Acidic leaching of steam gasified, pyrolyzed and incinerated PCB waste from LCD screen

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Abstract: In the recycling of WEEE, two approaches are common: a pyrometallurgical or hydrometallurgical treatment, preceded by a mechanical and/or physical separation. In this study, two-step processing of unmodified waste samples of LCD screen inverters was investigated: high-temperature processing followed by acidic leaching under fixed conditions (1M H2SO4, 90 °C, 1 bar). The analysis carried out concerned a correlation between the type of HT treatment (pyrolysis, incineration, or gasification) and the dynamics of metals’ leaching from samples pretreated this way. It was found that HT method can act as “thermal disintegration”, since it affects, to a varying degree, the structure of the samples and cause elimination of organics and carbonaceous residue (incineration/gasification). The greatest mass loss (~18%) and the most loosened structure was observed for the gasified sample. Varying oxygen potential in HT-processes correlates well with the leachability of thermally treated inverters. The incineration was found to be the most favorable for copper extraction (>95%) by acidic leaching due to oxidized form of Cu, whereas Cu leaching from pyrolyzed and gasified samples needed oxygen and was controlled by the oxygen supply achieving only 36/43% after 6 h. The course of Pd leaching was similar to copper, although with lower efficiencies; 47% of palladium was extracted from the incinerated sample, and only 4 or 7% from gasified and pyrolyzed samples, respectively. Au was leached immediately but only to a slight extent. Contrary to Pb, leaching of Zn, Sn, Sb, and Ni was gradual, probably due to the formation of alloys with copper.

Keywords: electronic waste, recycling, metals, thermal treatment, acidic leaching

1. Introduction

Used electric and electronic equipment is one of the fastest growing waste streams, thus the processing of e-waste became a growing issue and worldwide challenge. Currently, increasing attention is paid to the recycling of PCBs (Printed Circuit Boards) with a focus on waste treatment and recovery of valuable materials. PCBs are important parts of e-waste and are found in almost all electrical and electronic equipment. In general, PCBs are composed of polymers, ceramics, and metals in different proportions. A basic PCB consists of a flat sheet of insulating material and a layer of copper foil, laminated to the substrate. The PCB can have multiple copper layers, for instance, a two-layer board has copper foil on both sides of insulating material. It is estimated that Cu content in PCBs can vary from 10 to 27% (Ogunniyi et al., 2009). According to Yamane et al. (2011) the concentration of copper increases in mobile phones and remains constant in PCs. Taking into account the short life span of those devices, recycling of Printed Circuit Boards with the recovery of copper, metal with the highest content in this material, is an issue of great importance. On the other hand, approximately 30% of PCB corresponds to plastic components and during the recycling process, organic compounds can be released to the atmosphere.

DOI: 10.37190/ppmp/130068
Pollution of the environment and impact on human’s health caused by improper recycling of e-waste is an important issue in countries where adequate waste processing methods are not developed yet. Due to a lack of a proper recycling technology, e-waste treatment is mainly covered by an informal sector using simple and manual processes (Hai et al., 2017). Parts of electronic waste that are not properly recycled can also be either disposed or exported to other countries where e-waste management is also not sustainable (Tran and Salhofer, 2018). On the other hand, an informal e-waste recycling is a cause for environmental pollution by heavy metals and organic substances (Leung et al., 2006). Those pollutants have a negative impact on the health of people who work in such facilities and other inhabitants as toxic substances infiltrate to water, ground and bioaccumulate in environment. Because of those health and environmental risks it is essential to develop proper methods for electronic waste recycling.

Currently, many studies are focused on the recycling of e-waste due to the high content of metals and their potential value. The most attention attracts recovery of copper and precious metals (gold, palladium, silver) where the latter make up more than 70% of the PCB value. Cu represents much less value of the PCB (Paryk and Fray, 2009) but it has the highest content in this material among other metals and this fact makes the recycling of Cu also very important. Usually, the recovery of metals takes place through the separation methods (gravity, electrostatic, magnetic) combined with a hydrometallurgical or pyrometallurgical treatment (Rudnik et al., 2016; Ghosh et al., 2015). In hydrometallurgical processing, different leaching solutions are used, and usually, specific metals need to be selectively removed.

