THE INFLUENCE OF LEACHATE REAGENTS ON HYDROMETALLURGICAL RECOVERY OF METALS FROM SPENT PCBS

[1]Magdalena LISIŃSKA, [1]Mariola SATERNUS, [2]Silvie BROŽOVÁ

[1]Silesian University of Technology, Katowice, Poland, EU,
magdalena.lisinska@polsl.pl, mariola.saternus@polsl.pl

[2]VSB - Technical University of Ostrava, Ostrava, Czech Republic, EU, silvie.brozova@vsb.cz

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Abstract

For several years, continuous technological progress has been observed, resulting in a constantly growing number of e-waste. The diversified composition of e-waste causes the emergence of a large amount of hazardous waste, which is a threat to both health and life of people, as well as the environment. Nowadays, effective recycling of this type of waste has been recognized as a major challenge for every society. Spent printed circuit boards (PCBs) that are part of most electronic devices, including mobile phones and computers contain many metals. Printed circuit boards cause not only ecological threat, but also serious waste of resources, including copper. That is why new and effective ways to process these wastes and re-use of recovered metals are increasingly investigated. Interest in hydrometallurgical processing of used electronic equipment has increased in recent years due to its advantages - it is more accurate, more predictable and easier to control compared to pyrometallurgical methods. This method does not require the use of complicated and expensive devices. There are many leaching reagents that allow the dissolution of metals. Among the appropriate leaching agents, acids such as H_2SO_4, HCl and HNO_3 can be distinguished. Literature data show that a strong oxidizing agent should be used to increase the efficiency of the leaching process. This is justified by presented in the literature results of leaching with the addition of hydrogen peroxide and ozone. Own research confirms that among the best leaching agents the best results of copper leaching from electronic waste were obtained for H_2SO_4 and HCl, especially when the oxidizer in the form of hydrogen peroxide and ozone was added to the process. These conditions favor the dissolution of metals. The conducted research indicates a large potential of the PCB leaching method using HCl and H_2SO_4 with the addition of oxidants such as H_2O_2 or O_3.

Keywords: Printed circuit boards, leaching, oxidizing agent, ozone, hydrogen peroxide

1. INTRODUCTION

Electrical and electronic waste is becoming an increasing problem in the world. The waste is growing at an alarming rate through continuous technological progress and there are no signs of its slowdown. In addition, they are one of the fastest growing waste streams in the world in terms of quantity. By 2016, the world generated 44.7 million metric tons (Mt) of electronic waste. Only 8.9 Mt of e-waste has been documented worldwide, collected and recycled, which corresponds to 20 % of all electronic waste generated [1]. The diverse composition of electronic scrap has led to the formation of a large stream of hazardous waste, which is associated with the fact that they can pose a threat to both health and life of people, as well as the environment. This type of waste contains heavy metals, polymers, various kinds of organic compounds containing, among others: bromine, chromium, lead and mercury. Thus, recycling of this type of waste has been recognized as the main challenge [2,3]. The precious metals contained in electrical and electronic waste provide significant economic benefits, and the recovery of metals from these wastes can, to a certain extent, reduce the total global demand for primary metals production, while limiting the emission of greenhouse gases [3,4]. Recycling of electronic waste also helps reduce the amount of material stored in landfills. An example of a diversified composition of used electrical and electronic devices are computers and mobile phones that contain printed circuit boards (PCBs). These plates are the carrier of many metals, including precious metals, which is an attractive option for recycling [5]. Thus, PCBs included in mobile phones cause not only ecological threat, but also serious waste of resources, including copper. The main techniques for recycling electronic waste, including mobile phones, are pyrometallurgical and hydrometallurgical methods combined with mechanical pre-treatment [6,7]. However, recently most of the activities related to the recovery of these valuable metal waste concentrate on hydrometallurgical techniques, which are more accurate, predictable, easy to monitor and, what is more important, less energy-intensive compared to pyrometallurgical methods. Hydrometallurgical methods do not require complicated and expensive devices [8-11]. The pre-treatment of used cell phones usually involves manual disassembly (**Figure 1**), removal of hazardous substances from them and separation of other materials from PCBs. Then, the obtained product is processed by hydrometallurgical methods [12].

