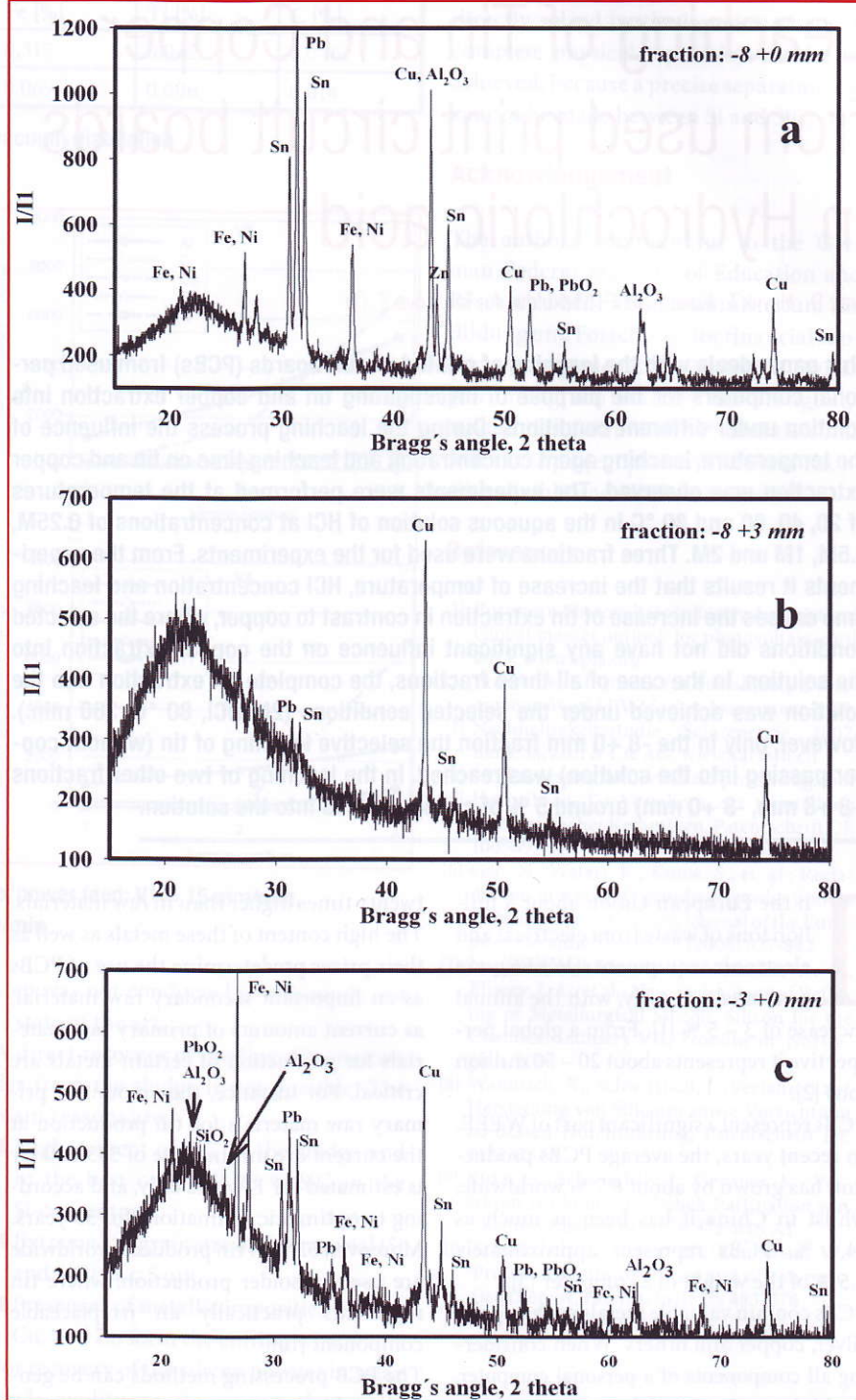


Fig. 2 a – c: XRD patterns of individual fractions of PCBs

tion from PCBs in HCl solutions with the aim to investigate the effect of the acid concentration and granularity. The highest tin extraction was achieved in 2M HCl and granularity of  $-0.24 +0$  mm. From the experiments it results that both the increasing acid concentration and decreasing granularity increase the tin extraction. The acid concentration and granularity changes did not have any significant influence on the copper extraction, and copper was practically not leached under the selected conditions.

Oishi et al. [16] dealt with copper recovering from PCBs. PCBs with the granularity from 0.5 to 3 mm were leached in  $[(\text{NH}_4)_2\text{SO}_4]$  solution or in  $(\text{NH}_4\text{Cl})$  medium, in the presence of  $\text{Cu}^{2+}$  ion.

The solution concentrations were 0.5, 1, 4 and 5M. Extractions of copper 21 %, tin 0 %, lead 2.6 %, manganese 27 % and zinc 11 % were achieved in the sulphate environment. In the chloride environment the extractions were as follows: Cu 12 %, Sn 0 %, Pb 9.1 %, Mn 38 % and Zn 57 %.



