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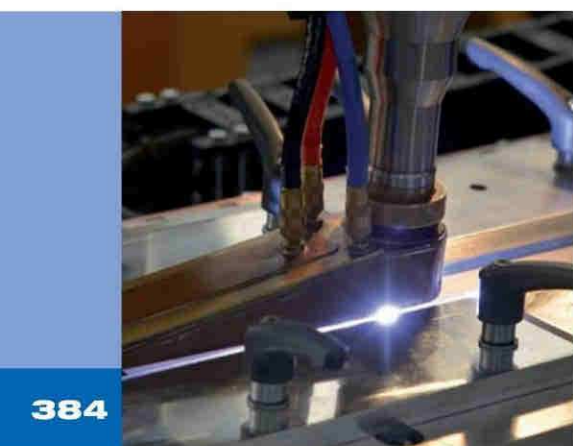
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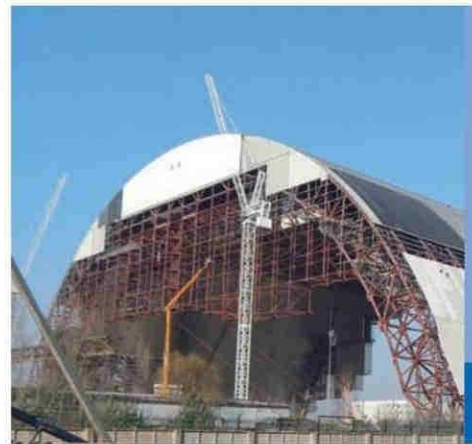
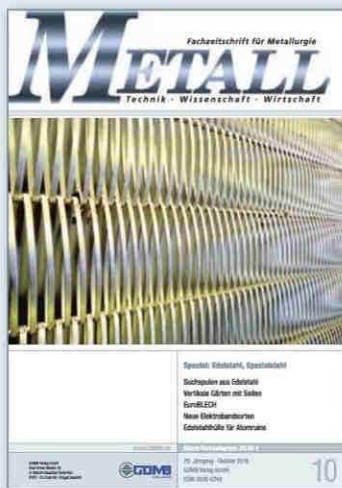
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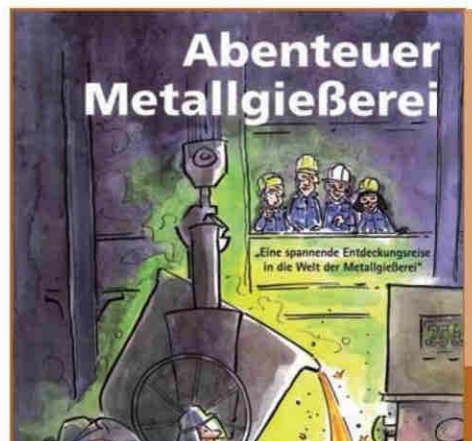
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The possibilities of precious metals recovery from used printed circuit boards - review

Takáčová, Z.; Oráč, D.; Havlík, T. (1)

The work deals with the precious metals recovery from used printed circuit boards (PCBs) from computers and mobile phones, which are considered as “high grade material” and contain high amount of copper and precious metals such as gold, silver and palladium. The paper describes the basic principles of PCBs treatment, their advantages and disadvantages. Furthermore, the work is focused on creating an overview of the investigated conditions and the results of current research in the PCBs recycling area. In this field, a trend is using hydrometallurgical processes, particularly a multi-stage leaching. By multi-stage leaching it is possible to obtain present non-ferrous metals and precious metals selectively. As the selective leaching agent for the efficient extraction of precious metals could be used ammonium or sodium thiosulfate, as well as thiourea with an oxidizing agent such as Fe^{3+} , Cu^{2+} , or others. In this way, nearly 100 % of precious metals extraction is possible to achieve. For selective recovery of precious metals from solution can be used precipitation, ion exchange or solvent extraction.

In recent years, technological innovation and intensive marketing strategies have caused rapid expansion of electrical and electronic equipment. The proportion of electrical and electronic equipment on the market is significant and their amortization is relatively high. This leads to the constant variation and subsequently to the formation of large amounts of waste electrical and electronic equipment (WEEE) [1].

WEEE is defined by Directive 2002/96/EC of the European Parliament and of the Council on waste electrical and electronic equipment (WEEE) as useless or old equipment which is dependent on electric currents or electromagnetic fields [2]. With the rapid economic growth, technological progress and obsolescence of electronic devices on the market, the volume of WEEE is increasing year to year. WEEE is a significant source of valuable materials, such as precious metals, especially gold and silver and other non-ferrous metals, mainly copper and tin. The main source of precious metals in WEEE is printed circuit boards which create 6 wt.% of the total quantity of electrical and electronic waste.

