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The effect of mechanical-physical pretreatment on hydrometallurgical extraction of copper and tin in residue from printed circuit boards from used consumer equipment



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1. Introduction

A key motivation for recycling of waste electrical and electronic equipment (WEEE) is the content of many types of valuable materials, as in other studies (Yamane et al., 2011; Veit et al., 2005; Kasper et al., 2011). Most WEEE includes printed circuit boards (PCBs) that are normally separated by hand-picking or sensor-based sorting. PCBs are sold to non-ferrous metal markets because they contain high grades of copper and other valuable metals (Yamane et al., 2011). However, PCBs also contain impurities such as silicon, aluminium, iron, which are slag materials in non-ferrous smelting processes, and other harmful elements such as zinc, lead, bromine and antimony.

At present, attention is focused mainly on processing of PCBs from used computers. The main reason is that these boards contain interesting quantities of metals (mainly precious metals) and are regarded as a "high grade" secondary raw material. The high level of attention corresponds to the number of scientific publications which are devoted to different methods of pretreating and processing with the aim to recycle these valuable elements (Table 1).

An overview of such publications (Table 1) shows which methods were used for mechanical pretreatment, namely various methods for comminution and sizing for initial treatment. These

ABSTRACT

This work is focused on studying mechanical-physical pretreatment of printed circuit boards from used consumer equipment followed by extraction of copper and tin from residue fractions by leaching in hydrochloric acid solutions. Mechanical-physical pretreatment was realized in three different procedures. Key processes were electro-dynamic separation, cross-flow air sifter separation and air table separation, respectively. Leaching experiments were carried out in 1 M and 2 M HCl at 80 °C. The results show that cross-flow air sifting leads to the highest accumulation of non-ferrous metals in a residue fraction. From this fraction, the highest extraction of tin with minimal copper extraction was achieved. © 2014 Elsevier Ltd. All rights reserved.

are followed by an array of magnetic and electro-static separation methods as well as sifting and density-based methods, but rarely electro-dynamic separation.

It follows from scientific papers, that using magnetic separation leads to complete separation of magnetic fraction. However, this magnetic fraction also contains part of non-ferrous metals, mainly due to insufficient liberation during comminution. An aluminium fraction can be recovered by using eddy-current separation (ECS). Electrostatic separation efficiency is influenced by many factors e.g. particle size (Zhang et al., 1998). Moreover, to avoid the influence of particles with different sizes during separation, authors used sieving to ensure optimal conditions for separation. For this reason, sieving and separation in several steps is needed, which makes processing expensive. In some articles, chemical analysis of samples after separation as well as comparison of different separation methods aiming to obtain pre-concentrate of non-ferrous metals are missing.

PCBs are not only present in personal computers but are now widespread in almost all electronic devices such as televisions, monitors, radios and others in the 4th category of WEEE: "consumer equipment". Statistics of WEEE collection for EU 27 countries show that approximately 620,000 tonnes were collected in 2010 (Fig. 1), which represents 19.5% of all WEEE categories (Fig. 2). The largest amount of equipment was collected in the category "large household appliances" (47.4%) and "IT and telecommunications equipment" with 22% (note: the last available data



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Table 1

Pretreatment	methods	of	electronic	waste	hv	several	authors
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Authors	Material	Used methods
Habib et al. (2013)	PC board scrap	Cutting mill, vibrating separator
Dey et al. (2012)	Scrap computers, television sets and mobile	Shredding, ball mill, density separator
	phone hand sets	
Lee et al. (2012)	PCBs from video recorders	Sizing, magnetic separation, dense medium separation
Chao et al. (2011)	PC motherboards scrap	Crushing, pneumatic separation, electrostatic separation, magnetic separation
Kasper et al. (2011)	Mobile phone scrap	Hammer mill, knife mill, magnetic separation, electrostatic separation
Yamane et al. (2011)	PC board scrap	Hammer mill, magnetic separation, electrostatic separation
Das et al. (2009)	PCBs scrap	Ball mill, hydrocyclone, flotation, multi-gravity separator, electrostatic separation
Wu et al. (2009)	PCBs scrap	Crushing, electrostatic separation
Eswaraiah et al. (2008)	PC board scrap	Hammer mill, air classification
Lu et al. (2008)	PCBs scrap	Electrostatic separation
Kers et al. (2008)	Consumer equipment PCBs scrap	Disintegrator mill, air classification, magnetic separation
Wu et al. (2008)	PCBs scrap	Crushing, electrostatic separation
Li et al. (2007)	Mixed PCBs	Crushing, Corona electrostatic separation
Veit et al. (2005)	PC board scrap	Cutting mill, electrostatic separation, magnetic separation
Zhang and Forssberg (1997, 1999)	PC board scrap	Hammer mill, eddy-current, density-based separation
Zhang et al. (1998)	PC scrap, mixture of PC scrap and PCBs	Ring shredder, hammer mill, eddy-current separation



