EXTRACTION OF METALS FROM ELECTRONIC WASTE BY BACTERIAL LEACHING

Electronic waste is usually processed by means of classical methods, i.e. in pyro- and hydrometallurgical processes. However, new solutions for more economically and ecologically efficient recovery of metals are constantly being searched for. Biohydrometallurgy can become a promising technology of recovering metals from industrial waste. Bioleaching – one of the methods applied in that technology – is the subject of particular interest of many scientific centres. The paper presents the results of laboratory tests of bacterial leaching of metals from electronic scrap. It describes the mechanisms of this process and the factors influencing the chemical reaction. The paper also presents preliminary results of experimental studies on the copper bioleaching from electronic waste with the participation of *Acidithiobacillus ferrooxidans* bacteria.

1. INTRODUCTION

Over the past decades, industrial biotechnology has become one of the fastest growing areas within biotechnology science. Enzymes, microorganisms, animal or plant cells are now widely used in manufacturing and processing chemicals, materials or energy. Microbiological processes are successfully used in mining and biohydrometallurgical recovery of metals from low-percentage ores (e.g. copper bioleaching from chalcopyrites).

Microbiological leaching uses a natural ability of microorganisms to transform metals present in the waste in a solid form (in the solid matrix) to a dissolved form. Apart from the possibility of bioleaching of metals in alkaline environment (involving cyanogenic bacteria), acidophilus microorganisms and conducting biological process of leaching in an acidic environment play a crucial role in the biohydrometallurgical techniques. Among major groups of bacteria, the most commonly used are: acidophi-
lus and chemolithotrophic microbial consortia of: *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, *Leptospirillum ferrooxidans* and heterotrophs, for example *Sulfolobus* sp. In addition, fungi such as *Penicillium* sp. and *Aspergillus niger* are examples of some eucaryotic microorganisms used in bioleaching during metal recovery from industrial wastes [1]. The bioleaching process is cheaper and easier to conduct in comparison to conventional techniques. Its advantage is flexibility – microorganisms easily adapt to changing and extreme living conditions.

Biohydrometallurgical processing of solid waste is similar to natural biogeochemical metal cycles and reduces the demand of resources, such as ores, energy and landfill space. This technology is environmentally friendly (in comparison to chemical method) and it is considered a green technology (generates less amount of waste) [2, 3]. This is why more and more scientists become interested in biohydrometallurgy, technology which can provide an attractive alternative to currently used physical and chemical methods to recover valuable metals from waste.

Researches on the possibility of use of biological methods for the extraction of metals from waste materials are also carried out on the waste electrical and electronic equipment (WEEE). It is estimated that WEEE is now one of the fastest growing waste streams in the world. According to estimates by the United Nations Environment Programme (UNEP), around the world some 50 million tonnes of e-waste is produced annually, of which only 10% is recycled [4]. Processing of waste is most justified not only because of the impact they can have on environment in case of uncontrolled handling [5], but is also connected with profits resulting from the possibility of recovery of valuable components. Undoubtedly, the quantitative composition of electronic waste equipment makes this type of waste material attractive in terms of possibility of metal recovery. Particularly, rich in these ingredients are printed circuit boards (PCBs), which are part of electronic devices, among which copper is the dominant component.

The paper presents results of laboratory work recently carried out on possibility of recovery of metals from e-waste by biohydrometallurgical methods with particular emphasis on copper. The mechanism of the process and factors affecting course and kinetics of bioleaching were described. In addition to the experimental results of bioleaching of base metals (e.g. Al, Zn, Ni), the attention was also paid to the possibility of extracting precious metals from electronic waste. The paper also presents preliminary results of bioleaching of copper from PCBs, obtained from spent cell phones, in the presence of acidophilus bacteria of *Acidithiobacillus ferrooxidans*.

2. BIOLEACHING OF ELECTRONIC WASTE

Studies on extraction of metals from waste materials were conducted with use of various microorganisms depending on the waste type (Table 1), containing basic met-
als, precious metals and hazardous substances. The electronic scrap is an interesting kind of waste, being a mixture of various metals (especially Cu, Al, Fe, Ni) and their alloys, and its components are covered or laminated with plastics and ceramics.

