

ROLE OF OXIDIZING AGENTS IN LEACHING PROCESS OF ELECTRONIC WASTE

New technologies and the globalization of the electrical and electronic equipment market cause a continuous increase in the amount of electrical and electronic waste. They constitute one of the waste groups that grows the fastest in quantity. The development of the new generation of electrical and electronic devices is much faster than before. Recently attention has been concentrated on hydrometallurgical methods for the recovery of metals from electronic waste. In this article the role of an oxidizing agent, mainly ozone and hydrogen peroxide was presented in hydrometallurgical processes. Leaching process of printed circuits boards (PCBs) from used cell phones was conducted. The experiments were carried out in the presence of sulfuric acid and ozone as an oxidizing agent for various temperatures, acid concentration, ozone concentration. As a result, the concentrations of copper, zinc, iron and aluminum in the obtained solution were measured. The obtained results were compared to results obtained earlier in the presence of hydrogen peroxide as an oxidizing agent and discussed.

Keywords: ozone, leaching process, electronic waste, metals recovery

1. Introduction

Recently, the electronics industry has revolutionized the world. Technological progress has caused the demand for electrical and electronic devices to grow steadily. Parallel to the demand, it is also growing the electronic waste stream, which probably is one of the fastest in the world. Waste electronic equipment is a mixture of different components: basic metals (Fe, Al, Ni, Zn, Se, In, Ga), precious metals (Cu, Au, Ag, Pd, Pt), dangerous substances (Hg, Be, Pb, As, Cd, Sb) as well as plastics, glass and ceramics [1]. The content of particular components in electronic scrap varies considerably. Iron and plastic are dominant in terms of mass content, however, the content of precious metals determines the value of electronic waste. The common element of electronic devices and the main carrier of most metals are printed circuit boards (PCBs) – metals and their alloys with ceramics are combined with the resin layers of the PCB laminate. Such a combination of metals and materials causes that it is not so easy to recover these metals and requires the appropriate waste treatment technology. However, taking into account the possible harmful environment impact the recycling of such devices is necessary and additionally gives a lot of economic benefits connected with limitation of primary production of metals, especially precious ones [2-5].

Today a huge contribution to the number of electronic waste has cell phones. Global smartphones sales in 2015 was 1500 million units and is constantly increasing [6]. This is due the fact, that from year to year the lifespan of phones decreases

(up to 8-12 months). After this time the phones gain “second life” or are recycled. Cell phone waste is a valuable source of metals, especially copper [7].

Recovery of metals from electronic scrap, including cell phones can be done using pyrometallurgical and hydrometallurgical methods. Fig. 1 presents general scheme of cell phone waste treatment. Today it is also possible to use biohydrometallurgical processes, especially bioleaching using microorganisms such as bacteria or fungi – this kind of treatment of PCB scrap gives possibility to extract base and precious metals [4].

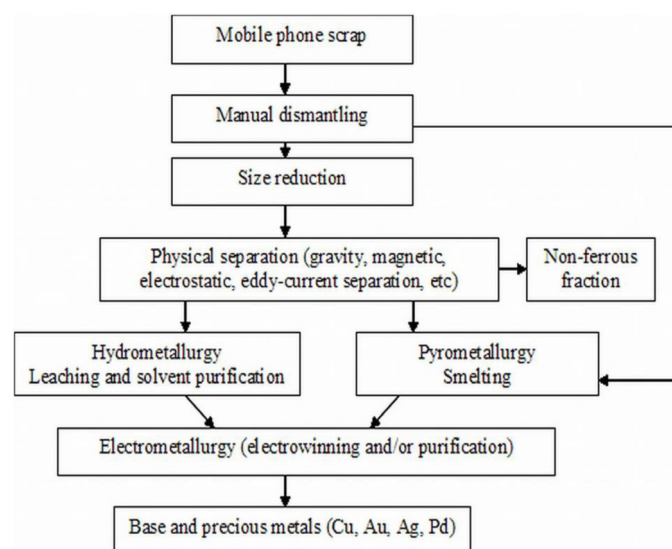


Fig. 1. General scheme of cell phone waste treatment [7,8]

* SILESIAŃ UNIVERSITY OF TECHNOLOGY, FACULTY OF ENGINEERING MATERIALS AND METALLURGY, KRASIŃSKIEGO 8, KATOWICE, POLAND

[#] Corresponding author: magdalena.lisinska@polsl.pl

However, at present, special attention has been paid to hydrometallurgical processes, which offer relatively low capital cost, reduced environmental impact and high metal recovery level; whereas pyrometallurgical processes are energy intensive and expensive. The main disadvantage of hydrometallurgical treatment is generation of wide range of harmful waste.