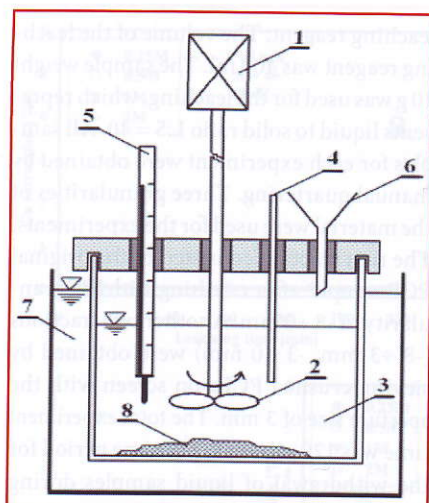


Fig. 3: The scheme of the leaching apparatus [22]; 1 – mechanical stirrer; 2 – propeller; 3 – leaching pulp; 4 – sampler; 5 – thermometer; 6 – feeder; 7 – water thermostat; 8 – crushed PCBs

Kinoshita et al. [17] leached PCBs in  $\text{HNO}_3$  solution. PCBs were cut into pieces with the dimensions of  $10 \times 20 \times 2$  mm before leaching. The highest extraction of metals was reached using  $1\text{M HNO}_3$  for 24 hours. Copper and nickel extractions were 95 % and 99.9 % respectively at  $80^\circ\text{C}$ . Gold remained in the form of flakes and its extraction was 98 %.

Ping et al. [18] leached copper from PCBs. First of all, PCBs were mechanically pre-treated and separated in order to get two fractions. The first fraction consisted of a

fine sample with the high copper content, and the second sample consisted of non-metallic material. The powder sample was subject to leaching in concentrated  $\text{H}_2\text{SO}_4$  with the addition of  $\text{NaCl}$  and  $\text{CuSO}_4$ . Moreover, air was blowing in. The sample was subject to classic leaching as well as to leaching with the aid of electrooxidation. The results showed that during the classic leaching the copper extraction reached

100 % after 330 minutes, whilst with the aid of electrooxidation the same extraction was achieved after 210 minutes.

Castro and Martins [19] obtained tin and copper from PCBs by leaching and precipitation. At first, PCBs were grinded, and the obtained powder sample was leached at the temperature of  $60^\circ\text{C}$  with L:S ratio = 10 for 120 minutes. The following solutions:  $2.18\text{N H}_2\text{SO}_4$ ,  $2.18\text{N H}_2\text{SO}_4 + 3.0\text{N}$

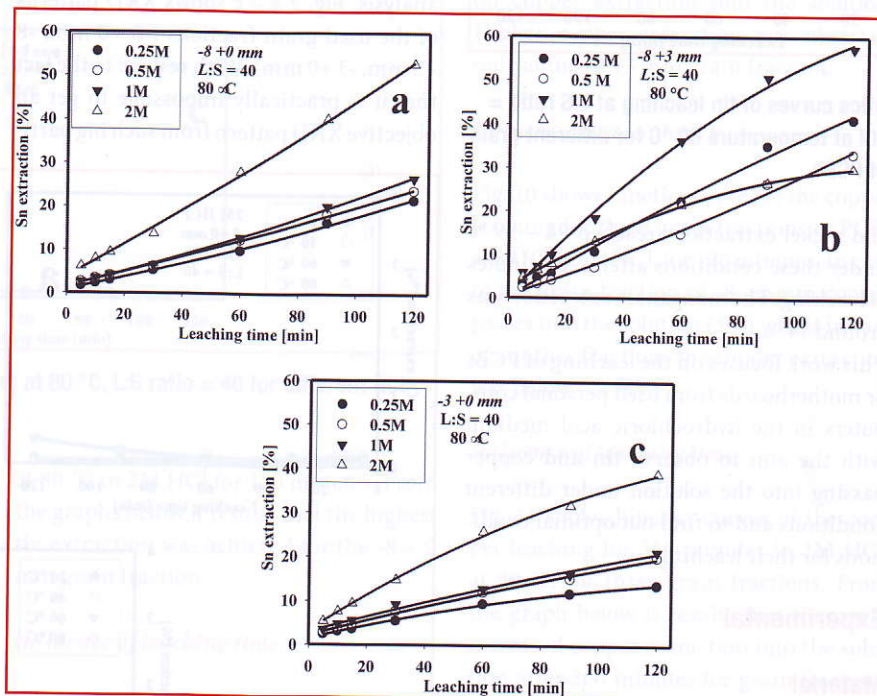


Fig. 5 a – c: Kinetics curves of tin leaching at  $80^\circ\text{C}$ , L:S ratio = 40, at different HCl concentrations and grain fractions of PCBs

