Politechnika Śląska

Wydział Inżynierii Materiałowej

mgr inż. Magdalena Lisińska

Badanie procesu odzysku metali z drukowanych płytek obwodowych na drodze dwustopniowego ługowania z użyciem H_2SO_4 i HNO_3

Praca doktorska

Promotor: **prof. dr hab. inż. Mariola Saternus**

Promotor pomocniczy: **dr inż. Joanna Willner**

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Abstract

The work as part of the literature review describes the recycling policy and legal regulations regarding the management of waste electrical and electronic equipment in Poland, the European Union and in the world. The paper presents characteristics of electronic scrap, in particular mobile phones and printed circuit boards (PCB) contained in them, which are carriers of many metals, are presented. Then, the available PCB recycling methods were reviewed (pyrometallurgical methods, hydrometallurgical methods and biohydrometallurgical methods). Hydrometallurgical techniques are discussed in detail as well as the analysis of the experimental research conducted in this field, published in many scientific articles. PCBs are a heterogeneous material containing many metals. This work focuses on the recovery of iron, copper, tin, zinc, nickel and lead due to their high concentration in PCBs and the increasing environmental and economic pressure on the recovery of these metals. The metal content was analyzed by atomic absorption spectrometry.

The preliminary leaching tests of the shredded PCB fraction with a grain size of 4-0.045 mm in H_2SO_4 solutions with concentrations: 2M and 5M in the temperature range: 313 K, 333 K, 353 K showed that the acid leaching process must be carried out in two steps and the iron must first be removed in order to be able to skip the magnetic separation step. It has been shown that an increase in the leaching agent concentration increases the leaching level of Fe and Ni. Increasing the temperature used in the tests causes an increase in the concentration of Fe, Ni and Sn in the solution.

The selection of 2M H_2SO_4 is confirmed by process rate studies based on kinetic models: control based on chemical surface reaction or control based on diffusion. In the case of Cu, Fe, Sn, Zn, Ni and Pb, the test results showed that the process was controlled on the basis of a surface chemical reaction. The experimental constants of the initial reaction rate k_a and the activation energy E_a were also determined. In the case of 5M H_2SO_4, the test results showed the instability of the process (no repeatability of the results), which ultimately determined the choice of 2M H_2SO_4 as the main leaching agent in the first stage of leaching. The main research consisted of 2 stages (stage I - application of 2M H_2SO_4 and stage II - application of 2M HNO_3 and oxidants such as: H_2O_2 and O_3 at various concentrations).

In the first phase of the main study, five identical leaching tests with 2M H_2SO_4 were carried out. The process temperature was 353 K, S/L = 1/10, mixing the system at 400 rpm, monitoring and sampling for analysis for 300 minutes. The leaching degree of Fe was 98.2%,

and the remaining metals were leached at the level of: Sn - 100%, Zn - 48.6%, Ni - 19.9%. Leaching of Cu (0.35%) and Pb (0.71%) was practically not observed. Moreover, a statistical analysis of the results for Cu and Fe was carried out, which showed a slight difference between the obtained results of Fe and Cu leaching research in H_2SO_4 solution. Therefore, it can be assumed that these processes are repetitive. Due to the use of the constant temperature in the main studies of the first stage, it was only possible to calculate the reaction rate constant and the dependence of the change in the reaction rate constant with time at one temperature).

In the second stage of the research, the residue of the leached printed circuit board material from the first stage was used. Five samples from the first stage were leached with 2M HNO_3 and with oxidants: 10% H_2O_2, 30% H_2O_2, 50% O_3 and 100% O_3. Ozone was used for the first time in this type of research. The process temperature was 298 K, S/L = 1/10, the mixing of the system was 400 rpm. Monitoring and sampling for analysis was performed for 300 minutes. It was found that when ozone was used, there was a clear intensification of the metal leaching process. Increasing the O_3 concentration to 100% increases the Pb leaching degree, while lowering it to 50% increases the Cu leaching rate. The remaining metals (Fe, Sn, Zn, Ni), both without and with the addition of oxidants, remain at a constant level of leaching (100%). The most optimal leaching variant is therefore the use of 2M H_2SO_4 at 353 K in the first stage, and in the second stage, 2M HNO_3 with the addition of 50% O_3 at ambient temperature, which allowed the recovery of 100% Fe, Cu, Sn, Zn, Ni in 100% and Pb at 88.9%.