European Union produced about 8 million tons of WEEE each year with annual growth of 3-5 wt.%. Worldwide production of WEEE is approximately 20 to 50 million

tons per year [3]. Such amount of waste is very important not only in terms of quantity, but also because it contains dangerous or potentially dangerous components, e.g. heavy metals or plastics. On the other hand, WEEE contains many valuable components, e.g. gold, silver, copper or tin.

Nowadays, current research in the field of WEEE recycling is mainly focused on the PCBs processing from discarded computers and mobile phones. The main reason is high content of precious metals. This kind of PCBs is considered as lucrative commodity known as “high grade material”. However, PCBs are not only a part of the personal computer. They are included in

almost all electronic devices, such as TVs, monitors, or radios as well. PCBs of these devices have lower content of valuable metal components and they are known as “low grade material” [4-6].

Tab. 1 shows the metals content in PCBs, compared with the content of primary raw materials. The metals content in the “high grade material” as well as “low grade material” PCBs is significantly higher than in the primary raw materials. Additionally, high price of present metals clearly justifies the attractiveness of this material as an important secondary raw material. Tab. 2 and Tab. 3 shows material potential of 3rd category (Information technology and telecommunications equipment) and 4th category (Consumer electronics) in Slovakia and in EU 27 countries.

Mechanical-physical pretreatment of PCBs may include: crushing, grinding, magnetic separation, separation of particles by size, air separation, separation by density, electrostatic separation and so on. The aim of mechanical pretreatment is material size reducing, releasing individual components or their sorting (e.g. by screening). The aim of physical pretreatment is separation of the components based on their different physical properties. In case of PCBs the goal is separation of metals from non-metal components in order to obtain a concentrate of metal, which can be subsequently processed.

The pyrometallurgical processes of PCBs recycling involve waste addition to some non-ferrous metals production, especially copper. Precious metals are concentrated in intermediate products. A second way for PCBs pyrometallurgical treatment is PCBs melting with addition collectors of precious metals, mainly copper, nickel or lead. The disadvantages of pyrometallurgical processes are the robustness, the loss

| Metals | Metal content [%] | | | Price [USD/t] 04/27/2016 |
|--------|----------------------|-----------------------|----------------------|-------------------------------|
| | Primary raw material | „High grade material“ | „Low grade material“ | |
| Cu | 0.5 – 1.0 | 7 – 20 | 3.4 – 21 | 4933 |
| Sn | < 1 | 2.9 – 4.9 | 0.72 – 1.4 | 17 225 |
| | Metal content [ppm] | | | Price [USD/oz*] 04/27/2016 |
| | | | | |
| Au | 5 – 7 | 16 – 566 | 10 – 20 | 1264 |
| Ag | 5 – 7 | 189 – 1380 | 115 – 280 | 17.5 |
| Pd | 3 – 5 | 3 – 210 | 4 – 10 | 624 |

Tab. 1: Comparison of metal content in the primary raw material and PCBs [5, 6]

* oz – troy ounce = 31.1 g

| Metal | Average content [%] | Collection in Slovakia (3 244 t, thence 210.9 t of PCBs*) | | Collection in EU 27 countries (698 220 t, thence 45 384 t of PCBs*) | |
|-------|---------------------|---|-----------------|---|-----------------|
| | | Content [t] | Price [\$/year] | Content [t] | Price [\$/year] |
| Cu | 13.5 | 28.47 | 140 442 | 6 126.88 | 30 223 504 |
| Sn | 3.9 | 8.22 | 141 589 | 1 769.99 | 30 488 077 |
| Au | 0.0291 | 0.06136 | 2 493 854 | 13.21 | 536 894 030 |
| Ag | 0.07845 | 0.1654 | 93 058 | 35.6040 | 20 031 700 |
| Pd | 0.01065 | 0.0225 | 451 386 | 4.8334 | 96 965 737 |
| Total | --- | --- | 3 320 329 | --- | 714 603 048 |