There are many studies on the leaching processes of PCBs for the recovery of the metallic phase (Quinet et al., 2005; Tuncuk et al., 2012; Lee and Mishra, 2018; Javed et al., 2018; Yazici and Devecli, 2013; Torres and Lapidus, 2016). These processes may differ in their parameters, such as the leaching solution and its concentration, temperature, pH, solid-liquid ratio, redox potential, etc. The main stages of hydrometallurgical processing include acidic or alkaline leaching processes. The solutions are then subjected to separation and purification processes such as precipitation, solvent extraction, adsorption, ion exchange. These processes are used to isolate and concentrate on individual metals. Subsequently, the solutions are subjected to electrorefining, chemical reduction or crystallization to recover the metal. Solutions of inorganic acids (e.g., H2SO4, HNO3, HCl) are commonly used as leaching agents often with the addition of H2O2 as an oxidizing agent. Cyanide leaching dominates in the gold mining industry and is also used to leach this metal from PCBs (Zhang et al., 2018). Currently, more attention is also paid to the leaching with thiourea, sodium or ammonium thiosulphate and halides. The use of H2SO4 leaching with chelation technology (Jadhao et al., 2016) Brønsted acidic ionic leaching (Huang et al., 2014) H2SO4 leaching with an additive of 30% H2O2 (Yang et al., 2011) have been currently investigated as methods for Cu extraction.

It is worth emphasizing that the effectiveness of leaching agents is limited by the compact structure of the PCB, which causes that the leaching of the original electronic waste stream leaves organic matter as a waste product in combination with a mineral residue. This organic matter, and the chemical nature of leaching solutions, is a major problem in the waste management. It is not an issue in thermal processing of compact PCB material, since HT treatment removes the organic fraction, thus the residue after leaching would be definitely less environmentally burdensome. In light of the above, the industrial processing of electronic waste is based on melting methods (for example: Boliden Ltd. (Theo, 1998), Umicore (Hagelüken, 2006), Aurubis (Tesféye et al., 2017)).

In the literature, one can find the proposals of two-step processing of electronic waste, where the first stage is high-temperature (HT) treatment of PCB that aims to remove organic compounds. However, it is usually focused on one or two types of HT treatment: pyrolysis (Mankhand et al., 2012) and pyrolysis vs. incineration (Havlík et al., 2010; Molto et al., 2009; Shen et al., 2018). Here, we covered also the steam gasification, which eliminates emissions to the atmosphere in favor of the production of energy gas during this process. In addition, an important advantage of thermal processes is the preservation of the original form of the material, with a definitely loose (stratified) structure, which facilitates access of leaching agents. Therefore, in our work, we used unmodified mechanically material (not crushed or ground, and without dismantling the built-in components), both in HT and leaching processes. The aim of this study was to analyze the correlation between a character of the HT treatment...
of electronic waste (pyrolysis, incineration and steam gasification) and dynamics of metals leaching from selected PCB material. Schematic diagram of experiments is shown in Fig. 1.

![Diagram of experimental design](image.png)

**Fig. 1.** Schematic diagram of experimental design. (Sol. – solution; SR – solid residue; O – original; L – leached; subscripts: I – leached in H$_2$SO$_4$; II – digested in aqua regia)

2. **Materials and methods**

2.1. **PCB**

Original LCD screen inverters NRP-25-DEQ18213 were used in experiments. The inverters act as a voltage converter, generating a voltage much higher than the supply voltage. They are used in backlighting of high-voltage fluorescent lamps in LCD screens. Inverters (FR-4 type multilayer PCB) were chosen as the test object because they are characterized by the integrated circuit structure typical of electronic waste and were available in large quantities in identical form. The selected type of waste was also characterized by a small amount of built-in components. The mass of a single inverter was about 5.85 g. Dimensions of a single inverter were: 190 (L) x 10(B) x 2(H) mm. The original samples of PCBs are shown in Fig. 2.