Figure 1 Parts of mobile phones after manual disassembly

Leaching reagents used for the recovery of metals in this method are, among others, acids. Most often, H_2SO_4, HCl and HNO_3 or combinations thereof were used. In order to increase the efficiency of the leaching process, additional oxidizing agents were used [13-15]. An example are PCB leaching processes using H_2SO_4 with the addition of hydrogen peroxide, obtaining satisfactory copper recovery results from these wastes (85-99 %) [9,10,16,17]. Another example is the use of ozone, which is known as one of the strongest oxidizers in acidic solutions [16,18,19]. Such an oxidant can be a viable alternative that gives a number of environmental benefits in the leaching of concentrates and wastes that contain metals, including precious metals, mainly due to the formation of oxygen as the only by-product of the reaction. Ozone was used in hydrometallurgical processes by many researchers. It was used, among others, as an oxidizer in combination with hydrochloric acid in the leaching of stibnite concentrates [18], leaching of tetrahedrite [20], leaching of a complex sulfidic antimony ore in hydrochloric acid solution [21], silver leaching from pyrargyrite [19], chalcopyrite leaching [22-24] and leaching metallic waste containing silver [25].

2. EXPERIMENTAL METHODOLOGY

Spent mobile phones of different producers were used as a material for research. Manual dismantling of them were carried out separating their particular elements (such as casing, battery, screens and others) from the printed circuit boards. The printed circuit boards were cut into pieces of 20-30 mm and then the pieces was milled in the cross beater Retsch SK100 hammer mill. Materials were prepared in such way as then leached. The experiments were carried out in a 600 ml flask using 2M sulfuric acid and 2M hydrochloric acid as a leaching agent with the addition of ozone and 30 % hydrogen peroxide. Ozone was produced, in concentration 140 mg/L and a volume of feed gas 8 L/min, by generator Korona L20 SPALAB. The process was conducted in the temperature range of 313 K and 353 K, providing mixing of the system with a mechanical stirrer of 400 rpm. The leaching process was carried out under continuous stirring for 6h and then each sample was left for another 18 h under static conditions without further stirring. Tests were carried out for a constant ratio of solids to liquid (S/L=1:4). During experiments the concentration of Cu, Fe, Zn, Al, Sn and Ni was constantly monitored after time: 2 h, 6 h, 10 h and 24 h. Content of metals in the sample was determined by the atomic adsorption spectrometry (AAS). **Figure 2** presents the scheme of the conducted research.

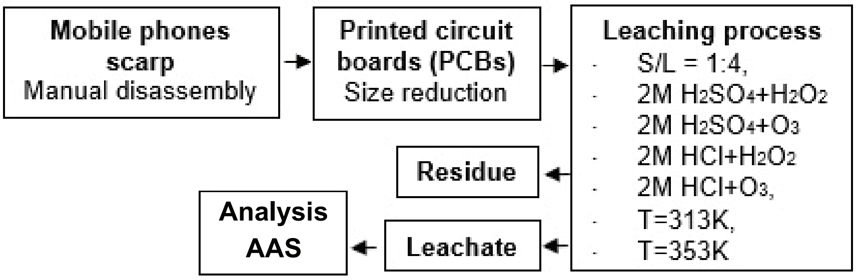

Figure 2 Scheme of the conducted research (stages of leaching process of PCBs)

3. RESEARCH RESULTS

Figure 3 shows the effect of copper concentration changes over 24 hours leaching in 2M sulfuric acid and 2M hydrochloric acid and the addition of ozone and hydrogen peroxide at 313 K and 353 K. The dissolution rate of copper was dependent on the temperature in the case of sulfuric acid. Already after 6h of the experiment an increase in Cu concentration at 353 K was observed, amounting to 21.48 g/dm^3 (for H_2SO_4+H_2O_2) and 15.82 g/dm^3 (for H_2SO_4+O_3). After 10h of the experiment it was obsreved the decrease in copper concentration by almost 4 g/dm^3 by the end of the experiment (for H_2SO_4+H_2O_2 in *T* = 353 K). The best copper leaching results during 24-hour leaching were obtained with 2M HCl+O_3 at 313 K and 353 K, corresponding to 26.22 g/dm^3 and 30.77 g/dm^3, respectively.