Fig. 1. Collection of WEEE in EU 27 countries in years 2007–2010 (Eurostat, http://epp.eurostat.ec.europa.eu).



Fig. 2. Collection of WEEE in 2010 in EU 27 countries (Eurostat, http://epp.eurostat.ec.europa.eu).

on the Eurostat website are from 2010) (Eurostat, http://epp.eurostat.ec.europa.eu).

The content of valuable metals in "consumer equipment" determines whether they are considered "low grade" of "high grade" secondary raw materials. More attention is being paid to processing of PCBs from used computers and practically no scientific papers are dealing with recycling of "low grade" secondary raw

Table 2												
Average	content	of	metals	in	ores,	high	grade	material	and	low	grade	material

(Tuncuk et al.,	2012; Cui an	d Forssberg, 2007; Cui and Zh	ang, 2008).
	Ores	High grade material	Low grade material

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

materials (Tuncuk et al., 2012). Nevertheless, the content of metals in "low grade" material is much higher (Table 2) than in primary raw materials (ores) and even higher for some metals than in high grade material. This clearly indicates the necessity for treatment of low grade PCBs. Moreover, the quantity of collected equipment in 4th category (consumer equipment) is approximately the same as in 3rd category (IT and telecommunications equipment), which are labeled as high grade material.

Table 3 shows the material potential of metals for the category "consumer equipment". In the table, average contents and prices of valuable metals such as copper, tin, gold, silver, palladium and steel are given. Based on the collected quantities of equipment for Germany, Slovakia and EU 27 countries, each amount of metals and their economic values were calculated. Table 3 clearly indicates the importance of recycling consumer equipment even if it is labeled as low grade material.

The main difference between ores and wastes, besides the quantitative contingent of elements is their form of appearance. Whereas metals in ores occur in form of chemical compounds, they are present in WEEE in metallic form or as alloys. This makes them especially suitable for mechanical–physical pretreatment before metallurgical processing.

The aim of this work is to compare three procedures of mechanical-physical pretreatment of PCBs from used consumer equipment and to determine the most effective procedure regarding hydrometallurgical recovery of copper and tin from pretreatment residue fractions by leaching in hydrochloric acid solutions.

2. Experimental part

The aim of the experimental part is to determine which procedure of mechanical-physical pretreatment of PCBs from used

Material po	terial potential of category "consumer equipment" (Tuncuk et al., 2012; Cui and Forssberg, 2007; Cui and Zhang, 2008; Eurostat, http://epp.eurostat.ec.europa.eu; MetalPrice											
http://www	w.metalprices.co	om).										
Metal	Price (\$/t)	Average content in equipment (%)	Germany collection (191 280 t)	Slovakia collection (2 545 t)	EU 27 collection (622 499 t)							

Metal	Price (\$/t)	Average content in equipment (%)	Germany collec	Germany collection (191 280 t)		ction (2 545 t)	EU 27 collectio	on (622 499 t)
			Amount (t)	Price (\$/year)	Amount (t)	Price (\$/year)	Amount (t)	Price (\$/year)
Cu	6 652	12.2	23336.16	155 232 136	310.49	2 065 379	75944.9	505 185 475
Sn	23 205	1.06	2027.568	47 049 715	26.977	626 001	6598.5	153 118 193
Steel	390	42.5	81294	31 704 660	1081.625	421 834	264562.1	103 179 219
Au	42 057 878	0.0015	2.8692	120 672 464	0.03818	1 605 770	9.3375	392 715 436
Ag	645 016	0.01975	37.7778	24 367 285	0.50264	324 211	122.9436	79 300 589
Pd	24 887 459	0.0007	1.3389	33 321 819	0.01782	443 495	4.3575	108 447 103
Sum	-		106699.7139	412 348 079	1419.65064	5 486 690	357550.0347	1 341 946 015

Note: Price of precious metals (09.04.2014): Au: 1308 \$/oz, Ag: 20.06 \$/oz, Pd: 1774 \$/oz, 1 oz = 31.1 g. The bold values represent material potential of category "consumer equipment".

consumer equipment produces a residue fraction most suitable for hydrometallurgical processing to obtain tin and copper. All procedures were fed with material from the same input sample, described in the following.