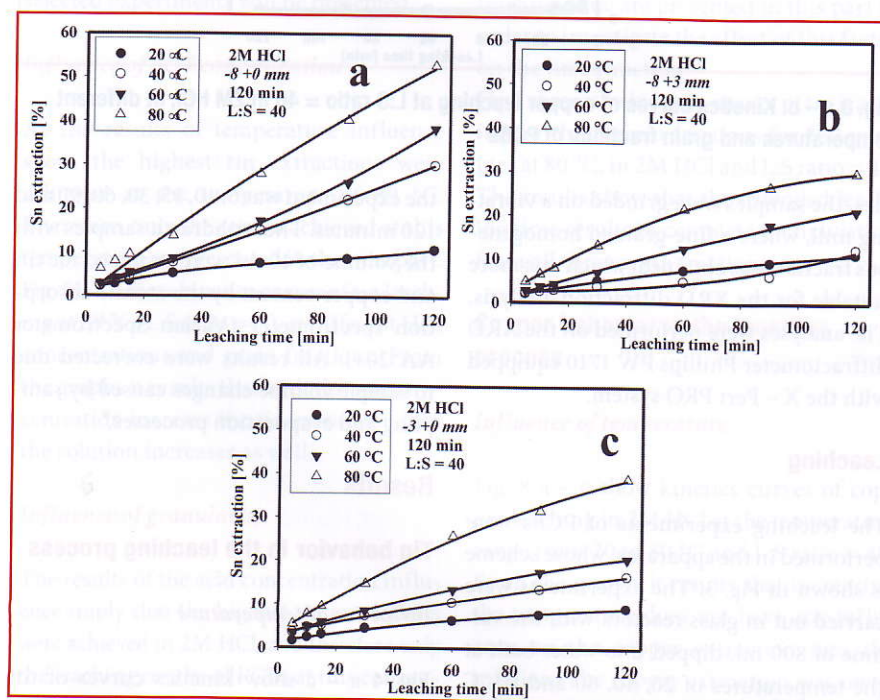


Fig. 4 a – c: Kinetics curves of tin leaching in 2M HCl, at L:S ratio = 40 at different temperatures and fractions of PCBs

HCl, 3.0N HCl and 3.0N HCl + 1.0N  $\text{HNO}_3$  were used as leaching reagents. The lowest extractions (2.7 % Sn, 0.01% Cu) were reached by using  $2.18\text{N H}_2\text{SO}_4$ ; and on the contrary, the highest extractions (98 % Sn, 93 % Cu) were reached by using  $3.0\text{N HCl} + 1.0\text{N HNO}_3$ . When using precipitation with NaOH, a maximum of 4.3 % Sn and 1.3 % Cu was obtained from the solution at pH = 3.3.

Bari et al. [20] leached PCBs in order to leach out Cu, Zn and Ni.  $\text{NH}_3$  solution with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  was used as a leaching reagent. The highest extractions of Cu (99 %), Zn (60 %) and Ni (9 %) were reached after 360 minutes of leaching in  $5\text{M NH}_3 + 0.5\text{M } (\text{NH}_4)_2\text{S}_2\text{O}_8$  solution. Consequently, the solution was submitted to electrolysis after leaching, where Cu with 99.97 purity % was obtained.

Veglio et al. [21] were recovering metals by leaching electronic and industrial waste. They used 0.05 – 0.15M  $\text{H}_2\text{SO}_4$  solution for the experiments. The temperature of the process was from  $30^\circ\text{C}$  to  $90^\circ\text{C}$ . Copper



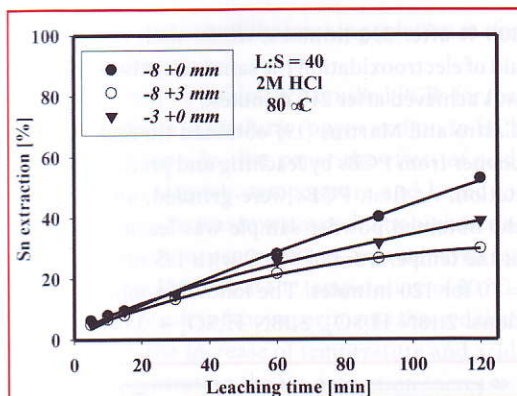


Fig. 6: Kinetics curves of tin leaching at L:S ratio = 40 in 2M HCl at temperature 80 °C for different grain fractions of PCBs

and nickel extractions reached 94 – 99 % under these conditions after 120 minutes of leaching. The manganese extraction was around 14 %.

This work focuses on the leaching of PCBs or motherboards from used personal computers in the hydrochloric acid medium with the aim to observe tin and copper passing into the solution under different conditions and to find out optimal conditions for their leaching.