Tab. 2: Material potential of 3rd category in Slovakia and in EU 27 countries

*Average content of PCBs in equipment is around 6.5 %

| Metal | Average content [%] | Collection in Slovakia (3 244 t, thence 210.9 t of PCBs*) | | Collection in EU 27 countries (698 220 t, thence 45 384 t of PCBs*) | |
|-------|---------------------|---|-----------------|---|-----------------|
| | | Content [t] | Price [\$/year] | Content [t] | Price [\$/year] |
| Cu | 12.2 | 15.52 | 76 560 | 3 797.25 | 18 731 834 |
| Sn | 1.06 | 1.35 | 23 253 | 329.93 | 5 683 044 |
| Au | 0.0015 | 0.001909 | 77 587 | 0.4669 | 18 976 216 |
| Ag | 0.01975 | 0.025132 | 14 139 | 6.1472 | 3 458 568 |
| Pd | 0.0007 | 0.0008911 | 17 876 | 0.2179 | 4 370 907 |
| Total | --- | --- | 209 415 | --- | 51 220 569 |

Tab. 3: Material potential of 4th category in Slovakia and in EU 27 countries

*Average content of PCBs in equipment is around 5 %

of metal in the process and environmental problems. In contrast, hydrometallurgy has several advantages as high flexibility, the possibility to process poor materials, high yield and low loss of metal in the process and is environmentally friendly. For these reasons, hydrometallurgical processing is regarded as more suitable procedure for PCBs treatment. These procedures are often combined.

It should be noted that the primary metallurgy of precious metals is based on hydrometallurgical or combined procedure as well. A typical example is cyanidation, which has been used for gold and silver obtaining from primary raw materials long time. Cyanidation is process simple and efficient but using dangerous toxic leaching agent is the problem. Alternative leaching agents which are safer and more environmentally friendly are thiourea, ammonium or sodium thiosulfate. Often used oxidizing agents are hydrogen peroxide, ozone, ferric ion, which provides effective extraction of precious metals into solution. Thiourea as leaching agent has advantages such as high yield of metals, high velocity of leaching, low toxicity, environmental friendliness and can fully replace cyanidation. The problem is the high consumption

of reagents. Thiosulphates provide similar benefits as thiourea [7-10].

The aim of this paper is to describe the trends of current research in the field of hydrometallurgical or combined treatment of PCBs from computers and mobile phones. The paper provides an overview of the procedures and the results of current research scientific works for complex PCBs processing, it means for recovery of all metals present with emphasis on precious metals that have the highest economic value.

Current state in the field of research of PCBs hydrometallurgical processing

In terms of quantitative content of metals, PCBs are suitable material intended for hydrometallurgical processing. In the following, a summary of results published in available scientific papers dealing with the hydrometallurgical treatment of PCBs is given. Subject of research is recovery of copper and precious metals.

Zhang and Zhang in [11] describe the synthesis of copper chloride and simultaneous recoveries of Ag and Pd from PCBs. PCBs were first subjected to a heat shock at 270 °C in order to break the compact structure as well as to release the metal components. The metals content in obtained metallic fractions was as follows: 94.30 wt. % Cu, 209 mg/kg of Ag, 307 mg/kg of Pd. CuSO_4 with the addition of NaCl was used as a leaching agent for metal extraction. In this way, 98.5 wt.% of copper can be obtained under the following conditions: $\text{VNaCl} : \text{mCuSO}_4 = 6 \text{ ml} : 1 \text{ g}$, a molar ratio of $[\text{Cu}] / [\text{Cu}^{2+}] = 0.95$; 30 min and 60 °C. Ag and Pd formed during leaching stable chlorine complexes and Cu^{2+} acts as an oxidant. Under these conditions, the authors report 94 wt.% of Ag extraction and 95 wt.% of Pd extraction in two steps leaching. The advantage of this process is using non-aggressive, non-corrosive agent, which is environmentally friendly. Copper from the leach-liquor can be obtained by hydrolytic precipitation in the form of CuCl ; Ag and Pd by liquid extraction.

Birloaga et al. [12] recovered the gold from PCBs by leaching in thiourea. The authors found that the presence of copper negatively affects the gold extraction. Therefore, in first leaching step, copper extraction was