2.1. Material

Table 3

The input sample consisted of pieces of electronic equipment (Fig. 3), which was classified as "consumer equipment" (4th category) according the Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment (WEEE). Part of the input sample was crushed below 1 mm and chemically analyzed using atomic absorption spectrometry (AAS, Varian Spectrometer AA 20+). Size reduction to below 1 mm for chemical analysis was identified yield sufficient metal liberation in other studies (Veit et al., 2005; Zhang and Forssberg, 1997; Kasper et al., 2011). To reduce statistical errors due to heterogeneity of the sample, chemical analysis was carried out three times and average values for calculations were considered. The results shown in Table 3 emphasize the potential of metals even in low grade PCBs. Most notably they contain 14.45 mass% of Fe and 10.32 mass% Cu on average. Concerning non-ferrous metals, these results correlate to findings of other studies where PCBs from personal computers (PC) (Veit et al., 2005; Yamane et al., 2011) and mobile phone (Kasper et al., 2011) were analyzed; for Fe, significantly higher contents found in the present study.

2.2. Mechanical-physical pretreatment

Based on the availability of devices, three procedures of mechanical-physical pretreatment were proposed. Each procedure contains magnetic separation aiming to remove an iron fraction and eddy-current separation to remove non-ferrous metals such



Fig. 3. Input material for mechanical-physical pretreatment experiments.

as aluminium. In addition, zig-zag separator and an air table were chosen for separation of non-ferrous metals from non-metals. For comparison of the separation effect, a basic scheme (*Procedure A*) was proposed. This scheme contains only magnetic and eddy-current separation. The two remaining procedures were created as variations of *Procedure A*.

In most other studies (see Table 1), electrostatic separation was used to remove non-ferrous metals from non-magnetic fractions; however, this was done for smaller particle sizes than in the present study: (Kasper et al., 2011) and (Veit et al., 2005) milled particles to below 1 mm, while (Yamane et al., 2011) comminuted to below 2 or 4 mm prior electrostatic separation. In the present study, the smallest grate opening during mechanical pretreatment was 20 mm, which is suitable for eddy-current separation. Particle sizes in the low mm-range become less responsive to ECS, as determined by (Zhang et al., 1998). Since eddy-current separation yielded mostly aluminium, the removed fraction is referred to as Al fraction in the following; however, other non-ferrous metals were present.

2.2.1. Procedure A

This procedure (flow chart in Fig. 4) consisted of comminution 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). Comminution 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 from which two fractions were obtained (an Al fraction and **Residue A**).

2.2.2. Procedure B

This procedure (flow chart in Fig. 5) consisted of comminution in three stages using a single shaft shredder (60 and 20 mm discharge grates) and a hammer crusher (20 mm discharge grate). These steps were carried out for initial liberation of materials from composites and for preparation for sorting operations that require smaller particles sizes. Comminution with 20 mm discharge grates was carried out twice to utilize selective comminution behavior, a single shaft shredder exerting cutting/tearing forces and a hammer crusher exerting impact/friction forces. Comminution was followed by magnetic separation, where the magnetic fraction was removed by a drum magnet. The non-magnetic fraction was further processed by electro-dynamic separation using a con-centric eddy-current separator from which two fractions were obtained (an Al fraction and residue). The residue fraction was further processed by cross-flow air sifting where a heavy and a light fraction were obtained. The goal of air sifting was removing low-density



Fig. 5. Scheme of Procedure B.

plastics, foils and dust into the light fraction, while keeping all metal parts in the heavy fraction (*Residue B*).