## Experimental

### Material

The PCBs used in the experiments were obtained from used personal computers produced in the years 1985 to 2000. 73 kg of used motherboards 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 mill. The representative sample of 2 kg was obtained from the crushed

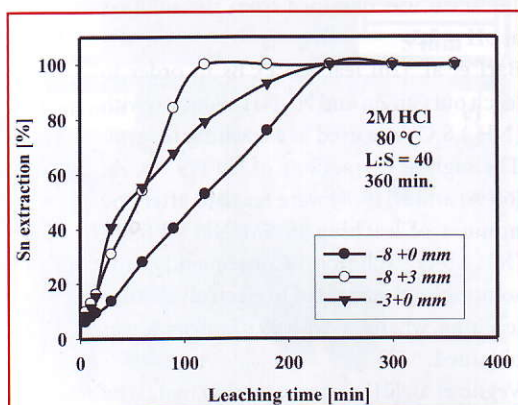


Fig. 7: Kinetics curves of tin leaching from PCBs in 2M HCl, at temperature 80 °C for 360 minutes for different grain fractions

material by quartering. From that sample (fraction -8 +0 mm, Fig. 1a) next sample for chemical analysis was taken. Remaining part was sieved into two fractions -8 +3 mm and -3 +0 mm (Fig. 1 b, c). Obtained products were submitted to chemical analysis by atomic absorption spectrometry (AAS), Tab. 1.

The phase composition was determined by the X-ray diffraction qualitative phase analysis. Fig. 2 a – c shows XRD patterns of the used grain fractions (-8 +0 mm, -8 +3 mm, -3 +0 mm). With respect to the fact that it is practically impossible to get an objective XRD pattern from such big parti-

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 (-8 +3 mm, -3 +0 mm) were obtained by sieving crushed PCBs on screen with the aperture size of 3 mm. The total experiment time was 120 minutes. The time period for the withdrawal of liquid samples during

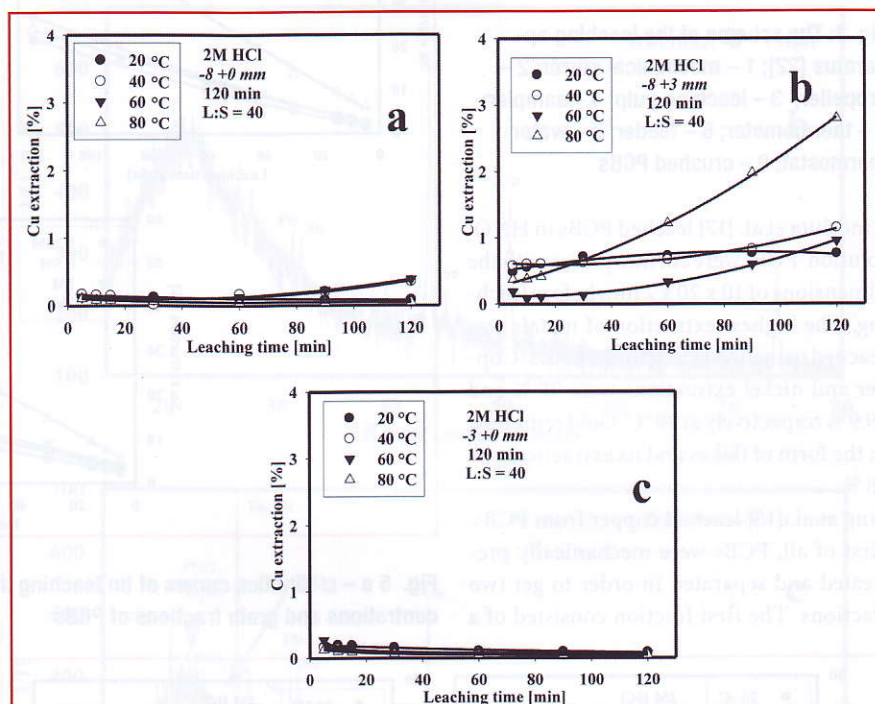


Fig. 8 a – c: Kinetics curves of copper leaching at L:S ratio = 40 in 2M HCl, at different temperatures and grain fractions of PCBs

cles, the samples were grinded on a vibrating mill, where a fine-grained homogeneous fraction was obtained, which was more suitable for the XRD diffraction analysis. The analyses were performed on the XRD diffractometer Phillips PW 1710 equipped with the X – Pert PRO system.

### Leaching

The leaching experiments of PCBs were performed in the apparatus, whose scheme is shown in Fig. 3. The experiments were carried out in glass reactors with the volume of 800 ml, dipped into water bath at the temperatures of 20, 40, 60 and 80 °C using constant stirring. The aqueous solution of hydrochloric acid at concentrations of 0.25M, 0.5M, 1M and 2M was used as a

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.

## Results

### Tin behavior in the leaching process

#### Influence of temperature

Fig. 4 a – c show kinetics curves of tin leaching from PCBs in 2M HCl at the temperatures of 20, 40, 60 and 80 °C for three grain fractions and at L:S ratio = 40. From