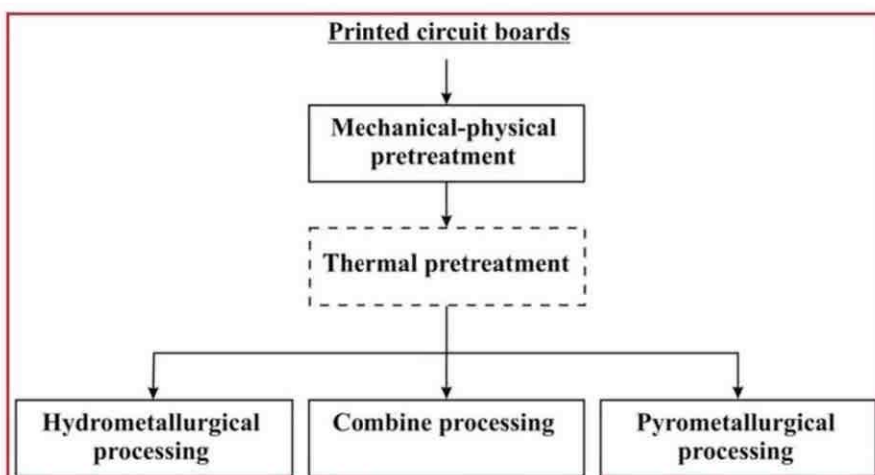


Fig. 1: Basic flowsheet for PCBs processing [6]

carried out. The effect of the concentration of H_2SO_4 , H_2O_2 addition as an oxidizing agent and the influence of temperature were investigated during leaching. The highest yield of copper was achieved using 2 M H_2SO_4 , with addition of 20 ml of 30 % H_2O_2 at 30 °C after 3 h leaching duration. The conditions for the subsequent gold recovery from leaching residue were following: leaching agent 20 g/L thiourea, 6 g/L Fe^{3+} , 10 g/L H_2SO_4 , 600 rpm. Gold extraction from PCBs containing 30.57 wt.% of copper, and gold 238 mg/kg was achieved 69 wt.% by two-steps oxidative leaching of PCBs with particle size of <2 mm, when the first leaching step removed 75 wt.% of copper. Finally, the authors evaluated that a small particle size is very important for recovery both of the metals - gold and copper, then a large contact area of leaching material with leaching agent is ensured. Oxidative leaching must be done with minimal agitation in order to prevent decomposition of H_2O_2 .

Li Jing-yin et al. [13] also studied the recovery of gold and silver from mobile phones PCBs using thiourea as leaching agent. Used PCBs contained 398.6 mg/g of Cu, 0.043 mg/g of Au and 0.54 mg/g of Ag. The authors investigated the effect of particle size, concentration of the leaching and oxidizing agent (Fe^{3+}) and the temperature on the interest metals extraction. High gold yield (90 wt.%) was obtained using a particle size <0.166 mm with leaching agent composed of 24 g/L of thiourea and 0.6 wt.% of Fe^{3+} at room temperature after 2 h of leaching.

Behnamfard et al. [4] investigated the selective recovery of Cu, Au, Ag and Pd from used PCBs. Copper and precious metals content was as follows: 19,187 wt.% of Cu, 130.25 mg/kg of Au, 704.31 mg/kg of Ag and 27.59 mg/kg of Pd. The highest extraction of copper (more than 99 wt.%) was achieved by two-stage leaching with 2 M H_2SO_4 in the presence of H_2O_2 . The leaching residue was subjected to leaching in thiourea with Fe^{3+} as an oxidizing agent, where maximum yield of Au was achieved almost 86 wt.% and of Ag 71 wt.%. Au and Ag were precipitated from solution with NaBH. In the last step of leaching, the residual Au and Pd were obtained by a mixture of NaCl - HCl - H_2O_2 . The yield of Pd and Au was increased with increasing concentration of HCl from 2 to 5 M. The best results for Au and Pd extraction in NaCl - HCl - H_2O_2 were obtained under following conditions: 5 M HCl, 1 vol. %

H_2O_2 , 10 vol. % NaCl, 63 °C, 3 h, l: s ratio = 10. Precipitation of Au and Pd from the leach liquor was carried out by NaBH. The maximum efficiency of the Au and Pd precipitation (100 wt.%) was achieved using with 2 g/L of NaBH at room temperature for 15 minutes. The authors report that this proposed method for PCBs treatment is environmentally acceptable because of low toxicity of reagents.

Gurung et al. [14] investigated the extraction of Au and Ag from used PCBs from mobile phones using thiourea followed by selective adsorption of metals on biomass, which consisted of available agricultural waste. At first, PCBs sample was subjected to the mechanical processing after calcination at 750 °C for 6 hours to combustion of the resin. During leaching was studied the effect of several parameters on the Ag and Au extraction: the concentration of thiourea and sulfuric acid, pulp density, temperature, and leaching time. Fe^{3+} was used as an oxidizing agent. It was found that the highest yield of metals was achieved during leaching of materials with particle size of 53-75 microns. Optimal conditions for the gold extraction (3.2 mg/g) were as follows: 0.5 M thiourea, 0.05 M H_2SO_4 , 45 °C, leaching time 6 hours. However, when 0.01 M Fe^{3+} was added in the system, the optimum leaching time was shortened to 2 hours. For the highest extraction of silver (6.8 mg/g) different optimum conditions were established: 0.5 M thiourea, 0.01 M H_2SO_4 , 60 °C, for less than 4 hours. For metal recovery from leach-liquor were used a cementation, adsorption on activated carbon and the adsorption of the biomass content of tannins. Cementation was not sufficiently effective. The biomass activated by H_2SO_4 was established as a promising material for obtaining Au and Ag from the solution.

