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RESEARCH OF LEACHING OF THE PRINTED CIRCUIT BOARDS COMING FROM WASTE MOBILE PHONES

The continuous changing technologies of electronic devices, mainly mobile phones cause that their life is shorten from year to year (even to 8-12 months); that is way there is a constantly increasing amount of generated waste. Such waste treatment to recover mainly copper and other base metals should be really profitable. The process of metals recovery could be done using different methods including pyro- and hydrometallurgical process. The paper describes the research of leaching process of Printed Circuit Boards (PCB) coming from waste mobile phones. As a leaching agent sulfuric acid was used with addition of hydrogen peroxides. Experiments were carried out for different temperature, acid concentration and addition of hydrogen peroxide. As a result the concentration of copper, zinc, iron and aluminium in the obtained solution was measured. The results were discussed.

Keywords: mobile phone waste, PCB, metals recovery, leaching

1. Introduction

In the modern world there is a huge increase in the use of information and communication technology products such as: mobile phones especially smartphones, computers, laptops, tablets, televisions, etc. The emergence of changing and more and more hi-tech and up-to-date technology causes a rapid aging of electrical and electronic equipment [1]. As a consequence the generation of huge amounts of waste around the world is observed. Waste electrical and electronic equipment is currently the fastest growing waste stream [2]. Nearly 42 million tons of electrical and electronic waste were registered in 2014. It is estimated that this figure will reach over 50 million tons by 2018 [3]. Electrical and electronic equipment may contain toxic metals such as lead, mercury, cadmium, nickel, chromium, which in case of uncontrolled handling with such waste may adversely affect the environment. However, next to the hazardous components, electronic waste is primarily the valuable source of precious metals like: gold, silver, platinum, palladium, copper [4]. Therefore, the recycling of electrical and electronic waste is justified not only due to possible harmful environmental impact, but about all due to the possibility of recovery the precious metals [5-7]. Among the wide range of electronic devices, mobile phones and particularly smartphones are a major part of them. Global smartphones sale in 2008 was at the level of 140 million units, whereas in 2015 it rapidly increased to 1500 million units [8]. It is assumed that each year about 400 million units of mobile phones are treated as waste (25% of that are contributed by China). Table 1 shows the content of particular components

of mobile phones. Although, the dominant part is ceramics and plastic, the value of electronic waste is the metals, especially precious metals. The printed circuit boards (PCB) are the main carrier of precious metals (Cu, Au, Ag) and basic metals (Fe, Al, Ni, Zn) in the electronic waste, accounting for only 6% of total mass of waste electrical and electronic equipment [10,11].

TABLE 1

Chemical composition of mobile phone [9]

Metals up to 40%	Cu (6-27%), Fe (1.2-2.8%), Al (2-7.2%), Sn (1-5.6%), Pb (1-4.2%), Ni (0.3-5.4%), Zn (0.2-2.2%), Au (250-2050 ppm), Ag (110-4500 ppm), Pd (50-4000 ppm)
Ceramics up to 30%	SiO ₂ (15-30%), Al ₂ O ₃ (6-9.4%), alkali-earth oxides (6%), titanates-micas (3%)
Plastics up to 30%	polyethylene (10-16%), polypropylene (4.8%), polystyrene (4.8%), Epoxy (4.8%), PVC polyvinyl chloride (2.4%), PTPE (2.4%), nylon (0.9%)

The printed circuit board is made of plastic complex with inorganic fill containing electrical connectors and soldering points [12]. The materials used to PCB production are glass-epoxy laminates or composite materials, which additionally contain layer of glass felt or paper. The remaining components of the board are transistors, integrated circuit, coils, connections, contacts. Table 2 and 3 present the content of basic and precious metals present in PCBs according to data published by different authors.

Recovery of metals from printed circuit boards is carried out using pyrometallurgical and hydrometallurgical methods.

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TABLE 2

Content of basic metals in PCBs in % wt. [13-24]

Researcher	Cu	Al	Pb	Zn	Ni	Fe	Sn
Shuey and Taylor	20	2	2	1	2	8	4
Kim et al.	15.6	—	1.4	0.16	0.28	1.4	3.2
Iji and Yokoyama	22	—	1.6	—	0.32	3.6	2.6
Ewaste-guide.info	6.9	14.2	6.3	2.2	0.85	20.5	1.0
Ficeriova et al.	47.5	2.7	1.4	1.1	0.85	10.4	3.3
Yamane	34.5	0.3	1.9	5.92	2.63	10.6	3.4
Park and Fray	16.0	5.0	2.0	1.0	1.0	5.0	3.0
Yang et al.	25.1	—	0.8	0.04	0.002	0.66	—
Guo et al.	26.8	4.7	—	1.5	0.47	5.3	1.0
Goosey and Kellner	16	—	—	—	2	3	—
Sum	20	—	2	1	2	8	4