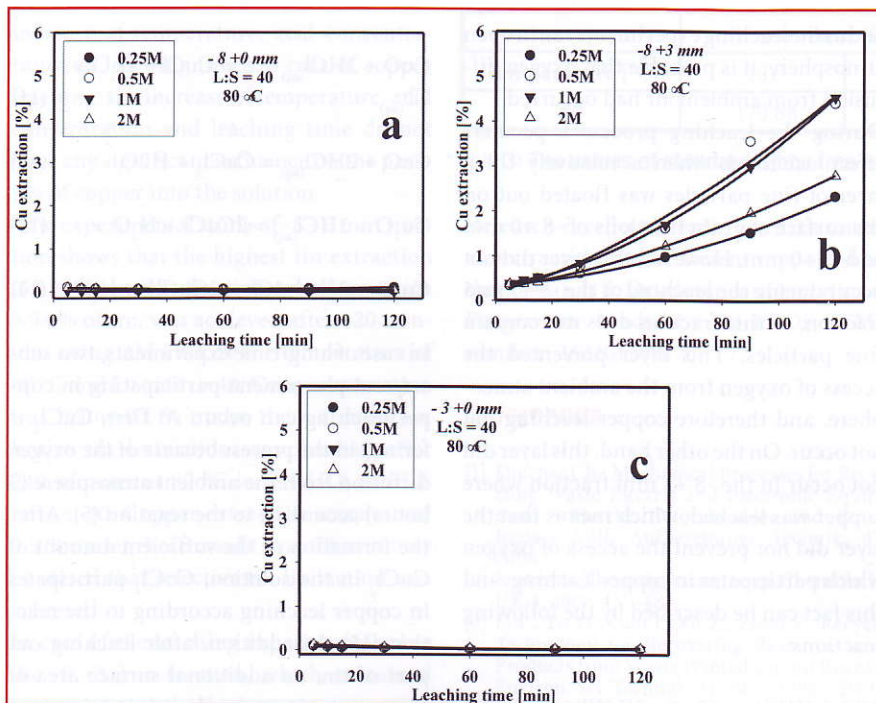


Fig. 9 a – c: Kinetics curves of copper leaching at 80 °C, L:S ratio = 40 for different HCl concentrations and grain fractions of PCBs

the graphs it results that the temperature change has a positive effect on the tin extraction into the solution. The highest tin extraction was achieved at 80 °C.

The tendency of the curves indicates that the extension of the leaching time could lead to a higher extraction. The leaching time for these experiments is 120 minutes, but in the next part the results of the leaching time influence on the tin extraction for selected experiments will be presented.

#### Influence of acid concentration

As the results of temperature influence show, the highest tin extractions were achieved at the temperature of 80 °C. Therefore, only the results achieved at this temperature are presented in the next part. Fig. 5 a – c show kinetics curves of tin leaching at 80 °C, L:S ratio = 40, at different HCl concentrations and grain fractions. From the graphs it results that with the acid concentration increase the tin extraction into the solution increases as well.

#### Influence of granularity

The results of the acid concentration influence imply that the highest tin extractions were achieved in 2M HCl, and therefore only the leaching results of PCBs at this concentration will be presented in the next part.

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 graphs below it results that the highest tin extraction was achieved for the -8 + 0 mm grain fraction.

#### Influence of leaching time

The current results of the tin leaching from PCBs were obtained after 120 minutes. Therefore, some results with the extended leaching time are presented in this part in order to investigate the effect of this factor on the tin extraction.

Fig 7 shows the kinetics curves of tin leaching for three grain fractions for 360 minutes at 80 °C, in 2M HCl and L:S ratio = 40. The results show that the extended leaching time results in complete tin lixiviation from all three grain fractions.

### Copper behavior in the leaching process

#### Influence of temperature

Fig. 8 a – c show kinetics curves of copper leaching in 2M HCl at the temperature range from 20 to 80 °C and L:S ratio = 40. From the graphs it results that increasing the temperature does not have any influence on the copper extraction into the solution. The copper extraction was up to 0.5 % and in some cases below 0.05 % at all temperatures and grain fractions -8 + 0 mm and -3 + 0 mm. Higher copper extrac-

tion up to 3 % was observed only at fraction -8 + 3 mm.

#### Influence of acid concentration

Fig. 9 a – c show kinetics curves of copper leaching at 80 °C, L:S ratio = 40, at different acid concentrations and grain fractions. The change in hydrochloric acid concentration did not have significant influence on copper extraction into the solution. Higher copper extraction was observed only at the -8 + 3 mm grain fraction.

#### Influence of granularity

Fig. 10 shows kinetics curves of the copper leaching for three grain fractions of PCBs at 80 °C in 2M HCl, for 120 minutes. In case of the grain fraction of -8 + 3 mm copper passes into the solution (3 %) whilst in case of another fractions the copper extraction was below 0.5 %.

#### Influence of leaching time

Fig. 11 shows kinetics curves of the copper leaching for 360 minutes in 2M HCl, at 80 °C for three grain fractions. From the graph below it results that there was increased copper extraction into the solution after 360 minutes for grain fractions of -8 + 3 mm a -3 + 0 mm.

### Discussion

From the leaching experiments of PCBs it results that tin and copper behavior during the leaching was different.