![Samples of PCB (inverter) before HT treatment](image2.png)

**Fig. 2.** Samples of PCB (inverter) before HT treatment

2.2. **HT processing**

HT processing was carried out in the reactor that consisted of a quartz tube with an inner diameter of 36 mm and length of 1200 mm, heated by four tube furnaces which formed four heating zones (Fig. 3).
The temperature in each zone was measured with K-type thermocouple and registered with digital recorder APAR AR 206/8. Furnaces were individually powered by electronic controllers RE31 or RE15 with SSR units (LUMEL S.A.). In the gasification process, water for the steam generation was fed with a peristaltic pump (201.SMA.150.050, Williamson Manufacturing Company Ltd.) Gases supplied to reactor in other two processes were: argon (Air Products, purity 99.999%) and air (Air Products, 20% O\textsubscript{2} + N\textsubscript{2}), for pyrolysis and incineration experiments, respectively. Gasses from the processes were cooled down in the Liebig condenser and washed with 0.10 M NaOH.

The reactor, containing 13 identical inverors, was placed horizontally and connected with other elements of the system. Before the experiment, the reactor was pre-heated overnight. Experiments started with the heating of the zone \textit{a} (catalyst) and \textit{d} (gas/water supply) until both zones achieved a temperature of 500 °C. At this moment gas/water supply to reactor and the heating of zone \textit{b} and \textit{c} were started. When zones with samples of waste reached a temperature of 850 °C, this temperature was maintained for 2 hours, then the reactor was cooled to the temperature of about 100 °C. All HT processes were conducted according to the above procedure. Detailed operating conditions of experiments are given in Table 1. Temperature profiles recorded during the pyrolysis process shows Fig. 4. Similar profiles were registered for two other processes (steam gasification and incineration) (Gurgul et al., 2018).

![Temperature profiles in the: waste sample zone (T\textsubscript{b}), gas/water supply zone (T\textsubscript{d})](image)

2.3. Leaching procedure

The experimental setup used in leaching tests is shown schematically in Fig. 5. The thermostated glass reactor was equipped with an automatic stirrer and a pipe tube for the oxygen supply. The leaching agent was 1M H\textsubscript{2}SO\textsubscript{4} with a volume of 800 cm\textsuperscript{3}. Leaching of the solid residues after HT processing was carried out at a temperature of 90 °C, S/L ratio = 1/160, and the oxygen supply of 50 dm\textsuperscript{3}/h. It was ensured during the process that the reaction mixture was continuously stirred at a speed of 200 rpm. The leaching parameters enabled essential stability of the leaching conditions (excess of sulfuric acid, intensive stirring and high flow of pure oxygen) as well as reaction rate (high temperature). The leaching
solution samples were taken at regular intervals from the start of the process, after 15 and 30 minutes respectively, then after 1, 2, 3, 4, 5 and 6 hours.

Fig. 5. Reactor used in the leaching experiments

2.4. Aqua regia digestion

The solid residues after leaching were digested by open-vessel wet digestion (DigiPREP Jr digestion block, SCP SCIENCE, with touch screen controller) at room temperature in 20 cm³ of aqua regia for 24 h. Next, the samples were additionally heated at 120 °C for 6 h, to complete dissolution, and filtered.

2.5. Chemical analysis

A Varian SpectrAA 20Plus single-beam flame absorption spectrometer, with a deuterium lamp for background correction was applied for the determination of Cu, Fe, Zn, Ni, Pb, and Ag content (analytical lines selected for measurements: 324.8, 248.3, 213.9, 232.0, 217.0, and 328.1 nm respectively). Working conditions (slit width, lamp current, fuel type, and optimum working range) for the instrument operation were selected according to recommendations of the spectrometer manufacturer.