	Chemical	analysis (mas		Insoluble residue (mass %)					
	Cu	Sn	Pb	Fe	Al	Zn	Au	Ag	
Analysis No. 1	12.05	1.51	0.58	16.84	5.8	1.63	0.003	0.01	37.5
Analysis No. 2	9.25	1.42	0.89	10.73	9.94	0.46	0.002	0.01	52.1
Analysis No. 3	9.65	1.41	0.46	15.78	9.97	0.61	0.002	0.005	47.8
Ø	10.32	1.44	0.64	14.45	8.57	0.9	0.00233	0.0083	45.8

Table 4Chemical composition of input sample.

air from this process. The heavy fraction was processed 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 (an Al fraction and **Residue C**).

The output from each procedure (*Residues A–C*) was transferred to a hammer crusher (8 mm discharge grate) and to hammer mill (1 mm discharge grate) to yield fractions of -8 + 0 mm and of -1 + 0 mm grain size. These two fractions of each residue were used for leaching experiments.

2.3. Leaching experiments

Leaching experiments were carried out in the apparatus shown in Fig. 7. Experiments were realized in glass reactors with a volume of 800 ml immersed in a water bath at 80 °C using constant stirring (300 rpm). Water solutions of hydrochloric acid with 1 M and 2 M concentrations were used as leaching reagents. The volume of the leaching reagents was 400 ml and the weight of each sample was 10 g (fractions -8 + 0 mm, -1 + 0 mm) which results in a liquidto-solid ratio (L:S) of 40. The total duration of each experiment was 120 min. During each experiment, liquid samples (10 ml) were withdrawn after 5, 10, 15, 30, 60, 90 and 120 min, and were analyzed by atomic absorption spectrometry to determine the content of copper and tin. All results were corrected for volume change and evaporation.

3. Results and discussion

3.1. Mechanical-physical pretreatment

Table 5 shows results of chemical analysis of final residual fractions (*Residue A–C*) using AAS and mass yields of these fractions. It must be noted that other studies (see Table 1) focus on middlings and products, not residual fractions. This is a distinct approach of the present study.

Between a fifth and a third of mass was transferred into the residue in each procedure. Compared to the chemical composition of the input sample (see Table 4) **Residue** C shows the least changes, while **Residue** A and B exhibit significant changes (Fig. 8). The share of Fe was reduced drastically (factor of approx. 70 to 80). This is due to relatively simple and effective removal of Fe into the magnetic fraction via drum magnet separation. The share of aluminium has decreased, presumably as a consequence of eddy-current separation that removes relatively large aluminium particles that stem from larger assembly parts such as Al casings or coolers.

Table	5
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Chemical composition of final residue fractions.



Fig. 8. Changes between metal content in input sample and **Residue A–C** respectively, (a) referring to non-ferrous metals and (b) referring to Fe.



Fig. 9. Separation efficiencies of metals from Residue A-C.

Among other metals, the content of Cu, Sn and Pb increased, most significantly for **Residue A** and **B**, while there was only marginal change for **Residue C**. Zinc, silver and gold showed slighter increases. Thus, all observed non-ferrous metal fractions besides

	Input		Input Output		Chemical	Chemical analysis of output (%)						
	(kg)	(mass %)	(kg)	(mass %)	Cu	Sn	Pb	Fe	Al	Zn	Au	Ag
Residue A	76.35	100	22.93	30.04	26.37	3.12	1.57	0.21	3.85	1.3	0.002	0.01
Residue B	76.35	100	25.87	33.9	29.55	4.2	2.22	0.18	5.28	1.36	0.004	0.02
Residue C	120	100	32.84	26.37	11.34	1.64	0.8	3.44	4.13	0.75	0.004	0.01



Fig. 10. Cumulative curves of material after different crushing steps.

aluminium were enriched in the residual fractions. This behavior may be a consequence of different particle shapes and sizes among non-ferrous metals resulting from their different applications on PCBs and peripheral components. Zhang (Zhang et al., 1998) confirms such strong influences of particle shape and size on ECS effectiveness. While aluminium is present in casings and coolers, other non-ferrous metals reside in smaller parts or unfavorable shapes, such as copper wiring.

Fig. 9 shows enrichment of non-ferrous metals in **Residue A–C**. From the graph it follows that highest enrichment were achieved by **Procedure B**. During zig-zag separation, a heavy fraction was obtained and a light fraction with minimal metals content was removed. Comparing overall metals content in the input sample with **Residue B** after mechanical–physical processing it was found that approximately 97% Cu, 98% Sn, 81% Ag and 58% Au were mechanically recovered. The effect of zig-zag separation is evident when the results are compared with **Procedure A**, where only magnetic and eddy-current separations were used. Using air table separation (**Procedure C**), a heavy fraction was also obtained (as in zigzag separation), but the loss of metals into the light fraction were higher.