Table 1 shows typical leaching reagents used in hydrometallurgical techniques [7]. The literature data show (see Table 2) that among the other leaching reagents the best results of metals extraction were obtained for sulfuric acid, especially when the leaching was carried out in the presence of an oxidizing agent as hydrogen peroxide [15]. Preliminary results of own research confirmed that statement.

TABLE 1

Typical leaching reagents used in hydrometallurgical techniques [9]

Kind of leaching	Examples
Chemical leaching	cyanide, halide, thiourea, thiosulphate
Involving ligands	EDTA, DTPA, NTA, oxalate
Involving acid treatment	H ₂ SO ₄ , HCl, aqua regia, H ₂ SO ₄ and HNO ₃ , sodium hypochlorite
Hydrometal. etching	FeCl ₂ , CuCl ₂ and HCl, organic solvents

TABLE 2

The results of metals extraction during leaching process of PCB with sulfuric acid and hydrogen peroxide

Ref.	Conditions	Recovery
[5]	2M H ₂ SO ₄ + 35% H ₂ O ₂ (1 step) 2M H ₂ SO ₄ + 35% H ₂ O ₂ (2 step) at 298K, in 3 h	(1) 85.8% Cu (2) 14.0% Cu
[10]	2M H ₂ SO ₄ , in 20 ml 30% H ₂ O ₂ (for 100 ml solution), 303K, 2 h	90.0% Cu
[11]	2M H ₂ SO ₄ + 35% H ₂ O ₂ , 298K, 200 rpm, 3 h	85.8% Cu
[12]	2M H ₂ SO ₄ + 0.2 M H ₂ O ₂ , 358K, in 8 h (Cu), in 12 h (Fe, Ni, Al)	100% Cu 95% Fe, Ni, Al
[13]	2M H ₂ SO ₄ + 5% H ₂ O ₂ , 298K, 200 rpm	87% Cu
[10]	2M H ₂ SO ₄ + 30% H ₂ O ₂ , 323K, pH 1.48, 3 h	46.3% Cu
[14]	1.2M H ₂ SO ₄ + 10% H ₂ O ₂ , 323K, 4 h	75.5% Cu

The obtained results show that addition of hydrogen peroxide to sulfuric acid enables to intensify the process of metal extraction [16]; thus improves considerably the recovery level. However, taking into account the slightly effect on leaching other metals than copper, alternative strong oxidizing agent as an addition to sulfuric acid should be carried out.

Ozone is used in hydrometallurgical processes by many researchers. Ozone with a standard redox potential of 2.07 V is known as one of the strongest oxidizing agent [17]. The oxidation-precipitation of cobalt (II) in a solution of cobalt chloride by ozone has been described in [18]. Other researchers investigated leaching process of tetraedrite in HCl solutions using ozone as an oxidizing agent [19]. It was also applied together with iron ions in the pyrite leaching process [20]. Table 3 shows review of research in which ozone has been used as an oxidizing agent. However, ozone

was not used as an additional oxidizing agent for the recovery of metals from spent PCBs. The preliminary test shows, that results of such experiments are promising, which allows to take up the proposed research topic. The subject of leaching PCBs with the participation of sulfuric acid and ozone is a new one in the country, and the proposed research could answer the question which oxidizing agent (hydrogen peroxide or ozone) gives better results.