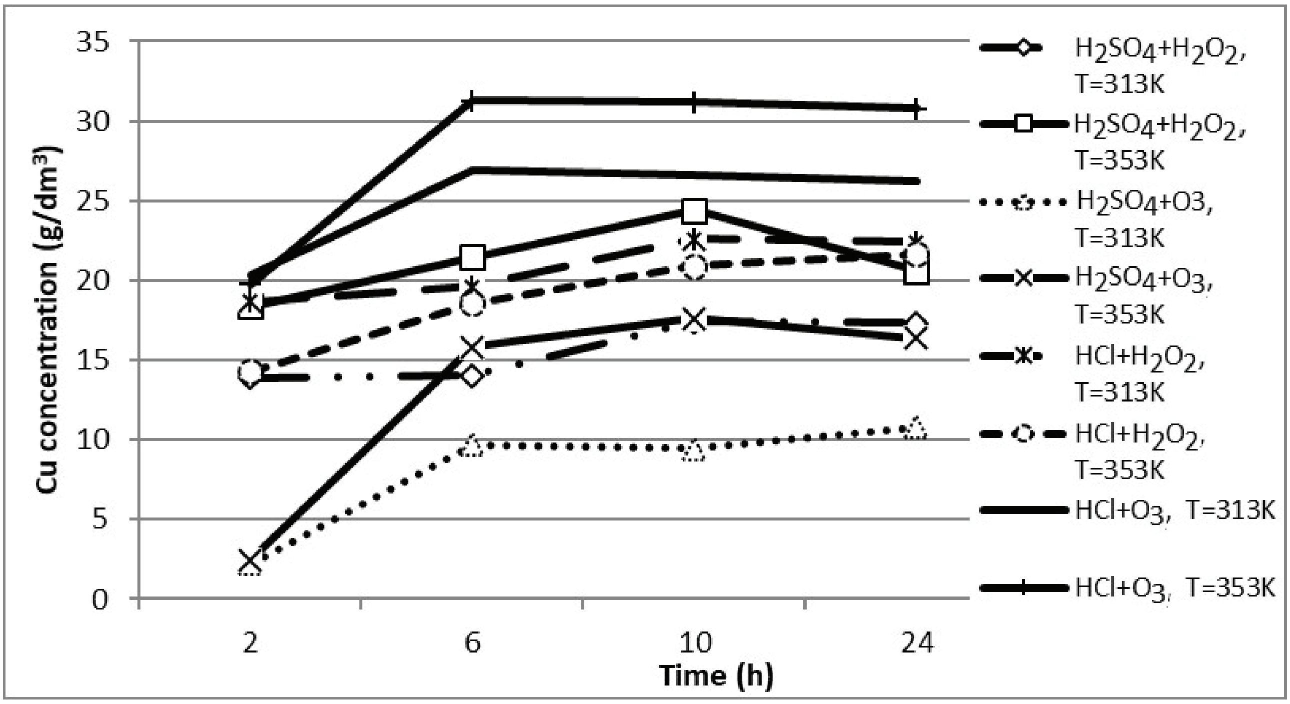

Figure 3 Copper concentration obtained after leaching in H_2SO_4 and HCl with the addition of oxidazer (H_2O_2 or O_3) during 24h of experiment

Figure 4 shows a comparison of tin leaching results in 2M sulfuric acid and 2M hydrochloric acid with the addition of 30 % hydrogen peroxide and ozone. It can be observed that the hydrogen peroxide works and ozone acts on the tin from the beginning of the experiment in a similar way. This is evidenced by the results obtained. The best results were obtained during 24-hour leaching in 2M $HCl+H_2O_2$ at T = 353 K, the Sn concentration was 9.25 g/dm^3, following 9.24 g/dm^3 in 2M $H_2SO_4+H_2O_2$ at T = 313 K. Slightly lower results were obtained by adding ozone. After 24-hour experiments with the use of ozone, the concentration of tin was 8.87 g/dm^3 (for $HCl+O_3$ in T = 313 K) and 8.32 g/dm^3 (for $H_2SO_4+O_3$ in T = 353 K). The increase in temperature has no effect on tin dissolution in these experiments.