An Agilent bench-top optical emission spectrometer, model 720, with an axially viewed Ar-ICP and a 5-channel peristaltic pump with conventional pneumatic sample introducing system was used for the determination of Au (267.6 nm), Pd (340.5 nm), Sn (283.9 nm), and Sb (206.8 nm). Operating conditions recommended by the manufacturer were applied.

3. Results and discussion

3.1. HT pre-treatment

Fig. 2 presents an original PCB sample and Fig. 6 shows the samples after HT treatment (pyrolysis, incineration, and gasification). In general, the structure of inverter was preserved but, depending on the HT process, changes in the color of the samples as well as weight losses (Table 1) could be observed.

High-temperature processing of the electronic waste (without melting) is generally applied for elimination of plastics and epoxy resins which consolidate printed circuit boards: (1) incineration – the process with high oxygen potential, (2) steam gasification – the process with moderate oxygen potential, controlled by steam and (3) pyrolysis – the process with low oxygen potential controlled by Boudouard reaction. This variation of oxygen potential (defined as $RT ln p_{O_2}$, where $p_{O_2}$ is the partial pressure of oxygen) in HT processing results in different products: combination of metals, metal oxides, minerals, and carbonaceous residue.

Oxygen potential of steam gasification was discussed in our paper on the PC ISA-card decomposition at temperature range 800 – 900 °C (Zablocka-Malicka et al., 2018). The difference in mass loss of samples subjected to pyrolysis and incineration (comparable losses - 7.65% on average) and gasification (18.15%) is a consequence of a combination of Cu oxidation and the presence or absence of fixed carbon. In the case of pyrolysis (Fig. 6a), fixed carbon was present in the sample and elements were preserved in metallic form. Hence, the mass loss is relatively low. The same effect can be found for incineration residue (Fig. 6b). Here, a lack of fixed carbon is compensated by the presence of oxidic metal forms, especially Cu. Both of these components (fixed carbon and oxides) are missing in the gasification residue (Fig. 6c), resulting in the highest weight loss.
On this basis, it was concluded that the content of organic matter (resins) at the level of 18% is appropriate in the thermally processed waste material.

Consequently, the differences described above correlate with the leachability HT-treated samples towards the most valuable metals.

![Fig. 6. HT processed PCB inverters. Samples after: a) pyrolysis, b) incineration, c) steam gasification, bottom photo shows open structure of PCB after this process](image)

| Table 1. Operating conditions and experimental stages for HT processes |
|--------------------------------------------------------------------|
| **Operating conditions** | **Pyrolysis** | **Gasification** | **Incineration** |
| Initial mass of waste sample, g | 76.11 | 75.71 | 75.92 |
| Mass loss (after process), % | 7.91 | 18.15 | 7.39 |
| Reaction gas/carrier gas | argon | steam | air |
| Pressure | Slightly exceeding atmospheric pressure (around 20-30 mm H₂O, due to scrubber with NaOH) |

| No. | Operation description | Parameters |
|-----|-----------------------|------------|
| 1.  | pre-heating of all reaction zones | 12 h at 100 °C |
| 2.  | heating of the catalytic zone (a) and steam generator (d) | 20 °C/min to 900 °C |
| 3.  | gas / water supply starts when temperature in zones (a) and (d) equals 500 °C, | 0.26 dm³/min | average 2.23 g/min | 2.78 dm³/min |
| 4.  | heating of the waste sample in zones (b) and (c) starts when temperature in zones (a) and (d) equals 500 °C, | 3 °C/min to 850 °C |
| 5.  | final heating (of the reactor) | 2 h |
| 6.  | cooling of the reactor | 20 °C/min approximately to 500 °C and inertly to 100 °C |
| 7.  | Disassembly of the reactor | at 50 – 100 °C |

(a)–(d) – reactor zones according to Fig. 3
3.2. Concentration of metals in the leached samples