TABLE 3

Review of research in which ozone has been used as an oxidizing agent

Ref.	Material	Application
[21]	Metallic scraps, metals powders (Au, Pd, Rh, Pt)	Leaching of Au and Pd by aqueous ozone in dilute chloride media at ambient temp. and low H ⁺ and Cl ⁻ concentrations (~0.1 M); under these conditions, Rh and Pt remain stable.
[19]	Tetraedrite Cu ₁₂ Sb ₄ S ₁₃	Leaching in 0.1-1 M HCl plus ozone as an oxidizing agent, which was supplied by blowing gas through the pulp.
[22]	Chalcopyrite CuFeS ₂	Microwave leaching with H ₂ SO ₄ in presence of ozone at T = 293K; results do not depend on acid concentrations; H ₂ SO ₄ is needed only to avoid iron hydrolysis; process is accelerated with the increasing ozone concentration.
[23]	Chalcopyrite CuFeS ₂	Leaching with 0.5 M H ₂ SO ₄ plus ozone as oxidizing agent in T = 277-348K; the most effective results were at T = 293K; content of ozone in O ₂ was 2.5 vol. %.
[24]	Chalcopyrite CuFeS ₂	Leaching with 0.1-1 M H ₂ SO ₄ and ozone as an oxidizing agent at room temperature; concentration of produced ozone varied from 20 to 60 g/m ³ .
[25]	Pyrrargyrite (Ag ₃ SbS ₃)	Ag dissolution (80%) was obtained when 1 gram of pyrrargyrite in 800 mL of 0.18 M H ₂ SO ₄ was oxidized with 1.2 L/min oxygen containing 0.079 g O ₃ /L at 298K and a stirring speed of 800 rpm.
[26]	Metallic scraps	Recycling of Ag from metallic scraps – O ₃ leaching at T = 283-333K and low (0.1 M) H ₂ SO ₄ concentration; Ag dissolved as Ag ²⁺ _(aq) in 10 ⁻³ -1 M H ₂ SO ₄ .
[27]	Sulfidic antimony ore containing pyrite	Ozonation leaching in HCl solution; the leaching efficiency (%) of Sb increases with temperature (308-338K) and HCl concentration (3.0-4.5 M). High Sb extraction (94.3%) with low Fe dissolution (2.3%) was achieved for: 4.5 M HCl, 2.0 L/min gas flow rate, 8:1 of the L/S ratio, 4.0 h, 338K.
[17]	Stibnite concentrates	Leaching with 4.5 M HCl and ozone as an oxidizing agent; liquid to solid ratio of 10:1 and gas flow rate from 1 L/min to 2.0 L/min, T = 308-353K.

2. Experimental methodology

As the research material spent cell phones were used. Manual dismantling of cell phones were carried out separating their particular elements from the printed circuit boards (see

Fig. 2), which then were cut into pieces of 20-40 mm. Material prepared in such way was then leached. The experiments were carried out in a 600 ml flask using 2M and 5M sulfuric acid as a washing agent with the addition of ozone in concentration 140 mg/L and a volume of feed gas 8 L/min (see Fig. 3). Ozone was produced by generator Korona L 20 SPALAB (see Fig. 4). The process was carried out in the temperatures: 298K, 313K and 343K, ensuring mixing of the system with a 340 rpm mechanical stirrer.



Fig. 2. View of dismantled cell phone with PCB pieces

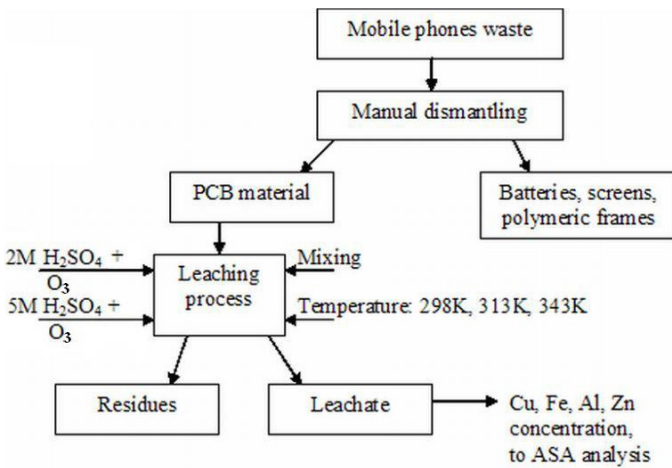


Fig. 3. Scheme of the conducted research



Fig. 4. Ozone generator Korona L 20 SPALAB

The leaching process was carried out by continuous mixing for 6 hours and introduction of ozone into the solution, and then each sample was left for 66 hours under static conditions

without further mixing and ozonation. Tests were carried out for a constant ratio of solid to liquid (S/L = 1:10). During the experiments, the concentration of copper, iron, zinc and aluminum was constantly monitored over time: 0.5h, 1h, 2h, 4h, 6h, 24h and 72 h. The metal content in the sample was determined using atomic adsorption spectrometry (AAS).