There are several possible reasons for increased contents of some metals in residue fractions, where they do not belong from a theoretical point of view. In particular, eddy-current separation requires a minimum grain size for sufficient forces to act upon particles to remove them from a material stream. Since surfacemounted devices and other metallic parts on PCBs are small themselves and become even smaller during comminution, they might fall below a critical grain size. This leads to de facto enrichment of such metals in residue fractions and makes these fractions particularly interesting for further metallurgical processing. Fig. 10 shows cumulative grain size curves after crushing of samples from individual procedures. From these curves it is possible to presume a liberation effect: the finer the material after crushing, the better liberation of metals will be achieved. From the curves it follows that after crushing B3 (hammer crusher) more than 80% of the material has a particle sizes under 6 mm and also approximately 40% less than 2 mm. After crushing, using single a shaft shredder (Crushing A2, B2, 20 mm sieve), the size of particles was larger (only 44% less than 6 mm and 10% under 2 mm). The result of Crushing C2 (single shaft shredder, 10 mm sieve) was approximately 80% under 6 mm (same as Crushing B3), but only 20% less than 2 mm. From a comparison of all three crushing steps it follows that after Crushing B3 (hammer crusher) finer particles were obtained, which means that better liberation of metals occurred.

3.2. Leaching experiments

Leaching curves of copper and tin of the individual fractions *Residue A, Residue B* and *Residue C* are shown in Figs. 11–13.

Leaching of all three residue fractions indicate the same tendency, meaning minimal copper extractions (less than 1%) and considerably higher tin extractions. However, tin extractions are significantly different from each other and achieved $\sim 60\%$ (*Residue* **A**), $\sim 80\%$ (*Residue* **B**) and $\sim 20\%$ (*Residue* **C**) after 120 min of leaching.

A common feature of all leaching experiments is that leaching efficiency increases with decreasing grain size, showing that grain size is more important than the concentration of acid. This is to be expected, as the reduction of grain size has resulted not only in an increase of interphase boundary, but also uncovers large amounts of metal particles by removing plastic from the surface. For this reason, an important finding is that extraction of tin is highest for procedure B, which is probably related to the use of a hammer crusher which certainly influenced morphology as well as surface properties of the material.

A reason, why copper is not significantly leached, is that copper as a relatively precious metal is not leached in a non-oxidative environment. Hydrochloric acid is non-oxidizing and as follows from the thermodynamic assumptions (Eqs. (1) and (2)), copper is not leached in such an environment. This is valid for the whole range of temperatures 0–100 °C, because the values of change of standard Gibbs free energy (ΔG°) in this temperature range are positive.

$$Cu + 2HCl_{(aq)} = CuCl_2 + H_{2(g)} \quad \Delta G_{80} = 92.58 \text{ kJ/mol}$$
 (1)

$$2Cu + 2HCl_{(aq)} = 2CuCl + H_{2(g)} \quad \Delta G_{80}^{\circ} = 1.68 \text{ kJ/mol}$$
(2)



Fig. 11. Leaching curves of copper (a) and tin (b) of sample Residue A.



Fig. 12. Leaching curves of copper (a) and tin (b) of sample Residue B.



Fig. 13. Leaching curves of copper (a) and tin (b) of sample Residue C.

Small amounts of copper in the solution are probably caused by leaching of copper oxides which naturally cover copper particles. Thermodynamically, this is probable according to Eqs. (3) and (4). The shape of copper leaching curves also indicates this mechanism, because these curves have tendencies to slow and stagnate, which indicates that oxide on surfaces was leached out and the process subsides.