The concentration of metals in samples of HT treated inverters was calculated assuming that the sum of the metal leached in sulfuric acid and extracted by aqua regia digestion (Table 2, rows “LI” and “LII”, respectively) is its total content in the sample. This concentration can be converted to the metal content in the original sample (Table 2, rows “O”). Because the investigation was focused on differences between samples from the I, G and P processes, absolute concentrations of metals was not evaluated (however, it seems reasonable to assume that absolute concentration is the highest one). Thus, the differences between leachability are an indication of “hiding” of metals in inert, non-leachable forms. It may be noticed that recalculated concentrations only for copper are well consistent, giving Cu content in the original inverter equal to 45.05 ± 0.72wt.%. However, this consistency of concentrations is lost in the case of other metals and there is no coherent tendency in the changes of concentrations. It may be a result of random variations in the composition of samples related to elements mounted on the main PCB. These elements were partially detached from the inverter during HT processing and formed a loose fraction, probably partially inhomogeneous. Therefore, the efficiency of leaching discussed below was presented as a relative for incineration, gasification, and pyrolysis separately.

Table 2. Metal content in the incinerated (I), gasified (G) and pyrolyzed (P) inverters, % of the metal leached in H$_2$SO$_4$ and digested by aqua regia. The table symbols (O, L, LI, LII) matches the legend in flow chart (Fig. 1)

| metal | Cu | Ag | Au | Pd | Zn | Pb | Sn | Sb | Fe | Ni |
|-------|----|----|----|----|----|----|----|----|----|----|
|       | concentration in the original inverter sample (O), wt.% |
| I     | 45.69 | 0.0025 | 0.089 | 0.011 | 0.31 | 0.14 | 0.45 | 0.0056 | 0.72 | 1.58 |
| G     | 45.41 | 0.0090 | 0.090 | 0.014 | 0.47 | 0.029 | 1.58 | 0.011 | 2.59 | 2.46 |
| P     | 44.04 | 0.012 | 0.068 | 0.0092 | 0.47 | 0.040 | 1.34 | 0.019 | 0.76 | 2.32 |
|       | concentration of leachable form in the original inverter sample (L), wt.% |
| I     | 49.34 | 0.0027 | 0.096 | 0.012 | 0.34 | 0.15 | 0.49 | 0.0060 | 0.78 | 1.71 |
| G     | 55.48 | 0.011 | 0.11 | 0.017 | 0.57 | 0.035 | 1.93 | 0.014 | 3.17 | 3.00 |
| P     | 47.82 | 0.013 | 0.074 | 0.010 | 0.51 | 0.043 | 1.46 | 0.021 | 0.83 | 2.52 |
|       | % of metal leached in H$_2$SO$_4$ (LI) |
| I     | 96.21 | 71.71 | 0.05 | 47.02 | 28.36 | 54.69 | 77.37 | 98.49 | 27.58 | 31.77 |
| G     | 42.68 | 26.22 | 0.28 | 4.01 | 72.83 | 80.24 | 74.61 | 86.62 | 13.74 | 50.31 |
| P     | 35.64 | 9.67 | 0.68 | 7.31 | 36.42 | 67.64 | 59.35 | 75.29 | 80.83 | 38.49 |
|       | % of metal digested by aqua regia (LII) |
| I     | 3.79 | 28.29 | 99.95 | 52.98 | 71.64 | 45.31 | 22.63 | 1.51 | 72.42 | 68.23 |
| G     | 57.32 | 73.78 | 99.72 | 95.99 | 27.17 | 19.76 | 25.39 | 13.38 | 86.26 | 49.69 |
| P     | 64.36 | 90.33 | 99.32 | 92.69 | 63.58 | 32.36 | 40.65 | 24.71 | 19.17 | 61.51 |

3.3. Cu leaching

Copper is undoubtedly the main component of the leached material, with a concentration of approximately 50wt.% (Table 2). It may be easily noticed from Fig. 7 that copper leaching from incinerated inverter ended after 1 hour, contrary to gasified or pyrolyzed ones. It is, of course, the result of almost total oxidation of copper during incineration (as it may be interpreted from 96/4% proportion in Table 2). Therefore, the respective general reactions may be written as:

$$\text{CuO}^{(*)} + 2\text{H}^+ = \text{Cu}^{2+} + \text{H}_2\text{O} \quad \Delta G_{r,90^\circ C} = -39.6 \text{kJ} \quad \text{(incinerated sample)} \quad (1)$$