3. Research results

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

The effect of copper concentration changes during 72 h of leaching in 2M and 5M sulfuric acid and addition of ozone at temperatures of 298K, 313K, 343K shows Fig. 5. Level of copper dissolution was strongly dependable on temperature. Already after 4 hours of the experiment an increase in Cu concentration in 2M and 5M H₂SO₄ and O₃ solution was observed. The best copper leaching results after 72 h of the experiment were recorded in 2M H₂SO₄ at 343K of 26.9 g/dm³, 2M H₂SO₄ at 313K of 15.32 g/dm³ and in 5M H₂SO₄ at 343K of 11.75 g/dm³. In 5M H₂SO₄ and ozone solution, after 24 hours at 343K, the concentration of copper was 12.3 g/dm³.

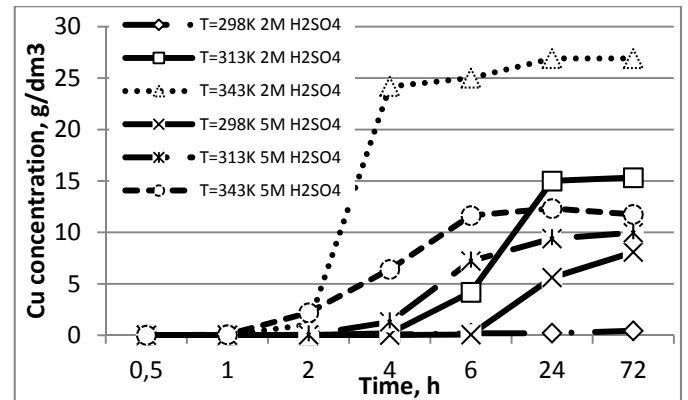


Fig. 5. Copper concentration obtained after leaching in 2M and 5M H₂SO₄ solution with O₃ as oxidizing agent during 72 h

Fig. 6 shows the influence of temperature on the iron concentration during 72 h process of leaching in 2M and 5M sulfuric acid and addition of ozone. Within 72 hours of the experiment, the concentration of Fe in the 2M and 5M solution of sulfuric acid and O₃ in T = 313K did not exceed 0.2 g/dm³. When the temperature was increased to 343K Fe concentration was also increased to 0.55 g/dm³ and 0.6 g/dm³ in 2M and 5M H₂SO₄ respectively. The highest concentration of Fe was reached after 24 hours of leaching in 5M sulfuric acid at 343K, which was 0.67 g/dm³. Ozone does not significantly affect the process of iron leaching.

Fig. 7 presents results of zinc concentration changes with temperature during 72 h process of leaching PCB in 2M and 5M sulfuric acid with addition of ozone. During 72 hours of leaching,

Zn concentration in a 2M and 5M solution of sulfuric acid and ozone did not exceed 0.70 g/dm³. After raising the temperature to 343K, an increase in Zn leaching was observed. The best zinc leaching effect was obtained with 2M H₂SO₄ and ozone at 343K (0.68 g/dm³). During 72 hour leaching in 2M H₂SO₄, the zinc concentration was 0.13 g/dm³ and 0.52 g/dm³, respectively for 298K and 313K, and in 5M H₂SO₄, the zinc concentration was 0.09 g/dm³ and 0.32 g/dm³. At both temperatures (313 and 343K) and after 24 h zinc concentration was (0.68 and 0.41 g/dm³) higher than after 72 h (0.49 and 0.35 g/dm³).