TABLE 3

Content of precious metals in PCBs in ppm [12-15,17,18,21,22]

Researcher	Au	Ag	Pd
Shuey and Taylor	1000	2000	50
Kim et al.	420	350	20
Iji and Yokoyama	1240	—	200
Ficeriova et al.	140	800	30
Park and Fray	250	1000	100
Goosey and Kellner	300	500	100
Sum	1000	2000	50

Pre-treatment of electronic waste is usually disassembly, removal of toxic substances and separation of particular components into categories of materials such as metals, glass, plastics, printed circuit boards [25]. Pyrometallurgical methods include incineration, sintering, smelting at high temperature in a shaft furnace or a plasma arc furnace. Hydrometallurgical processes require various steps including series of acid and caustic leaching media followed by various separation and purification procedures such as solvent extraction, adsorption and ion exchange [11]. The most commonly used leaching agents in hydrometallurgical methods are: HNO_3 , H_2SO_4 , HCl , aqua regia, thiourea, cyanides, NaCl [26]. Table 4 presents the chosen leaching agents used for recovery different metals especially precious ones from electronic waste. Hydrometallurgical methods do not require using complicated and expensive metallurgical aggregates, which should ensure the appropriate temperature and processing parameters.

In the article the research of leaching copper and associated metals (such as iron, zinc, aluminium) from waste material (printed circuit boards) was carried out using sulfuric acid. According to the literature sulfuric acid with hydrogen peroxides gives better metallurgical performance than nitric acid alone [9]. Therefore, the purpose of the experiments was to determine the effect of temperature and oxidation agent in the form of H_2O_2 on the metals extraction. Hydrogen peroxide is strongly oxidant, which is commonly applied in combination with acids to enhance metal extraction [34]. In the case of sulfuric acid also it was tested the influence of acid concentration (2M or 5M) on the process efficiency.

TABLE 4

Leaching agents used for recovery different metals from electronic waste [20,27-33]

Leaching agent	Recovered metals	Ref.
Aqua regia	Au, Ag and Pd	[20]
HNO_3 , epoxy resin, aqua regia	Au	[27]
H_2SO_4 , chloride, thiourea, cyanide leaching	Au, Ag, Pd and Cu	[28]
HNO_3 and aqua regia	Au	[29]
HCl , H_2SO_4 and NaClO_3	Ag, Au and Pd	[30]
HCl , MgCl_2 , H_2SO_4 and H_2O_2	Al, Sn, Pb, Zn, Cu, Ni, Au, Ag, Pd, Pt	[31]
Aqua regia and H_2SO_4	Cu	[32]
HNO_3	Pb and Cu	[33]

2. Experimental methodology

Spent mobile phones derived from different producers were used as a material for research. Manual dismantling of mobile phones were carried out separating their particular elements (such as casing, battery, screens) from the printed circuit boards. Fig. 1 shows the components of the mobile phone together with the PCB. The printed circuit boards were cut into pieces of 20-40 mm (Fig. 2). Materials prepared in such way was then leached.

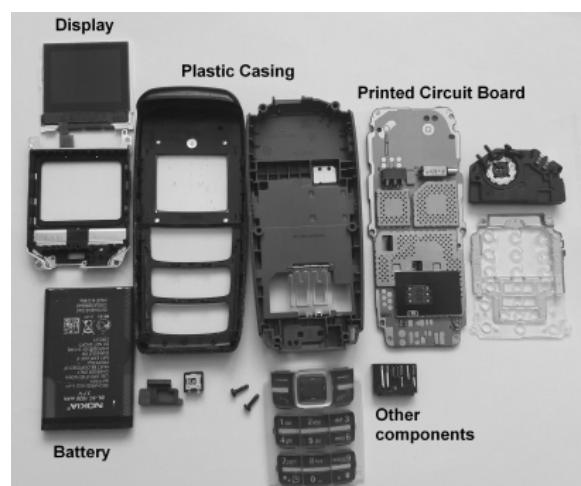


Fig. 1. View of dismantled mobile phone elements with printed circuit board

The experiments were carried out in a 600 mL flask using 2M and 5M sulfuric acid as a leaching agent. The process was conducted in the temperature range of 298K, 313K and 343K, providing mixing of the system with a mechanical stirrer of 340 rpm. The leaching process was carried out under continuous stirring for 6h and then each sample was left for another 66h under static conditions without further stirring.