(*) - CuO is a thermodynamically representative form of copper in incineration and dominated in the incinerated sample, $p_{O_2} = 4.56 \times 10^{-3}$ bar for reaction $4\text{CuO} = 2\text{Cu}_2\text{O} + \text{O}_2$ at 850 °C, and:
\[
2\text{Cu} + \text{O}_2 + 4\text{H}^+ = 2\text{Cu}^{2+} + 2\text{H}_2\text{O} \quad \text{with } \Delta G^{0}_{r,90^\circ\text{C}} = -323.3 \text{ kJ (pyrolyzed and gasified samples)} \quad (2)
\]

Fig. 7. Cu leaching from HT processed inverters vs. the leaching time

The rate of copper (copper oxide) dissolution from the incinerated sample was obviously controlled by circumstances of the inverter penetration by solution, whereas dissolution of copper from gasified and pyrolyzed samples depended on the oxygen transfer in the leaching solution and the rate of leaching was similar for both experiments. A small acceleration of the copper leaching from these samples and a bit higher leaching from the gasified sample may be related to a higher concentration of Fe\(^{3+}\) ions (discussed later in the text) and the lack of the carbonaceous substance in the sample.

3.4. Au, Pd and Ag leaching

It may be evaluated from data in Table 2 that concentrations of Cu, Au, and Pd in original (not HT processed) inverters were equal to 45.0 ± 0.7, 0.082 ± 0.010, and 0.011 ± 0.002 wt.\%, respectively. Ag concentration seems to be similar to Pd, taking into account pyrolysis and gasification experiments – approximately 0.011 wt.\%. The progress of Pd and Ag leaching is presented in Fig. 8. It is easy to notice that the leaching is well correlated with the metal affinity to oxygen:

\[
a\text{M} + \text{O}_2 = b\text{M}_2\text{O}_3 \quad \text{at } 850^\circ\text{C}: K_{\text{Pd}} = 4.64 \cdot 10^{-1}, K_{\text{Ag}} = 2.79 \cdot 10^{-4}, K_{\text{Au}} = 1.05 \cdot 10^{-9} \quad (3)
\]

Fig. 8. Precious metals leaching from HT processed inverters vs. the leaching time

Palladium, with the highest oxygen affinity, was leached identically to copper (although with lower efficiency – 47\%). Leaching curves similarity suggests that Pd was at least partially oxidized during incineration, contrary to pyrolysis and gasification. The metal was also slowly oxidized under leaching conditions. The leaching of Ag from incinerated sample was very high at the beginning and decreased gradually to approximately 70\% at the end of the experiment. Contrary, the silver leaching from gasified and pyrolyzed samples, even if relatively low, increased up to 20-30\%. A very low content of the metal,
lower than concentration of Au (Table 2), is a suggestion that Ag was alloyed admixture to the copper foil. Oxidation of copper would enable high leaching of silver (first measurement after 15 minutes of leaching) due to the fast dissolution of the copper oxide. Further decrease of silver concentration in the leaching solution seems a result of possible sorption or precipitation effects. On the other hand, leaching of Ag from gasified and pyrolyzed samples proceeded similarly to copper. The leaching of a small amount of gold was observed during the beginning of the process, then the concentration of Au did not change in the solution, and eventually the overall leaching efficiency was negligible (below 1%).