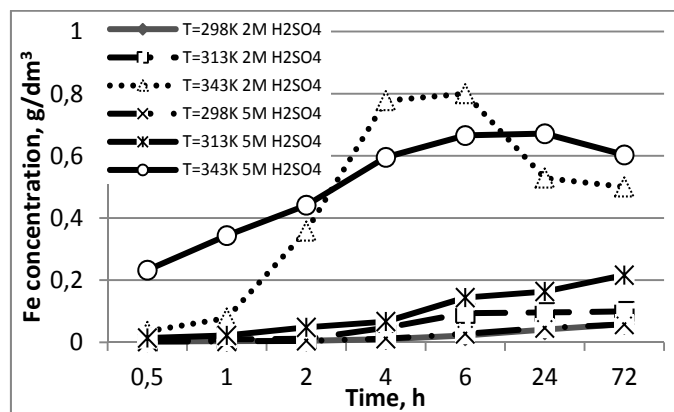


Fig. 6. Iron concentration obtained after leaching in 2M and 5M H₂SO₄ solution with O₃ as oxidizing agent during 72 h

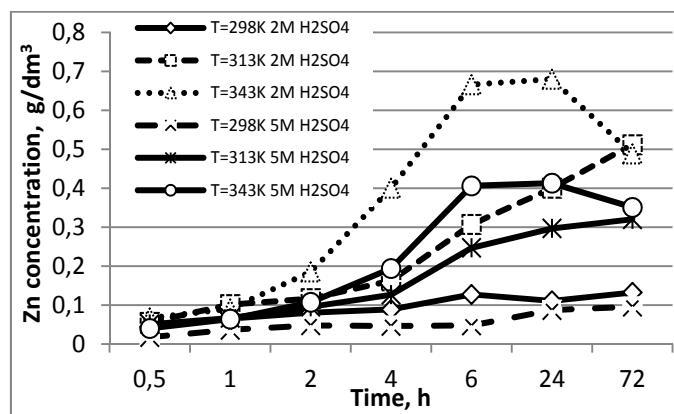


Fig. 7. Zinc concentration obtained after leaching in 2M and 5M H₂SO₄ solution with O₃ as oxidizing agent during 72 h

Fig. 8 presents results of changes the aluminium concentration with temperature during 72 h process of leaching PCB in 2M and 5M sulfuric acid with addition of ozone. During 72 hours of leaching, the concentration of Al in 2M and 5M solution of sulfuric acid and ozone did not exceed 1.7 g/dm³. After raising the temperature to 343K, an increase in aluminium leaching was observed. The best aluminium leaching effect was obtained with 2M H₂SO₄ and ozone at 343K (1.7 g/dm³). During the 72 hour leaching in 2M H₂SO₄, the aluminium concentration was 0.086 g/dm³ and 0.060 g/dm³ respectively (for 298K and 313K), and in 5M H₂SO₄, Al concentration was 0.063 g/dm³ and 0.826 g/dm³. At both temperatures (313 and 343K) 5M H₂SO₄

and after 24h the concentration of aluminum (0.875 g/dm³ and 1.52 g/dm³) was higher than after 72h (0.826 g/dm³ and 1.42 g/dm³).

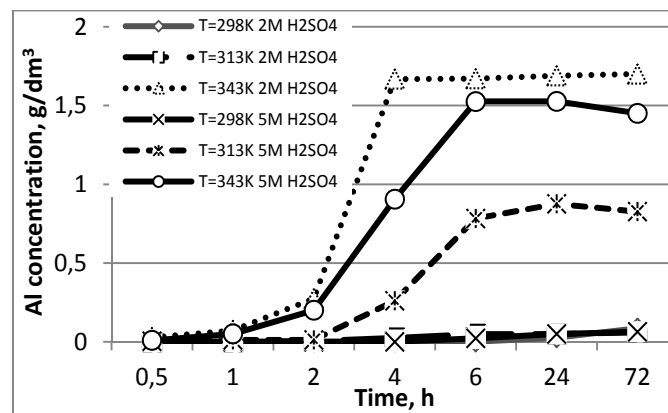


Fig. 8. Aluminium concentration obtained after leaching in 2M and 5M H₂SO₄ solution with O₃ as oxidizing agent during 72 h