In addition, copper, iron, zinc and aluminium were leached with 10% and 30% H_2O_2 in the presence of 5M H_2SO_4 at 343K. Tests were conducted at the condition that there is a constant solid-liquid mass ratio ($S/L = 1:10$) with H_2O_2 in the volume of 25 mL. During experiments the concentration of copper, iron,

zinc and aluminium was constantly monitored after time: 0.5h, 1h, 2h, 4h, 6h and 72h. The metals content in the sample was determined by the atomic adsorption spectrometry (AAS). Fig. 3 presents the scheme of the conducted research.

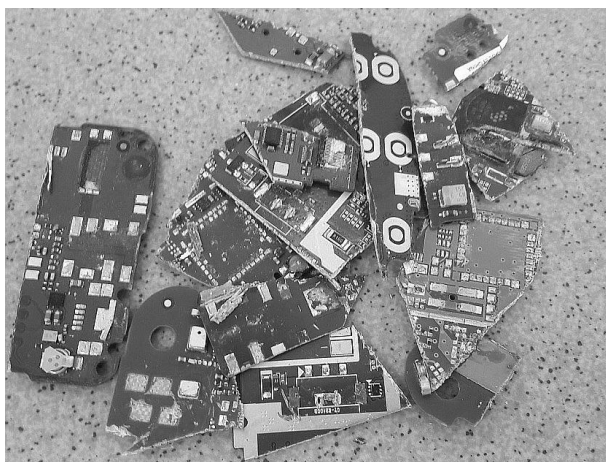


Fig. 2. PCB pieces prepared for tests

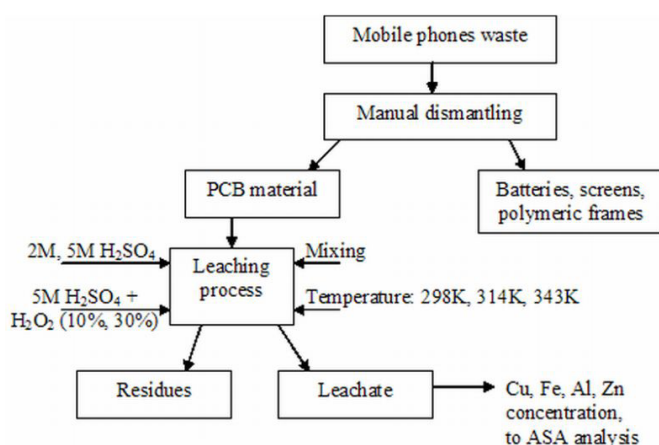


Fig. 3. Scheme of the conducted research (stages of leaching process of Cu, Fe, Zn and Al from PCBs)

3.1. Temperature influence on the leaching process of Cu, Fe, Zn and Al

Figs. 4 and 5 show the effect of copper, iron, zinc and aluminium concentration changes during 72 h of leaching in 2M and 5M sulfuric acid at temperatures of 298K, 313K, 343K. For all metals, their solution was significantly limited within the range of assumed temperatures. Within 72 hours of conducting the experiment, Cu and Fe concentration in solution of 2M and 5M sulfuric acid did not exceed 0.3 g/dm³ (for Cu, T = 343 K) and even 0.1 g/dm³ (for Cu, Fe, temperature: 298K, 313K). The exception is iron, for which concentration of 0.47 g/dm³ for 5M H₂SO₄ (Fig. 5) was obtained at 313 K, while the increase of temperature to 343 K visibly increased the leaching level of iron. Increase of iron concentration in 2M as well as in 5M H₂SO₄ solution was observed, the value of which after 72h was 6.36 g/dm³ and 3.87 g/dm³, respectively.

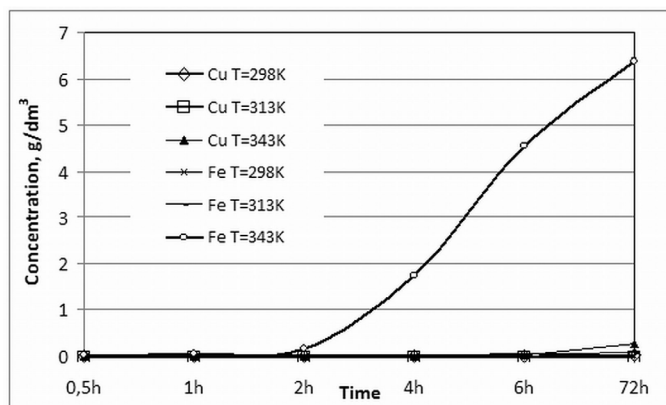


Fig. 4. Copper and iron concentration obtained after leaching in 2M H₂SO₄ solution during 72h