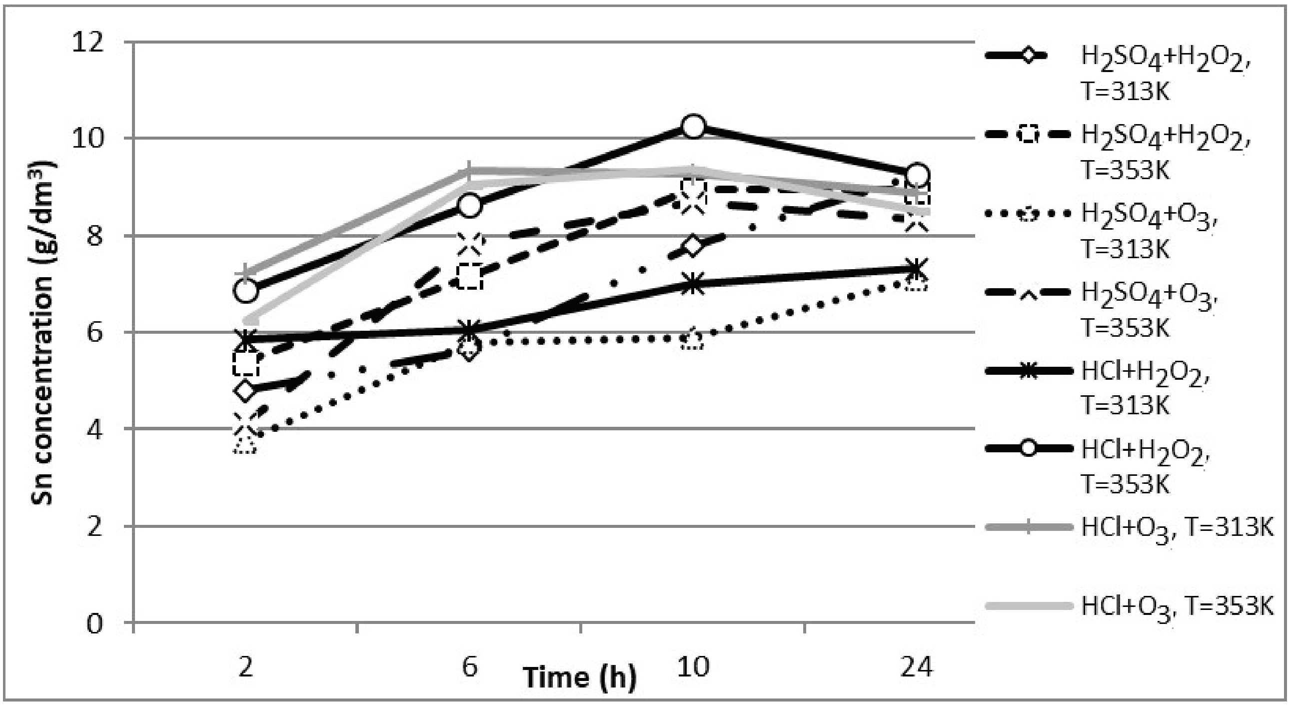

Figure 4 Tin concentration obtained after leaching PCBs in H_2SO_4 and HCl with the addition of oxidizer (H_2O_2 or O_3) during 24h of experiment

Figure 5 shows a comparison of the best results of leaching of iron, aluminum and nickel in 2M sulfuric acid and 2M hydrochloric acid with the addition of 30 % hydrogen peroxide and ozone. It can be seen that the majority of those selected among the best results come from leaching experiments with the addition of ozone. It can also be observed that the remaining samples under static conditions for a further 14 hours do not significantly affect the increase in nickel, aluminum and iron concentrations. Hydrochloric acid combined with hydrogen peroxide and ozone act on iron from the beginning of the experiment, but the ozone result is slightly lower. After 2h it was 6.24 g/dm^3 for 30 % H_2O_2 in T = 353 K and 5.01 g/dm^3 for O_3 in T = 313 K. After 24h, the results were 11.06 g/dm^3 and 8.76 g/dm^3, respectively. In research [14], the effect of sulfuric acid alone and the addition of ozone and hydrogen peroxide was compared for iron, the best result (6.36 g/dm^3) was achieved without the use of an additional oxidizing agent using H_2SO_4. The leaching results of HCl with the addition of hydrogen peroxide are as good as the use of ozone.

The results of iron leaching using hydrogen peroxide and ozone differ slightly. In the case of iron, the addition of hydrogen peroxide and ozone to sulfuric acid and hydrochloric acid had no significant effect on increase in their concentration in solution after the leaching process. After 24 hours of the experiment the aluminum concentration was respectively 7.37 g/dm^3, 5.65 g/dm^3, 5.30 g/dm^3 (for 2M HCl in 353 K with the addition of ozone, 2M $H_2SO_4+O_3$ in 353K and 2M H_2SO_4 with the addition of 30 % hydrogen peroxide at 353 K). The best result was obtained for a solution with ozone. The results of nickel leaching using hydrogen peroxide and ozone differ slightly. The best result of nickel concentration after 24 hours of experience amounting to 6.46 g/dm^3 was achieved by using 2M HCl+H_2O_2 in T = 353 K, immediately after it 5.83 g/dm^3 using 2M HCl+O_3 in T = 353 K. Only the minimum increase in Zn concentration after 24h of leaching is visible - this concentration was 1.58 g/dm^3, when HCl+O_3 was used in T = 353 K and 1.27 g/dm^3 in HCl+O_3 T=313 K. Due to the low concentration of Zn in the solution at the other parameters of the results processes, it has not been shown in the figure.