3.2. Comparison of results obtained for hydrogen peroxide and ozone as oxidizing agents

Figs. 9-12 show the comparison of the best results of leaching of copper, iron, zinc and aluminum in 2M and 5M sulfuric acid with the addition of 30% and 10% hydrogen peroxide and ozone. It can be observed that hydrogen peroxide works on copper just from beginning of the experiment, but ultimately the results with ozone are much better. After 30 minutes the copper concentration in the experiment without additional oxidizing agent was only 0.0007 g/dm³. During the experiment with the addition of 10% hydrogen peroxide Cu concentration was at the level of 1.47 g/dm³. In the experiment with ozone after 30 minutes, the copper concentration was only 0.0043 g/dm³. The noticeable Cu concentration is observed after 2 hours. After 72 hours of experiment, the concentration of copper was 0.278 g/dm³, 6.55 g/dm³ and 26.9 g/dm³ for alone H₂SO₄ and with the addition of 10% H₂O₂ and O₃, respectively. The results of ozone leaching are fourth as good as using hydrogen peroxide.

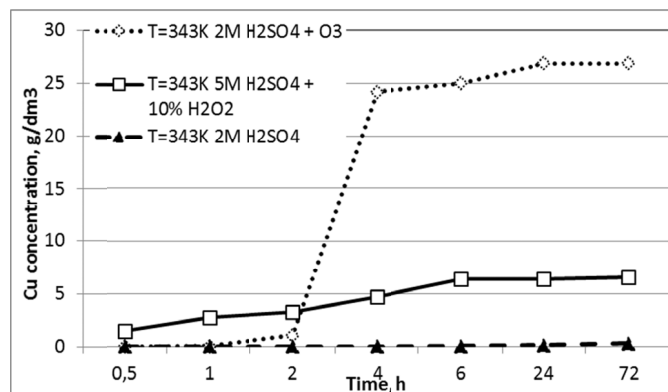


Fig. 9. Copper concentration obtained after leaching in only H₂SO₄ and with addition H₂O₂ or O₃ solution during 72 h

The results of the iron leaching applying hydrogen peroxide and ozone differ slightly. The best result was achieved without the use of an additional oxidizing agent. After 72 hours of experiment, the iron concentration was respectively 6.36 g/dm^3 , 0.82 g/dm^3 , 0.60 g/dm^3 (for $2\text{M H}_2\text{SO}_4$ without the addition of an oxidizing agent, $5\text{M H}_2\text{SO}_4$ with the addition of $30\% \text{H}_2\text{O}_2$ and O_3).

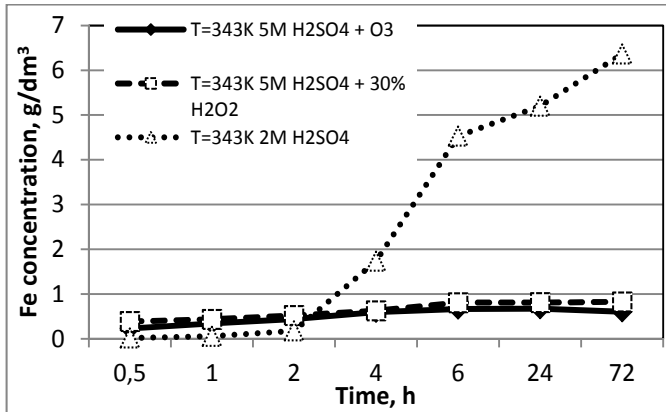


Fig. 10. Iron concentration obtained after leaching in only H_2SO_4 and with addition H_2O_2 or O_3 solution during 72 h

The selected zinc leaching test ($2\text{M H}_2\text{SO}_4$ in $T = 313\text{K}$) with the addition of ozone shows the best results compared to hydrogen peroxide ($5\text{M H}_2\text{SO}_4$ in $T = 343\text{K}$) and pure $2\text{M H}_2\text{SO}_4$ in $T = 343\text{K}$. In the experiment with O_3 , the concentration was 0.512 g/dm^3 , and with $30\% \text{H}_2\text{O}_2$ it was 0.45 g/dm^3 and 0.42 g/dm^3 without addition of oxidizing agent.