Hydrochloric acid is a non-oxidizing acid. The XRD patterns showed that tin and copper were present in the metallic form in the PCBs, and therefore only this form

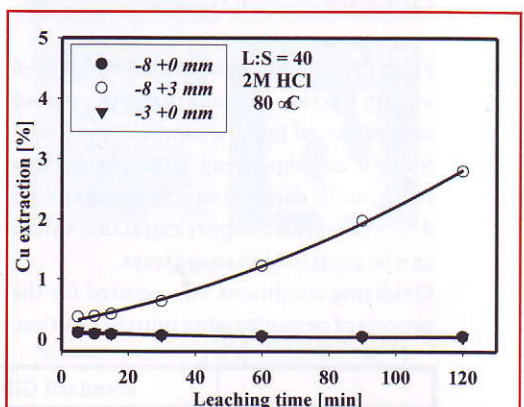


Fig. 10: Kinetics curves of copper leaching at L:S ratio = 40 in 2M HCl, at 80 °C for different grain fraction of PCBs



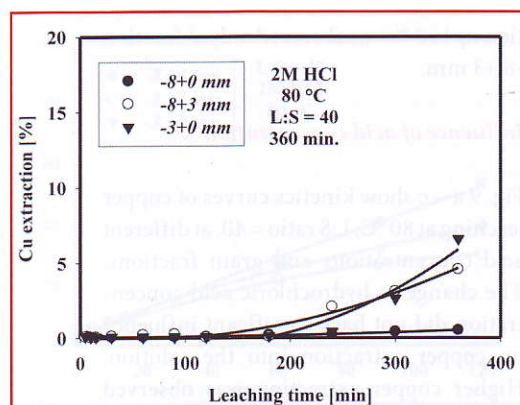
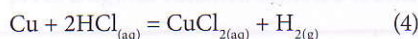


Fig. 12: Reduction of the impurities by gas purging ( $t = 15$  min,  $V = 2.2$  l/min,  $p = 0.8$  bar,  $T = 1500$  °C)

was considered during calculations. From the thermodynamic calculations of tin and copper leaching for reactions (1) – (4) 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  $\Delta G^\circ$  (Tab. 2), which means that from the thermodynamic point of view they are likely to run in the direction of product creation. This fact is also confirmed by the results of tin leaching experiments under different conditions (Fig. 4 – 7). On the other hand, the reactions of metallic copper leaching, (3) and (4), show a positive value of  $\Delta G^\circ$  (Tab. 2), which means they will not run. This fact is confirmed also by the results of copper leaching in Fig. 8 a, c.

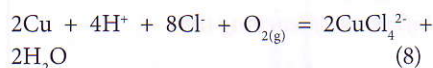
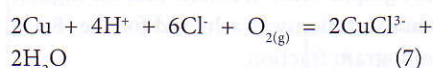
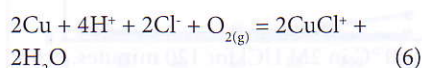
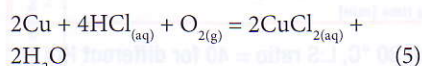


From the leaching experiments using the -8 +3 mm fraction it results that also a part of copper passed into the solution, and therefore an accompanying phenomena must occur, as the copper extraction was around 4 %. The elevated copper extraction values can be explained in many ways.

Oxidizing conditions are required for the process of copper passing into the solution,

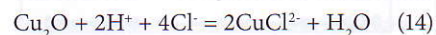
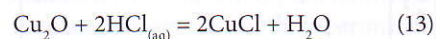
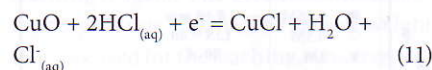
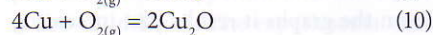
and as the leaching experiments ran in open atmosphere, it is probable that oxygen diffusion from ambient air had occurred.

During the leaching process a peculiar effect occurred, when a relatively thick layer of fine particles was floated out on the surface at grain fractions of -8 +0 mm and -3 +0 mm. However, this layer did not occur during the leaching of the -8 +3 mm fraction, as this fraction does not contain fine particles. This layer prevented the access of oxygen from the ambient atmosphere, and therefore copper leaching did not occur. On the other hand, this layer did not occur in the -8 +3 mm fraction where copper was leached, which means that the layer did not prevent the access of oxygen which participates in copper leaching; and this fact can be described by the following reactions:

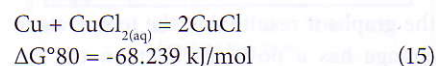


The reactions of copper leaching in hydrochloric acid solutions at oxygen presence (5) – (8) show a negative value of  $\Delta G^\circ$  (Tab. 3), and therefore from the thermodynamic point of view it is probable that they will run, as opposed to copper leaching without the oxygen presence (reactions 3 and 4), where the values of  $\Delta G^\circ$  were positive.

Another explanation for copper leaching can be given by leaching of the oxidized layer of copper, which was created as a result of storing crushed PCBs. The reactions of copper oxide formation (9) and (10) show negative values of  $\Delta G^\circ$ . Additionally, leaching of copper oxides can run also under non-oxidizing conditions, as shown by the values of  $\Delta G^\circ$  for reactions (11) – (14) in Tab. 4.