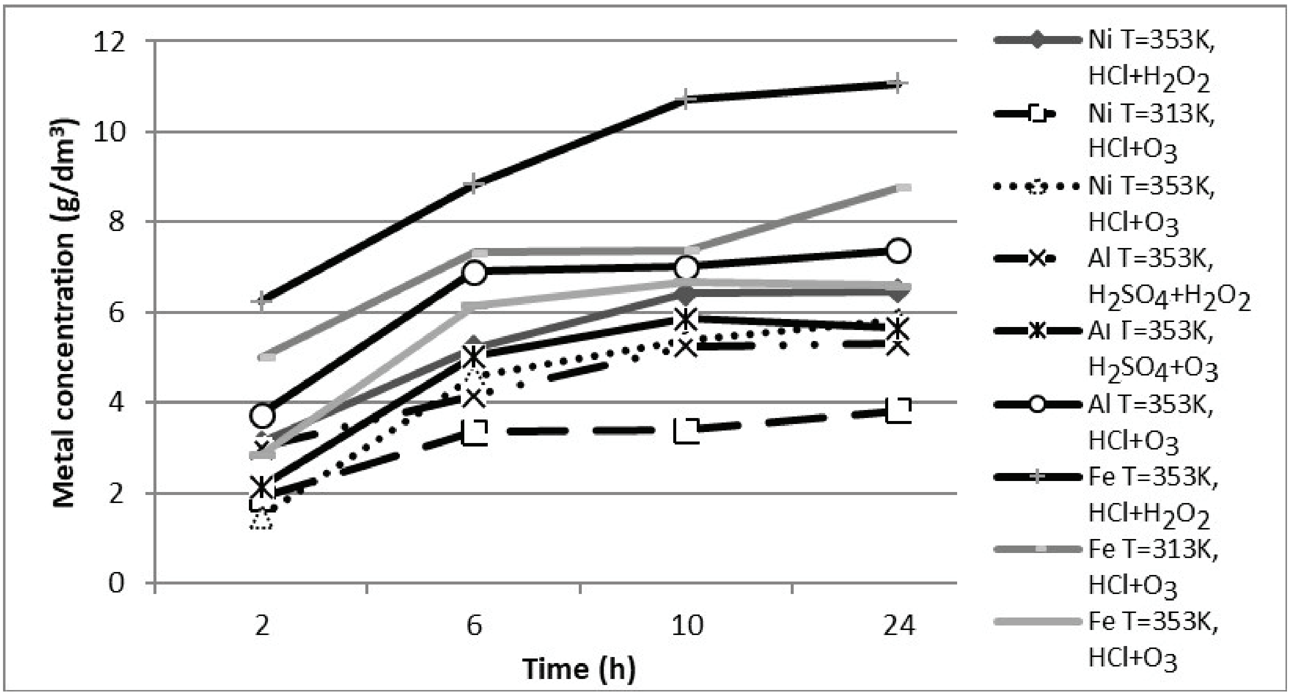

Figure 5 Nickel, aluminum and iron concentration obtained after leaching PCBs in H_2SO_4 and HCl with the addition of oxidizer (H_2O_2 or O_3) during 24h experiment

4. CONCLUSION

To increase the efficiency of the leaching process, strong oxidizing agent should be added to the acid - two of them are hydrogen peroxide and ozone. This is evidenced, inter alia, by the results of tests carried out with the addition of hydrogen peroxide and ozone [7,8,14-19]. Own experiments were carried out using these oxidizing agents. The obtained results showed intensification of the process of leaching printed circuit boards from used cell phones with the use of H_2SO_4 and HCl with the addition of hydrogen peroxide and ozone as an oxidizer. The best results of the copper leaching process were observed for 2M hydrochloric acid and ozone, the results obtained are around 27 % better than using hydrogen peroxide. The process of tin, iron and nickel leaching was the best when using HCl and H_2O_2, however slightly lower results were obtained with HCl and O_3. For aluminum, the efficiency of this process was best with HCl and O_3. In the case of zinc the addition of hydrogen peroxide and ozone to the sulfuric acid and hydrochloric 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 24 hours of leaching - this concentration was 1.58 g/dm^3 when HCl and O_3 was used. The obtained positive results indicate the potential of the PCB**s** leaching method using O_3 and are the basis for the continuation of research in this field. The leaching of PCBs with the participation of acid and ozone is new in the country, and the continuation of research will recognize the phenomena occurring in this process and select its appropriate parameters for the effective recovery of copper and associated metals from electronic waste, such as mobile phones.

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