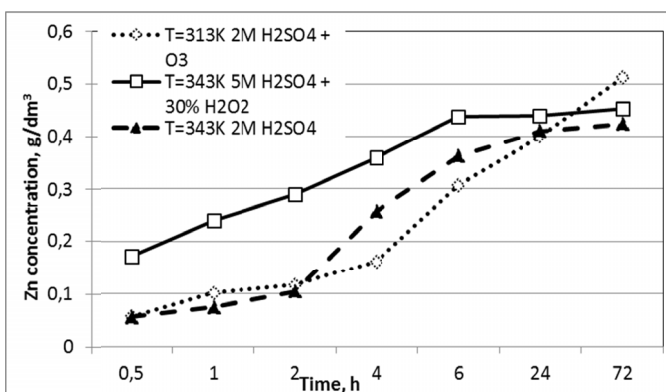


Fig. 11. Zinc concentration obtained after leaching in only H_2SO_4 and with addition H_2O_2 or O_3 solution during 72 h

Fig. 12 shows the best results obtained for aluminum leaching in sulfuric acid without an additional oxidizing agent and with the addition of $30\% \text{H}_2\text{O}_2$ and O_3 . The best result was obtained for solution with ozone. After 72 hours of experiment, the aluminum concentration was 1.45 g/dm^3 , 0.47 g/dm^3 , 0.16 g/dm^3 , respectively (for $5\text{M H}_2\text{SO}_4$ in 343K with the addition of ozone, $2\text{M H}_2\text{SO}_4$ in 343K without the addition of an oxidizing agent and $5\text{M H}_2\text{SO}_4$ with addition of $30\% \text{H}_2\text{O}_2$).

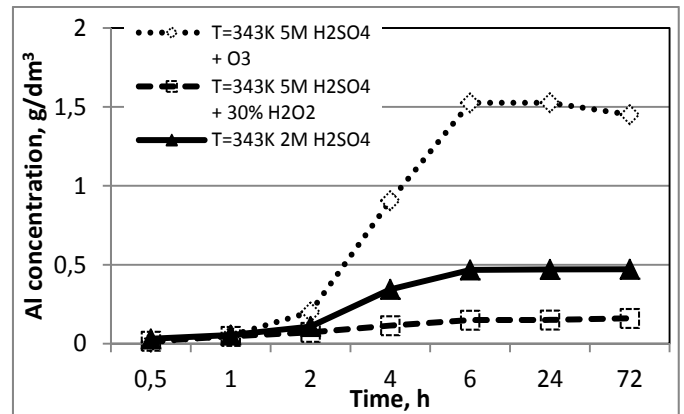


Fig. 12. Aluminium concentration obtained after leaching in only H_2SO_4 and with addition H_2O_2 or O_3 solution during 72 h

4. Conclusions

Hydrometallurgical treatment of PCBs from used cell phones seems to be justified both economically and ecologically to recover selected metals. Among other leaching reagents sulfuric acid is popularly used for such kind of research. However, the results of tests confirmed the negligible efficiency of leaching using only sulfuric acid. The literature data show that in order to increase the efficiency of leaching process, a strong oxidizing agent should be applied – for example hydrogen peroxide or ozone. The conducted research can draw the following conclusions:

- the obtained results experiments carried out using H_2O_2 in various concentration ranges showed intensification of the leaching process, especially for copper, but still leave a large margin in the scope of the possibility of increasing the degree of transition of metals from the solid phase to the solution,
- the best results of copper leaching process was observed for the 2M sulfuric acid and ozone, the obtained results is 3-4 times better than using hydrogen peroxide; the obtained positive results indicate the potential of the PCBs leaching method with the use of O_3 and are the basis for the continuation of research in this field,
- the leaching process of iron was the best using alone sulfuric acid, for zinc the efficiency of this process is similar in all used solutions, whereas for the aluminium the best result was obtained for 5M sulfuric acid with ozone.

The subject of leaching PCBs with the participation of sulfuric acid and ozone is in the country quite new, and the continuation of the research will allow to recognize the phenomena occurring during this process. In further studies, the choice of process parameters will allow a comprehensive approach to the problem of recovering metals from used cell phones.

Acknowledgements

This paper was created with the financial support of Polish Ministry for Science and Higher Education under internal grant BK-221/RM0/2018 for Faculty of Materials Engineering and Metallurgy, Silesian University of Technology, Poland.