Camelino et al. [15] compared the effect of two leaching agents - ammonium thiosulfate and thiourea on the gold and silver extraction from mobile phones PCBs. Sample of PCBs contained nearly 66 wt.% of Cu, 0.0168 wt.% of Au and 0.0285 wt.% of Ag. Pre-treated PCBs with a particle size <2 mm were subjected to the leaching with thiosulfate and thiourea, but at first was realized leaching of the accompanying non-ferrous metals, particularly copper, in sulfuric acid with the addition of oxidizing agent. Investigated conditions were as follows: 0.08-0.12 M ammonium thiosulfate, 0.1 - 0.2 M NH_4OH , 20 °C, pH = 10.5-15 and 15 mM Cu^{2+} . During the leaching in thiourea the effect of the concentration

(20-28 g/l) was investigated. The authors found that ammonium thiosulfate is more appropriate leaching agent for gold extraction (maximum yield 70 wt. %). In contrast, the highest yield of gold in thiourea was achieved 40 wt. %.

Ving Hung Ha et al. [16] focused on PCBs processing using 0.06-2 M ammonium thiosulfate with the addition of 5-3 mM copper sulfate and 0.1-0.4 M ammonia in order to gold recovery. PCBs used in the experiments had an average content of 12 wt.% of Au, 35.1 wt.% of Cu, 4 wt.% of Sn, 2.7 wt.% of Pb. The highest yield of gold (98 wt.%) was reached in 0.1-0.14 M thiosulfate by addition of 15-20 mM copper sulfate and 0.2-0.3 M ammonia for 2 hours. The authors report that the gold yield is strongly dependent on the Cu^{2+} concentration. If the Cu^{2+} concentration is decreased below 15 mM, the gold yield is very low. These authors in another work [17] optimized this process as well as studied its kinetics, and found that the activation energy was in the range of 20-50 °C 78.6 kJ mol⁻¹, indicating that the process is controlled by chemical reaction rate.

Park and Fray [18] investigated the leaching of PCBs in aqua regia with l: s phase ratio = 20. The silver does not dissolve in aqua regia, therefore is obtained by other conventional procedures with creation of AgCl. Maximum silver yield was achieved 98 wt.%. Palladium (93 wt.%) was obtained as a black precipitate of $\text{Pd}(\text{NH}_4)_2\text{Cl}_6$. Gold was recovered from solution by solvent extraction (97 wt. %).

Kin et al. [19] investigated the leaching of gold from mobile phones PCBs using electrically generated chlorine as an oxidizing agent and its recovery from the solution by ion exchange. Input sample contained 66 wt.% of Cu, 0.045 wt.% of Au, 2.30 wt.% of Ni and 31.66 wt.% of residue which included ceramics and resin. The experiments were carried out in leaching apparatus where chlorine gas was fed from Cl_2 generator. Gold extraction was increased with increasing temperature, even at low acid concentration. Copper extraction was increased with increasing acid concentrations and decreased with increasing temperature. Leaching was carried out in two steps. In the first step, maximum copper yield was achieved nearly 97 wt.% in 2 M HCl for 165 minutes at 25 °C, where Cl_2 was generated by current density of 714 A/m². At the same time only 5 wt.% of gold was obtained. In the second step, 93 wt.% of gold yield was achieved from

the leaching residue using 0.1 M HCl and gaseous chlorine. Authors used the ion exchanger Amberlite XAD-7HP for gold separation from leach liquor and obtained 95 wt.% of gold with maximum adsorption of gold 46.03 mg/g of the ion exchanger. Final solution contained 6034 mg/l of gold with 99.9 % of purity.