 $Cu_{2}O+2HCl_{(aq)}=2CuCl+H_{2}O\quad \Delta G_{80}^{^{o}}=-81.306\ kJ/mol \eqno(3)$

$$CuO + 2HCl_{(aq)} = CuCl_2 + H_2O \quad \Delta G_{80}^{\circ} = -33.73 \text{ kJ/mol}$$
 (4)

The systematic behavior for tin was different from that of copper. Tin was leached out at relatively high rates of extraction, but in different quantities. From a thermodynamic point of view, leaching of tin is accompanied by negative values of change of standard Gibbs free energy (Eqs. (5) and (6)).

$$Sn + 2HCl_{(aq)} = SnCl_2 + H_{2(g)} \quad \Delta G_{80}^{\circ} = -56.09 \text{ kJ/mol}$$
 (5)

$$Sn + 4HCl_{(aq)} = SnCl_{4(aq)} + 2H_{2(g} \quad \Delta \mathring{G_{80}} = -20.96 \text{ kJ/mol}$$
(6)

The shape of tin leaching curves, unlike copper, is progressive within the examined time span and it can be expected, that an extension of leaching time would help to achieve higher rates of tin extractions.

Tin is a relatively reactive metal and its surface is certainly oxidized. From thermodynamic calculations follows (Eqs. (7) and (8) that SnO will be leached in HCl solutions, but not SnO₂.

$$SnO + 2HCl_{(aq)} = SnCl_{2(aq)} + H_2O \quad \Delta G_{80}^{\circ} = -37.77 \text{ kJ/mol}$$
 (7)

$$SnO_2 + 4HCl_{(aq)} = SnCl_2 + 2H_2O + Cl_{2(g)} \Delta G_{80}^{\circ} = 243.02 \text{ kJ/mol}$$
 (8)



Fig. 14. Comparison of leaching efficiency of tin for each sample.

From the comparison of leaching curves of tin for all three residue fractions follows (Fig. 14) that sample **Residue B** achieved highest tin extraction. One of the possible reasons, except statistics, could be that the sample was crushed three times, which is once more than **Residue A** and **Residue C**, which could cause better liberation of tin as well as more breaches of surface.

After mechanical pretreatment, individual residue fractions basically represent pre-concentrate of non-ferrous metals, as described above. They originated from gradual removal of iron, aluminium, plastics, ceramics, etc. Figs. 15–17 show pictures of individual samples of **Residue A, B, C** before and after the leaching process. In these figures, oxidized particles of copper can be seen in



Fig. 15. View of the fractions before leaching (a) and after leaching (b) of *Residue A* (60× zoom).



Fig. 16. View of the fractions before leaching (a) and after leaching (b) of *Residue B* ($60 \times zoom$).



Fig. 17. View of the fractions before leaching (a) and after leaching (b) of *Residue C* (60× zoom).

the samples before leaching and shiny particles after leaching, from which oxide was leached out, confirming the above hypothesis.

4. Conclusions

Different mechanical-physical pretreatment procedures of PCBs from used consumer equipment were tested and compared. Initially, comminution by single shaft shredding and hammer crusher was carried out, followed by magnetic and electro-dynamic separation combined with cross-flow air sifting or air table separation, respectively, to create three different procedures. Each resulting residue fraction after mechanical removal of metals was further comminuted and used for leaching experiments.

The results show that **Procedure B** exhibited the highest enrichment of non-ferrous metals in its residue fraction, aside from

aluminium which was largely removed by eddy-current separation. From **Residue B** the highest extraction of tin through leaching was achieved. Using **Procedure B**, 34 mass% of input was obtained as residue compared to 30 mass% (**Residue A**) and 26 mass% (**Residue C**). From chemical analysis follows that **Residue B** contains most copper, tin and lead.

The highest tin extraction (more than 80%) was achieved in 2 M HCl at 80 °C after 120 min of leaching. Furthermore, the shape of the curves is progressive and an extension of leaching time would help to achieve higher tin extractions. Copper extractions were low, less than 1%.

Concentrates of iron, aluminium and other non-ferrous metals can most effectively be obtained from residue originating from **Procedure B** of mechanically pretreating PCBs of used consumer equipment. These concentrates can be further recycled by pyrometallurgical, hydrometallurgical or combined methods.