REFERENCES

- [1] J. Willner, A. Fornalczyk, *Przemysł chemiczny* **91**, 4, 517-522 (2012).
- [2] A. Fornalczyk, J. Willner, K. Francuz, J. Cebulski, *Arch. Mater. Sci. Eng.* **63**, 87-92 (2013).
- [3] M. Saternus, A. Fornalczyk, J. Willner, H. Kania, *Przemysł chemiczny* **95**, 1, 78-83 (2016).
- [4] J. Cui, L. Zhang, *J. Hazard. Mater.* **158**, 228-256 (2008).
- [5] M. Kaya, *Waste Management* **57**, 64-90 (2016).
- [6] C. Xu, W. Zhang, W. He, G. Li, J. Huang, *Waste Management* **58**, 341-347 (2016).
- [7] M. Saternus, M. Lisińska, J. Willner, *IaSM Conference, Horni Beeva, Czech Republic, Conf. Proc.* 121-127 (2017).
- [8] A. Tuncuk, V. Stazi, A. Akcil, E.Y. Yazici, H. Deveci, *Minerals Engineering* **25**, 28-37 (2012).
- [9] Z. Ahamd, *Extracion of Metals from Electronic Waste, Final Report (CPT-II Mini Project), Dept. of Chem. Eng., COMSATS Institute of Information Technology, Defense Road, Lahore* (2015).
- [10] I. Birloaga, I. De Michelis, F. Ferella, M. Buzatu, F. Vegliò, *Waste Manag.* **33**, 935-941 (2013).
- [11] H. Cui, C.G. Anderson, *J. Adv. Chem. Eng.* **6**, 142 (2016).
- [12] C.J. Oh, D.O. Lee, H.S. Yang, T.J. Ha, M.J. Kim, *J. Air Waste Manag. Assoc.* **53** (7), 897-902 (2003).
- [13] A. Akcil, C. Erust, C. Gahan, M. Ozgun, M. Sahin, *Waste Management* **45**, 258-271 (2015).
- [14] M. Kumar, J. Lee, M. Kim, J. Jeong, K. Yoo, *Envir. Eng. and Manag. J.* **13** (10), 2601-2606 (2014).
- [15] A. Behnamfard, M.M. Salarirad, F. Veglio, *Waste Management* **33**, 2354-2363 (2013).
- [16] A. Khaliq, M.A. Rhamdhani, G. Brooks, S. Masood, *Resources* **3**, 152-179 (2014).
- [17] Q. Tian, H. Wang, Y. Xin, Y. Yang, D. Li, X. Guo, *Hydrometallurgy* **165**, 295-29 (2016).
- [18] Q.-H. Tian, X.-Y. Guo, Y. Yi, Zh.-H. Li, *Trans. Nonferrous Metals Soc.* **20**, 42-45 (2010).
- [19] M. Ukasik, T. Havlik, *Hydrometallurgy* **77**, 139-145 (2005).
- [20] Q.-C. Li, D.-X. Li, F.-J. Qian, *Hydrometallurgy* **97** (1), 61-66 (2009).
- [21] J. Viñals, E. Juan, M. Ruiz, E. Ferrando, M. Cruells, A. Roca, J. Casado, *Hydrometallurgy* **81**, 142-151 (2006).
- [22] T. Havlik, *Metall.* **64**, 5, 25-28 (2010).
- [23] T. Havlik, M. Skrobian, *Canadian Metallurgical Quarterly* **29**, 133-139 (1990).
- [24] T. Havlík, J. Dvořčíková, Z. Ivanová, R. Kammel, *Metall.* **53**, 1-2, 57-60 (1999).
- [25] C. Rodríguez-Rodríguez, F. Nava-Alonso, A. Uribe-Salas, *Hydrometallurgy* **149**, 168-176 (2014).
- [26] J. Viñals, E. Juan, A. Roca, M. Cruells, J. Casado, *Hydrometallurgy* **76**, 225-232 (2005).
- [27] Q. Tian, H. Wang, Y. Xin, D. Li, X. Guo, *Hydrometallurgy* **159**, 126-131, (2016).