In case of long-time experiments, two subsequent phenomena participating in copper leaching can occur. At first,  $\text{CuCl}_2$  is formed in the process because of the oxygen diffusion from the ambient atmosphere (3 hours) according to the reaction (5). After the formation of the sufficient amount of  $\text{CuCl}_2$  in the solution,  $\text{CuCl}_2$  participates in copper leaching according to the reaction (15). In addition, after leaching out part of tin, an additional surface area of copper was uncovered and reactive area grown larger, whereby the trend of curves in Fig. 11 can be explained.



The reason why higher copper extractions were not achieved may be caused by copper cementation on metallic parts of less noble metals, which occurs during the leaching process. As all the metals in PCBs are practically less noble than copper, except for Au and Ag, this fact must be taken into consideration.

A possible reaction between hydrochloric acid and the organic phase can be considered a totally unexplored area, because some compounds (epoxide, polyester, nylon) contain oxygen within their polymer chains. As the elevated copper extraction into the solution occurred only at increased temperatures and in 2M HCl, it is possible that oxygen from the polymeric chain could be released under these aggressive conditions.

## Conclusion

Based on the experiments it was found out that the behavior of individual fractions during the leaching is different, and also tin and copper leaching run in different ways. From the leaching of individual grain fractions (-8+0 mm, -8 +3 mm, -3 +0 mm) it results that the leaching process of tin depends on temperature, hydrochloric acid concentration and on leaching time, where tin extraction raises with the

	standard Gibbs free energy change $\Delta G^\circ$ [kJ/mol]			
Temperature [°C]	(1)	(2)	(3)	(4)
80	-56.09	-59.42	26.75	57.44

Tab. 2: The values of standard Gibbs free energy change for the reactions (1) – (4) [23]



increase of temperature, acid concentration and leaching time. In case of copper leaching, the increase of temperature, acid concentration and leaching time do not have any significant influence on the passing of copper into the solution.

The experimental study of -8 +0 mm fraction shows that the highest tin extraction (53 %) from this fraction, which contains 5.94 % of tin, was achieved after 120 minutes using 2M HCl, at the temperature of 80 °C and L:S ratio = 40. Copper extraction was below 0.1 % under these conditions. Entire tin lixiviation was reached after 240 minutes at 80 °C in 2M HCl and L:S ratio = 40. Copper extraction was around 0.5 % under these conditions. Thus it may be stated that selective tin lixiviation was achieved.

In case of the leaching experiments using the -8 +3 mm fraction, which contained 1.32 % of tin, the highest tin extraction 29.85 % was achieved after 120 minutes in 2M HCl at 80 °C. However, during the leaching also around 4 % of copper passed into the solution, which is not very desirable from the practical point of view. Another fact, which is not in favor of leaching this fraction, is that the absolute amount of tin to be leached out is lower than in -8 +0 mm fraction. It was found out that during the leaching of the -3 +0 mm fraction with tin content of 4 %, the highest tin extraction (40 %) was achieved after 120 minutes in 2M HCl, at 80 °C and L:S ratio = 40. Copper extraction was under 0.1 % under these conditions.

Following the results of leaching of three fractions it can be stated that the sieving of crushed PCBs in this process step with the aim of selective tin leaching turned out to be ineffective. The entire tin lixiviation was reached after 360 minutes in all three grain fractions; but in the -8 +3 mm and -3 +0 mm fractions copper was passing into the solution as well. The selective leaching of tin without copper passing into the solution was achieved only in the -8 +0 mm fraction. This fact has a real impact on the practical implementation, because costs and energy consumed by sieving are saved.

## Acknowledgements

This work was supported by Ministry of Education of the Slovak republic under grant MS SR 1/0123/11 project No. APVV-20-013405. This contribution is also the result of the project implementation

standard Gibbs free energy change $\Delta G^\circ$ [kJ/mol]				
Temperature [°C]	(5)	(6)	(7)	(8)
80	-170.88	-167.31	-148.09	-128.79

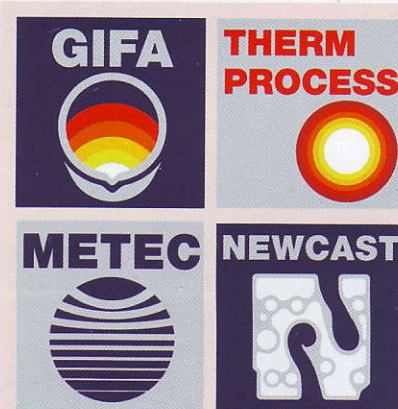
Tab. 3: The values of standard Gibbs free energy change for the reactions (5) – (8) [23]

Research excellence centre on earth sources, extraction and treatment supported by the Research & Development Operational Programme funded by the ERDF, ITMS number: 26220120017.