3.5. Zn, Pb, Sn and Sb leaching

The results of nonferrous metals leaching are presented in Fig. 9. It is characteristic that the metals were systematically leached during the experiment, with the exception of lead. This metal was transferred to the solution at the beginning of the leaching, however, its extraction varied between 55 and 80%. It may be noticed that the leaching of Zn from gasified sample and Sb from the incinerated one was somewhat similar. It may be stated that Zn, Sn, and Sb were trapped in the forms which were gradually destroyed during leaching. The uniqueness of Pb seems an indication that alloying with copper may be responsible for such behavior. This is the only metal (from the discussed group) which does not form a solid solution with copper. Therefore, forming of such alloys (bronzes) would be the reason for the leaching specificity observed in Fig. 9 and this formation would not depend on the HT process. Of course, it is only a hypothesis and needs to be further investigated.

3.6. Ni and Fe leaching

The course of the two ferrous metals leaching is similar to nonferrous ones, i.e. there was observed gradual extraction of metals, with the exception of Fe leaching from the pyrolyzed sample (Fig. 10). Interpretation of this phenomenon may be also similar – there is a continuous solid solution in the Cu-Ni system and relatively low solubility of Fe in a solid Cu at higher temperatures. However, an alternative interpretation of the leaching results may be proposed for Fe. It consists in the oxidation of iron during incineration and steam gasification and formation of inorganic phases non- or low soluble in sulfuric acid. During pyrolysis Fe generally preserved metallic form and could be leached by the acid.
Fig. 10. Ni and Fe leaching from HT processed inverters vs. the leaching time

4. Conclusions

The correlativity between high-temperature processing of LCD waste inverters and efficiency of metals’ leaching was analyzed, and the following conclusions were drawn:

1) The differences between high-temperature processes (incineration, gasification, and pyrolysis), applied in the presented study, are reflected in the noticeable differences in appearance of the samples, as well as weight losses or structure uniformity.

2) The highest weight losses were observed for gasified sample, as a consequence of removal of carbonaceous residue, in the absence of oxide phases.

3) The varying oxygen potential in the HT-processes correlates well with the leachability of thermally-treated inverter samples.

4) Incineration process was found to be the most favorable for leaching of copper (the main waste component), and was relatively fast (1h), resulting in the highest extraction efficiency (>95%). Leaching efficiency of gasified or pyrolyzed samples was unsatisfactory, reaching only 42 and 35%, respectively.

5) In case of precious metals (Au, Ag, Pd), it was noticed that leaching process was correlated with the metal affinity to oxygen. The leaching course of palladium, with the highest oxygen affinity, was similar to copper (after incineration), although with lower efficiency (47%). This may suggest that Pd was partially oxidized during incineration. Leaching distribution curves for silver and copper had similar shape after gasification and pyrolysis.

6) The rate of nonferrous metals (Zn, Sn, and Sb) leaching was relatively slow, in contrast to Pb, which was extracted immediately from samples after gasification and pyrolysis, and relatively fast (1h) from the sample after incineration. This unique behavior of lead (comparing to the rest of the group) indicates that it is highly probable that alloying with copper took place for Zn, Sn, and Sb.

7) The leachability of nickel and iron was very similar to the group of nonferrous metals – the gradual extraction with time was observed. Although, in the pyrolyzed sample, iron was leached much quicker - during the first hour of the process. There are two possible reasons for such behavior. Either alloys of Ni and Cu were formed (slowing down the leaching), or iron was oxidized during gasification or incineration, and was transformed to phases of non- or low solubility in sulfuric acid.

8) Presented work is a starting point for extended research aiming optimization of the leaching process coupled with a high temperature sample treatment. Moreover, such a combination of pyro- and hydrometallurgical processes can be very advantageous for technological reasons.

9) Considering the overall performance under investigated leaching conditions, incineration seems the best HT pre-treatment process. However, at the same time, incineration appears to be potentially most inconvenient due to immediate emission of flue gasses to the atmosphere (even after cleaning). Gasification and pyrolysis do not exhibit this inconvenience, additionally gasification eliminates carbonaceous residue from the HT product.

Acknowledgments

The work was financed by statutory activity subsidies from the Polish Ministry of Science and Higher Education for the Faculty of Environmental Engineering and Faculty of Chemistry of Wroclaw University of Science and technology.
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