Petter et al. [20] studied the leaching of Au and Ag from PCBs from mobile phones in a conventional agent - aqua regia and nitric acid and in the alternative leaching agents - sodium and ammonium thiosulfate. The sample contained approximately 273 g/t of Ag and 880 g/t of Au. It was investigated the effect of addition of various oxidizing agents to alternative leaching media - CuSO_4 , NH_4OH , H_2O_2 on interest metals extraction. It was found that by commercial cyanide leaching agent approximately 500 g/t of gold from PCBs can be obtained. The highest silver extraction (100 wt.% = 3.494 g/t) was achieved by using nitric acid as leaching agent. In alternative leaching agents, the best results (15 wt.% of Au) were achieved in 0.1 M sodium thiosulfate with the addition of 0.2 M NH_4OH and 0.015-0.03 M of copper concentration. The use of H_2O_2 as an oxidizing agent does not increase the gold yield. The maximum yield of the silver was only 3 % in both of alternative agent, even without the addition of Cu^{2+} as oxidizing agent.

Bas et al. [21] studied the leaching of silver and copper from the television PCBs using nitric acid. Input sample was crushed and milled for size reduction (250 microns) and contained 11.2 wt.% of Cu and 48 g/t of Ag. Leaching in HNO_3 was carried out for 120 minutes, at 30-70 °C. The highest silver yield was achieved almost 70 wt.% using 5 M nitric acid. At the same time copper yield was 99 wt.%.

Fu Rong Xiu et al. [22] investigated the possibility of gold, silver and palladium extraction from crushed mobile phones PCBs with a particle size <4 mm. Iodide leaching agent was used, but at first it was realized pre-treatment of PCBs with water in a supercritical state ($T = 374^\circ\text{C}$). During supercritical conditions of water oxidizable substances are very turbulent oxidized, where the water acts as a catalyst. Result is removing organic components from the PCBs and metal content enrichment. Subsequently, the modified PCBs were leached in hydrochloric acid for 100 minutes in order to remove the copper, lead, zinc, iron and nickel. The last procedure was iodide leaching for 30-180 min for sil-

ver, gold and palladium extraction. It was found that leaching time, phase ratio, temperature and pH significant effect precious metals extraction. The highest yield of the metals - almost 100 wt.% were achieved at 20 mM of KI and 40 mM of I_2 concentrations at pH= 9.

Tab. 4 provides an overview of the results, described conditions and procedures for the precious metals extraction from PCBs.

Conclusion

Current research focuses on the development and optimization of complex proc-

esses for the metals recovery from PCBs, including precious metals, which significantly increase the economic attractiveness of this kind of waste. There are investigated the methods as an alternative to conventional cyanidation of gold and silver and are solved the related problems, such as the aggressive nature of leaching agents, long time leaching, large consumption of leaching agents, presence of strong oxidants, large amount and problematic treatment of waste water, etc. The aim of the research is to ensure selective leaching and maximum yield of precious metals using less aggressive leaching agents, without using strong oxidizing agents and so on.