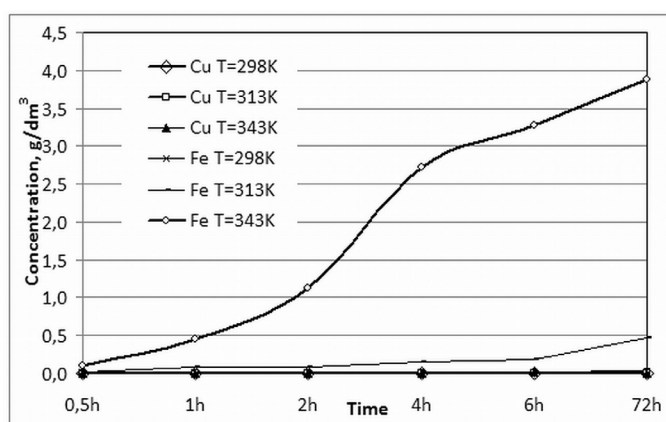


Fig. 5. Copper and iron concentration obtained after leaching in 5M H₂SO₄ solution during 72h

Under the experimental conditions, zinc and aluminium behaved in the same way (Figs. 6 and 7). During 72 h of leaching, the concentration of Zn and Al in solution of 2M and 5M sulfuric acid did not exceed 0.06 g/dm³ (for Zn, Cu, temperature: 298K and 313K). When raising the temperature to 343K it was noticed the increase of leaching level of Zn and Al. The best effect of zinc and aluminium leaching was achieved using 2M H₂SO₄ (Fig. 6). During 72 h leaching process the concentration of aluminium and zinc was 0.42 g/dm³ and 0.47 g/dm³, respectively.

In the 5M H₂SO₄ solution after 72 h the zinc concentration was 0.1 g/dm³ and the aluminium concentration was 0.09 g/dm³. It is difficult to explain the sudden decrease in zinc concentration (Fig. 7) at 343 K, in 5M H₂SO₄ after 6h. For this processing parameters the trial should be done again.

It is evident, that when the temperature is raising from 313K to 343K the increase of iron, zinc and aluminium transfer from solid phase to solution is observed, applying 2M H₂SO₄ as well as 5M H₂SO₄. In the case of copper, it is generally known that metals with the positive potentials are soluble in oxidative acids but these acids have to be really strong oxidant agents. Therefore, the sulfuric acids was not enough to leach all the copper contained in PCBs material and even the temperature does not improve the processing conditions.

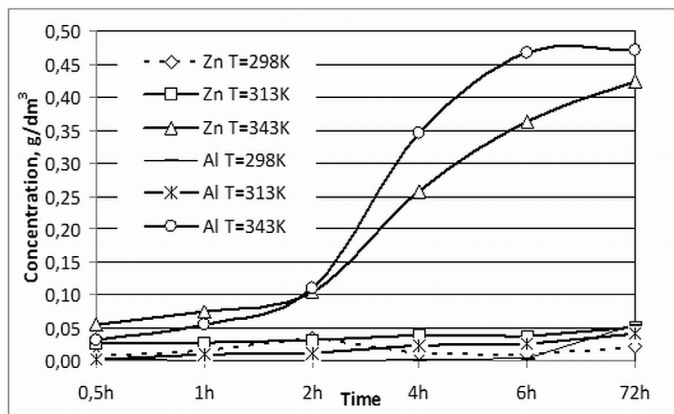


Fig. 6. Zinc and aluminium concentration obtained after leaching in 2M H₂SO₄ solution during 72h

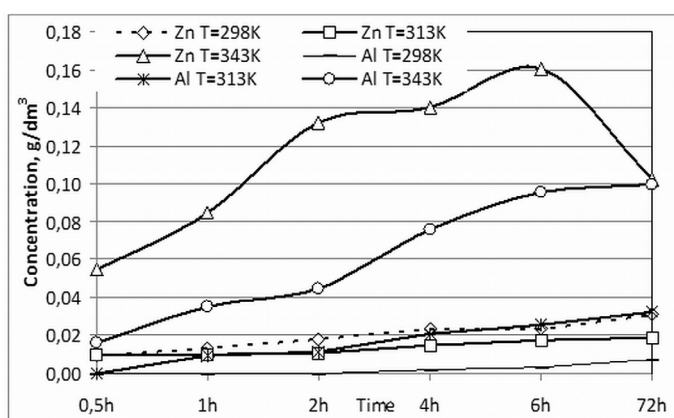


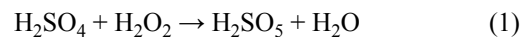
Fig. 7. Zinc and aluminium concentration obtained after leaching in 5M H₂SO₄ solution during 72h

That is why, due to the limited degree of copper dissolution, experiments of leaching copper and associated metals were conducted using hydrogen peroxide. In the series of experiments with hydrogen peroxide, the conditions were assumed, for which the highest metals leaching rates were reached: 5M H₂SO₄, T = 343K.