## References

- [1] Drechse Ch.: Mechanical Processes for Recycling Waste Electric and Electronic Equipment with the Rotorshredder and Rotor Impact Mill, Aufbereitungs Technik, 47, 2006.
- [2] Burke M.: The gadget scrap heap, ChemWorld UK 4, 2007, 45 – 48.
- [3] Li L., Lu H., Guo J., Xu Z., Zhou Y.: Recycle Technology for Recovering Resources and Products from Waste Printed Circuit Boards, Environ. Sci. Technol. 41, 2007, 1995 – 2000.
- [4] Goosey M., Kellner R.: A Scoping Study End-of-Life Printed Circuit Boards, Website, 2007, [http://www.cfsd.org.uk/seeba/TD/reports/PCB\\_Study.pdf](http://www.cfsd.org.uk/seeba/TD/reports/PCB_Study.pdf).
- [5] Cui J.: Mechanical Recycling of Consumer Electronic Scrap, Website, 2008, <http://epubl.luth.se/1402-1757/2005/36/LTU-LIC-0536-SE.pdf>.
- [6] Zhang H. – Ch., Ling F.: A Decision-Making Model for Materials Management of End-of-Life Products in the Pantex Plant, Website, 2008, [www.uraweb.org/reports/anrc9927.pdf](http://www.uraweb.org/reports/anrc9927.pdf).
- [7] Shuey S., Taylor P.: A Review of Pyrometallurgical Treatment of Electronic Scrap, SME Annual Meeting and Exhibit February 23 – 25, Denver, 2004.
- [8] Lehto H., Tohka A., Saeed L., Zevenhoven R., Heiskanen K.: Minimising environmental impact and improving synergism between mechanical and thermal processing of waste from electrical and electronic equipment, Metals and Energy Recovery, Skellefteå, Sweden, 2003.
- [9] Hagelucken Ch., Van Kerckhoven T.: Maximising returns from e-scrap recycling, Website, 2008, [http://www.preciousmetals.unicore.com/publications/presentations/e\\_scrap/show\\_SanFranciscoIERI2006.pdf](http://www.preciousmetals.unicore.com/publications/presentations/e_scrap/show_SanFranciscoIERI2006.pdf).
- [10] Mineral Commodity Summaries 2009, Website, 2010, <http://minerals.usgs.gov/minerals/pubs/mcs/2009/mcs2009.pdf>.
- [11] Oh Ch. J., Lee S. O., Yang H. S., Ha T. J., Kim M. J.: Selective Leaching of Valuable Metals from Waste Printed Circuit Boards, Air & Waste Management Association 53, 2003, 897 – 902.
- [12] Rabah M., Mosa M., Aly G.: Recovery of Metals Values from Useless Printed Circuit Boards, Eurasian Chem J. 9, 2007, 129 – 137.
- [13] Mecucci A., Scott K.: Leaching and electrochemical recovery of copper, lead and tin from scrap printed circuit boards, J. Chem. Technol. Biotechnol. 77, 2002, 449 – 457.
- [14] Orac D., Hoang Trung Z., Miskufova A., Havlik T.: Hydrometallurgical processing of printed circuit boards from used personal computers, Waste Recycling 11, 2007, 133 – 137.
- [15] Orac D., Kukurugya F., Havlik T.: Hydrometallurgical treatment of printed circuit boards from used computers, Acta Metallurgica Slovaca 14, 2008, 1335 – 1532.
- [16] Oishi T., Koyama K., Alam S., Tahala M., Lee J.-C.: Recovery of high purity copper cathode from printed circuit boards using ammonia-cal sulfate or chloride solutions, Hydrometallurgy 89, 2007, 82 – 88.
- [17] Kinoshita T., Akita S., Kobayashi N., Nii S., Kawaizumi F., Takahashi K.: Metal recovery from non-mounted printed wiring boards via hydrometallurgical processing, Hydrometallurgy 69, 2003, 73 – 79.
- [18] Ping Z., ZeYun F., Jie L., Qiang L., GuangRen Q., Ming Z.: Enhancement of leaching copper by electro-oxidation from metal powders of waste printed circuit board, Journal J. Hazard. Mater. 166, 2009, 746 – 750.
- [19] Castro L. A., Martins A. H.: Recovery of tin and copper by recycling of printed circuit boards from obsolete computers, Brazilian Journal of Chemical Engineering 26, 2009, 649 – 657.
- [20] Bari F., Begum N., Jamaludin S. B., Hussein K.: Selective leaching for the recovery of copper from PCB, Website, 2010, <http://dspace.unimap.edu.my/dspace/bitstream/123456789/7476/1/Selective%20leaching%20for%20the%20recovery%20of%20Copper.pdf>.
- [21] Veglio F., Quaresima R., Fornari P., Ubaldini S.: Recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning, Waste Management 23, 2003, 245 – 252.
- [22] Havlik T.: Hydrometallurgy: Principles and applications, TU Kosice, 2005, p. 485, ISBN 80-8073-337-6.
- [23] Roine A.: HSC chemistry\*, ver. 6.0 – software Outotec Research Oy.

(1) Orac D., Havlik T., Kukurugya F., Miskufova A., Takacova Z., Technical University of Kosice, Faculty of Metallurgy, Department of Non-ferrous Metals and Waste Treatment, Letna 9, 042 00 Kosice, Slovak Republic



Vorschau:

Schwerpunkt **M**ETALL 6/11

Messehighlights von Gifa, Metec, Thermprocess und Newcast