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References

- Chao, G., Hui, W., Wei, L., Jiangang, F., Xin, Y., 2011. Liberation characteristic and physical separation of printed circuit board (PCB). Waste Manage. (Oxford) 31, 2161–2166.
- Cui, J., Forssberg, E., 2007. Characterization of shredded television scrap and implications for materials recovery. Waste Manage. (Oxford) 27, 415–424.
- Cui, J., Zhang, L., 2008. Metallurgical recovery of metals from electronic waste: a review. J. Hazard. Mater. 158, 228–256.
- Das, A., Vidyadhar, A., Mehrotra, S.P., 2009. A novel flowsheet for the recovery of metal values from waste printed circuit boards. Resour. Conserv. Recycl. 53, 464–469.
- Dey, S.K., Ari, V., Das, A., 2012. Processing of electronic waste in a counter current teeter-bed separator. J. Environ. Manage. 107, 45–51.
- Eswaraiah, C., Kavitha, T., Vidyasagar, S., Narayanan, S.S., 2008. Classification of metals and plastics from printed circuit boards (PCB) using air classifier. Chem. Eng. Process. 47, 565–576.
- Eurostat, available on website <http://epp.eurostat.ec.europa.eu/portal/page/ portal/waste/key_waste_streams/waste_electrical_electronic_equipment_weee>.

- Habib, M., Miles, N.J., Hall, P., 2013. Recovering metallic fractions from waste electrical and electronic equipment by a novel vibration system. Waste Manage. (Oxford) 33, 722–729.
- Havlik, T., 2008. Hydrometallurgy Principles and Applications. CRC Press, Cambridge, ISBN 978-1-4200-7044-6, p. 536.
- Kasper, A.C., Berselli, G.B.T., Freitas, B.D., Tenório, J.A.S., Bernardes, A.M., Veit, H.M., 2011. Printed wiring boards for mobile phones: characterization and recycling of copper. Waste Manage. (Oxford) 31, 2536–2545.
- Kers, J., Kulu, P., Goljandin, D., Kaasik, M., Ventsel, T., Vilsaar, K., Mikli, V., 2008. Recycling of electronic wastes by disintegrator mills and study of the separation technique of different materials. Mater. Sci. (MEDŽIAGOTYRA) 14, 296–300.
- Lee, J., Kim, Y., Lee, J.-Ch., 2012. Disassembly and physical separation of electric/ electronic components layered in printed circuit boards (PCB). J. Hazard. Mater. 241-242, 387-394.
- Li, J., Xu, Z., Zhou, Y., 2007. Application of corona discharge and electrostatic force to separate metals and nonmetals from crushed particles of waste printed circuit boards. J. Electrostat. 65, 233–238.
- Lu, H., Li, J., Guo, J., Xu, Z., 2008. Movement behavior in electrostatic separation: recycling of metal materials from waste printed circuit board. J. Mater. Process. Technol. 197, 101–108.
- MetalPrices.com, available on website < http://www.metalprices.com/>.
- Tuncuk, A., Stazi, V., Akcil, A., Yazici, E.Y., Deveci, H., 2012. Aqueous metal recovery techniques from e-scrap: hydrometallurgy in recycling. Miner. Eng. 25, 28–37.
- Veit, H.M., Diehl, T.R., Salami, A.P., Rodrigues, J.S., Bernardes, A.M., Tenório, J.A.S., 2005. Utilization of magnetic and electrostatic separation in the recycling of printed circuit boards scrap. Waste Manage. (Oxford) 25, 67–74.
- Wu, J., Li, J., Xu, Z., 2008. Electrostatic separation for multi-size granule of crushed printed circuit board waste using two-roll separator. J. Hazard. Mater. 159, 230– 234.
- Wu, J., Qin, Y., Zhou, Q., Xu, Z., 2009. Impact of nonconductive powder on electrostatic separation for recycling crushed waste printed circuit board. J. Hazard. Mater. 164, 1352–1358.
- Yamane, L.H., de Moraes, V.T., Espinosa, D.C.R., Tenório, J.A.S., 2011. Recycling of WEEE: characterization of spent printed circuit boards from mobile phones and computers. Waste Manage. (Oxford) 31, 2553–2558.
- Zhang, S., Forssberg, E., 1997. Mechanical separation-oriented characterization of electronic scrap. Resour. Conserv. Recycl. 21, 247–269.
- Zhang, S., Forssberg, E., 1999. Intelligent liberation and classification of electronic scrap. Powder Technol. 105, 295–301.
- Zhang, S., Forssberg, E., Arvidson, B., Moss, W., 1998. Aluminum recovery from electronic scrap by high-force[®] eddy-current separators. Resour. Conserv. Recycl. 23, 225–241.