| Metals content in PCBs | Studied leaching conditions | Maximum yield | Source |
|--|--|--|--------|
| metal fraction of PCBs Cu 94.30 wt. %, Ag 209 mg/kg Pd 307 mg/kg | CuSO_4 with NaCl addition V NaCl/ $\text{mCuSO}_4 = 6 \text{ ml/g}$, $[\text{Cu}]/[\text{Cu}^{2+}] = 0.95$; 30 min, 60 °C | Cu 98.5 wt.% Ag 94 wt.% Pd 95 wt.% | [11] |
| Cu 30.57 wt.% 238 mg/kg Au | 1st step: 2 M H_2SO_4 , 20 ml 30 % H_2O_2 , $T = 30^\circ\text{C}$, 3 h 2nd step: 20 g/l thiourea, 6g/l Fe^{3+} , 10 g/l H_2SO_4 , 600 rpm | Cu 75 wt.% Au 69 wt.% | [12] |
| Cu 398.6 mg/g Au 0.043 mg/g Ag 0.54 mg/g | 24 g/l thiourea + 0.6 % Fe^{3+} , room temperature, 2 h, particle size < 0.166 mm = optimal conditions | not specified | [13] |
| Cu 19.187 wt. %, Au 130.25 mg/kg, Ag 704.31 mg/kg, Pd 27.59 mg/kg | 1st step: $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ 2nd step: thiourea + Fe^{3+} 3rd step: NaCl + HCl + H_2O_2 | Cu 99 wt.% Au 86 wt.% Ag 71 wt.% Pd – not specified | [4] |
| Au, Ag – not specified | thiourea + Fe^{3+} | Au 3.2 g/g Ag 6.8 mg/g | [14] |
| Cu 66 wt.% Au 0.0168 wt.% Ag 0.0285 wt.% | 0.08 – 0.12 M ammonium thiosulfate; 0.1 – 0.2 M NH_4OH , 20 °C, pH = 10.5-15 a 15 mM Cu^{2+} 20 – 28 g/l thiourea | Au 70 wt.% | [15] |
| Au 12 wt.% Cu 35.1 wt.% | 0,06 – 2 M ammonium thiosulfate + 5-3 mM CuSO_4 + 0.1 – 0.4 M NH_3 | Au 98 wt.% | [16] |
| Au, Ag – not specified | Aqua regia, l:s = 20 | Ag 98 wt.% Pd 93 wt.% Au 97 wt.% | [18] |
| Cu 66 wt.% Au 0.045 wt.% Ni 2.30 wt.% | 1st step: 2 M HCl + Cl_2 2nd step: 0.1 M HCl + Cl_2 | Cu 97 wt.% Au 98 wt.% | [19] |
| Ag 273 g/t Au 880 g/t | sodium thiosulfate, ammonium thiosulfate, oxidizing agent – CuSO_4 , NH_4OH , H_2O_2 | Au 15 wt.% Ag 3 wt.% | [20] |
| Cu 11.2 wt.% Ag 48 g/t | 1-5 M HNO_3 , 120 min., 30-70 °C | Ag 70 wt.% Cu 99 wt.% | [21] |
| Cu 40.8 wt.% Au 0.0065 wt.% Ag 0.106 wt.% Pd 0.005 wt.% | 1. Pretreatment under supercritical water conditions 2. HCl – recovery of Cu, Pb, Zn, Fe, Ni 3. KI+ I_2 – recovery of Ag, Au, Pd | ~ 100 % Au, Ag, Pd | [22] |

Tab. 4: Overview of conditions and results of studied procedures for obtaining precious metals from PCBs [11-22]

From the study of the current research of hydrometallurgical processing of PCBs result following conclusions:

- Trends in this area is two and multi-stage leaching. In the first are removed accompanying non-ferrous metals and subsequently, in the next steps precious metals are gradually transferred to leach liquor.
- The most common metal which is obtained in the first step of leaching is copper. Copper extraction is usually carried out by conventional leaching agents, mainly sulfuric acid with the addition of hydrogen peroxide as oxidant. In this way it is possible to obtain almost 100 wt.% of copper.
- Preferred alternative leaching agent for gold and silver extraction is thiourea with the addition of ferric ion as oxidizing agent, possibly hydrogen peroxide or cupric ion.
- The paper states that the main advantage of using thiourea is non-toxic nature, the disadvantage is low stability.
- For extraction of platinum group metals from PCBs (in particular palladium is present), it is appropriate to use the chloride leaching agent, which is supplied to the chlorine gas as the oxidizing agent. Palladium extraction is third step of PCBs leaching, after copper, silver and gold extraction.
- Precious metals from the leach liquor may be recovered by precipitation, liquid extraction, ion exchange, adsorption on biomass, etc.