3.2. Influence of hydrogen peroxide on leaching process of copper, iron, zinc and aluminium

Figs. 8 and 9 present the change of results of copper, iron, zinc and aluminium concentrations obtained during 72h of leaching process in 5M sulfuric acid in temperature 343K with addition of 10% and 30% of hydrogen peroxide. The considerable increase of copper concentration is observed applying 10% H₂O₂ as well as 30% H₂O₂. During the 6 h of leaching process with stirring the copper concentration in solution was 6.4 g/dm³. The next hours of leaching (to 72h) in the condition when there was no stirring do not influence considerably the further copper extraction.

In the presence of hydrogen peroxide sulfuric acids forms peroxysulfuric acid, which act as a strong oxidant for the copper:



Molecular oxygen obtained from the increased rate of decomposition of hydrogen peroxide is adsorbed onto the copper surface. The presence of oxygen on the copper surface improves the contact with sulfuric acid [35,36].

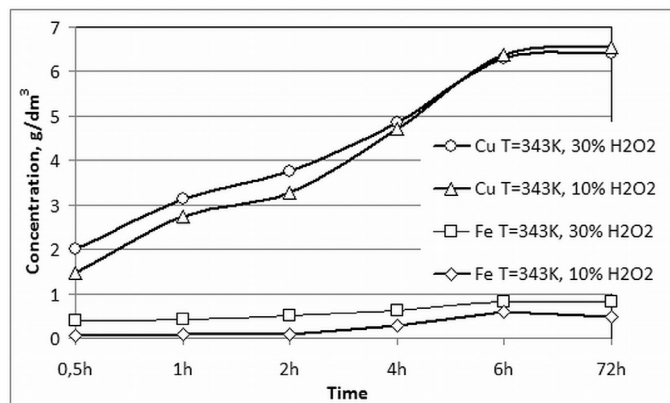


Fig. 8. Copper and iron concentration obtained after leaching in 5M H₂SO₄ with addition of 10% and 30% H₂O₂ solution during 72h

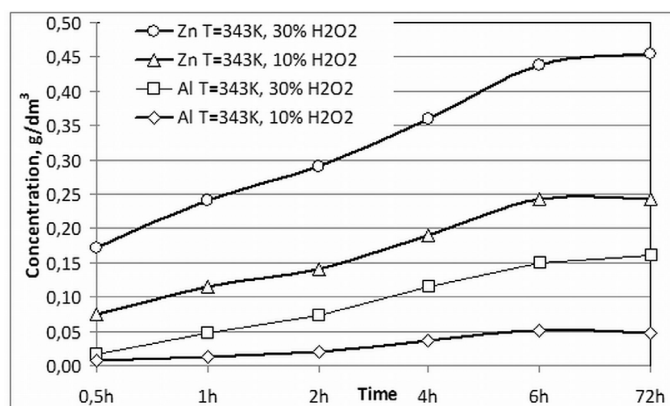


Fig. 9. Zinc and aluminium concentration obtained after leaching in 5M H₂SO₄ with addition of 10% and 30% H₂O₂ solution during 72h

In the case of iron, zinc and aluminium the addition of hydrogen peroxide to the sulfuric acid did not substantially influence the increase of their concentration in the solution after leaching process. There is seen only minimal increase of zinc concentration after 72 hours of leaching – this concentration was 0.24 g/dm³ when 10% H₂O₂ was used and 0.45 g/dm³ for 30% H₂O₂.

4. Conclusions

Mobile phones waste is a precious source of metals, which can be recovered using hydrometallurgical methods. Among other available leaching agents sulfuric acid is commonly used because of its availability and relatively low price. It seems

obvious that temperature and hydrogen peroxide are efficient factors influencing the process of copper extraction from electronic waste. In the conducted research the best level of copper leaching was obtained for 5M sulfuric acid in temperature 343K with addition of hydrogen peroxide. However, it occurs that the concentration of hydrogen peroxide did not influence considerably the obtained copper concentration in solution after leaching process. Thus, from economic point of view applying of 30% hydrogen peroxide is not effective in increasing the leaching level of metals in solution. Taking into account the cost of hydrogen peroxide and the slightly effect on leaching other metals than copper, the further research should be carried out using alternative strong oxidant as an addition to the sulfuric acid.

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