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References

- [1] Onwughara N. I., Nnorom I. C., Kanno O. C. and Chukwuma R. C.: Disposal Methods and Heavy Metals Released from Certain Electrical and Electronic Equipment Wastes in Nigeria: Adoption of Environmental Sound Recycling System, *International Journal of Environmental Science and Development*, 1, 4, 2010, ISSN: 2010-0264.
- [2] Directive 2002/96/ C of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment (WEEE).
- [3] Oráč D., Havlík T., Maul A., Berwanger M.: Acidic leaching of copper and tin from used consumer equipment, *Journal of mining and metallurgy*, 51 (2) B (2015) 153 – 161.
- [4] Behnamfard, A., Salarirad M.M., Veglio F.: Process development for recovery of copper and precious metals from waste printed circuit boards with emphasize on palladium and gold leaching and precipitation, *Waste Management*, 33, 11, 2013, 2354-2363.
- [5] Oráč D., Havlík T., Kukurugya F., Mišková A., Takáčová Z.: Leaching of tin and copper from used print circuit boards in hydrochloric acid, *METALL* 65, 5, 2011, 211-217.
- [6] Oráč D.: Complex processing of printed circuit boards used, in Slovak. Habilitation thesis, Faculty of Metallurgy, Technical University of Košice, 2014, s. 99.
- [7] Tuncuk, A., Stazi, V., Akcil, A., Yazici, E.Y., Deveci, H.: Aqueous metal recovery techniques from e-scrap: hydrometallurgy in recycling, *Minerals Engineering*, 25, 2012, 28-37.
- [8] Cui, J., Forssberg, E.: Characterization of shredded television scrap and implications for materials recovery. *Waste Management*, 27, 2007, 415-424.
- [9] Cui, J., Zhang, L.: Metallurgical recovery of metals from electronic waste: a review. *Journal of Hazardous Materials*, 158, 2008, 228-256.
- [10] Jing-ying, Xu Xiu-li, Liu Wen-quan: Thiourea leaching gold and silver from the printed circuit boards of waste mobile phones, *Waste management*, 32, 2012, 1209-1212.
- [11] Zhiyuan Zhang, Fu-Shen Zhang: Synthesis of cuprous chloride and simultaneous recovery of Ag and Pd from waste printed circuit boards, *Journal of Hazardous Materials*, 261, 2013, 398-404.
- [12] Birloaga I., de Michelis I., Ferella F., Buzatu M., Veglio F.: Study on the influence of various factors in the hydrometallurgical processing of waste printed circuit boards for copper and gold recovery, *Waste Management* 33, 2013, 935-941.
- [13] Li Jing-ying, Xu Xiu-li, Liu Wen-quan: Thiourea leaching gold and silver from the printed circuit boards of waste mobile phones, *Waste Management* 32, 2012, 1209-1212.
- [14] Manju Gurung, Birendra Babu Adhikari, Hidetaka Kawakita, Keisuke Ohto, Katsutoshi Inoue, Shafiq Alam, *Hydrometallurgy* 133, 2013, 84-93.
- [15] Vinh Hung Ha, Jae-chun Lee, Jinki Jeong, Huynh Trung Hai, Manis K. Jha: Tiosulphate leaching of gold from waste mobile phones, *Journal of Hazardous Materials* 178, 2010, 1115-1119.
- [16] S. Camelino a kol.: Initial studies about gold leaching from printed circuit boards (PCB's) of waste cell phones, *International Congress of Science and Technology of Metallurgy and Materials, SAM – CONAMET 2014, Procedia Materials Science* 9, 2015, 105 – 112.
- [17] Vinh Hung Ha, Jae-chun Lee, Huynh Trung Hai, Jinki Jeong, B.D. Pandey: Optimizing the tiosulphate leaching of gold from printed circuit boards of discarded mobile phone, *Hydrometallurgy* 149, 2014, 118-126.
- [18] Young Jun Park, Derek J. Fray: Recovery of high purity precious metals from printed circuit boards, *Journal of Hazardous Materials* 164, 2009, 1152-1158.
- [19] Eun-young Kim, Min-seuk Kim, Jae-chun Lee, B.D. Pandey: Selective recovery of gold from waste mobile phone PCBs by hydrometallurgical process, *Journal of Hazardous Materials* 198, 2011, 206-216.
- [20] P.M.H. Petteer, H.M. Veit, A.M. Bernardes: Evaluation of gold and silver leaching from printed circuit board of cellphones, *Waste Management* 34, 2014, 475-482.
- [21] A. D. Bas a kol.: Treatment of manufacturing scrap TV boards by nitric acid leaching Separation and Purification Technology 130 (2014) 151-159.
- [22] Fu Rong Xiu a kol.: Leaching of Au, Ag, and Pd from waste printed circuit boards of mobile phone by iodide lixiviant after supercritical water pre-treatment, *Waste Management*, 41 (2015) 134-141.

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Stahl-Service-Center stärkt seinen Marktauftritt in Europa

Mit Wirkung zum 1. Juli 2016 firmierte die Stahl-Service-Center-Gruppe von thyssenkrupp in thyssenkrupp Materials Processing Europe um. Die neue Namensgebung des Anarbeitungsspezialisten spiegelt die vielfältige Werkstoffkompetenz in den Bereichen Carbon- und Edelstahl sowie Aluminium wider. Die

Geschäftsaktivitäten wurden ausgebaut. Neben dem Stahl-Service-Center im ungarischen Győr wurde im Frühjahr auch das Edelstahl-Service-Center Willich übernommen. Darüber hinaus ist zum Ende des Geschäftsjahres die organisatorische Integration des Metallcenter Wörth geplant, die das Angebot um

maßgeschneiderte Aluminiumprodukte bereichert.

Die gesamte Produktionskapazität des Netzwerks wächst mit den neu hinzu gekommenen Standorten Győr und Willich auf über zwei Millionen Tonnen - 40 % davon werden mittlerweile im Ausland umgesetzt.