**Table 1**

Table 1 Examples of industrial waste treated with bacterial leaching

<table>
<thead>
<tr>
<th>Waste</th>
<th>Leached metal</th>
<th>Used microorganisms</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium batteries</td>
<td>Li, Co</td>
<td>Acidithiobacillus ferrooxidans</td>
<td>[6]</td>
</tr>
<tr>
<td>Fly ashes</td>
<td>Zn, Al, Cd, Cu, Ni, Cr, Pb, Mn, Fe</td>
<td>Thiobacillus thiooxidans +</td>
<td>Thiobacillus ferrooxidans, Aspergillus niger</td>
</tr>
<tr>
<td>Tannery</td>
<td>Cr</td>
<td>Acidithiobacillus thiooxidans</td>
<td>[8]</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>Cu, Ni, Zn, Cr</td>
<td>Iron oxidizing bacteria</td>
<td>[9]</td>
</tr>
<tr>
<td>Used cracking catalysts, hydro-processing catalysts</td>
<td>Al, Ni, Mo, V, Sb</td>
<td>Aspergillus niger, Acidithiobacillus thiooxidans</td>
<td>[3, 10]</td>
</tr>
<tr>
<td>BOF slag from steelmaking, slag from copper production</td>
<td>Zn, Fe, Cu, Ni</td>
<td>Acidithiobacillus spp., Leptospirillum spp.</td>
<td>[11]</td>
</tr>
<tr>
<td>Jewellery waste, automobile catalytic converter, electronic scrap</td>
<td>Ag, Au, Pt</td>
<td>Chromobacterium violaceum, Pseudomonas fluorescens, Pseudomonas plecoglossicida</td>
<td>[12]</td>
</tr>
<tr>
<td>Electronic scrap</td>
<td>Cu, Ni, Al, Zn</td>
<td>Acidithiobacillus ferrooxidans + Acidithiobacillus thiooxidans</td>
<td>[13]</td>
</tr>
</tbody>
</table>

**Table 2**

The level of various metals leached by means of bioleaching from electronic scrap

<table>
<thead>
<tr>
<th>Species of microorganisms</th>
<th>Level of leached metal</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. ferrooxidans + A. thiooxidans</td>
<td>Cu, Ni, Al, Zn &gt;90%</td>
<td>[13]</td>
</tr>
<tr>
<td>A. ferrooxidans</td>
<td>Cu 99%</td>
<td>[16]</td>
</tr>
<tr>
<td>A. ferrooxidans</td>
<td>Cu 99%</td>
<td>[17]</td>
</tr>
<tr>
<td>A. thiooxidans</td>
<td>Cu 74.9%</td>
<td></td>
</tr>
<tr>
<td>A. ferrooxidans + A. thiooxidans</td>
<td>Cu 99.9%</td>
<td></td>
</tr>
<tr>
<td>Sulfohiobacillus thermosulfidooxidans</td>
<td>Ni 81%, Cu 89%, Al 79% Zn 83%</td>
<td>[18]</td>
</tr>
<tr>
<td>Chromobacterium violaceum,</td>
<td>Au 68.5%</td>
<td>[12]</td>
</tr>
<tr>
<td>Aspergillus niger,</td>
<td>Cu, Sn 65%</td>
<td></td>
</tr>
<tr>
<td>Penicillium simplicissimum</td>
<td>Al, Ni, Pb, Zn &gt;95%</td>
<td>[13]</td>
</tr>
<tr>
<td>Thermosulfidooxidans sulfohiobacillus + Thermoplasma acidophilum</td>
<td>Cu 86%, Zn 80%, Al 64%, Ni74%</td>
<td>[19]</td>
</tr>
</tbody>
</table>

Printed electronic circuit boards are the main carrier of valuable metals in the waste. For example, metal content in the elements of mobile phones is about 28%, including 10–20% of copper, 1–5% of lead, 1–3% of nickel, content of precious metals (Ag, Pt, Au) about 0.3–0.4%, and the rest: glass and ceramics [14]. Apart from
traditional methods of electronic scrap processing (pyro- and hydrometallurgical methods), also microorganisms have recently been applied to recover metals from electronic waste. Experimental work was conducted with bacterial leaching for the extraction of copper, zinc, lead, nickel, tin, aluminum from electronic waste. Bioleaching of precious metals (Ag, Au) with ground electrowastes was also carried out in the presence of cyanogenic bacteria (e.g. *Chromobacterium violaceum*, *Pseudomonas fluorescens* [12,15]). These bacteria have an ability to produce of hydrocyanic acid (HCN) which can dissolve gold. A detailed information about microorganisms and level of various metals leached from electronic scrap is given in Table 2.

### 2.1. MECHANISM OF THE PROCESS AND THE FACTORS AFFECTING THE REACTION RATE

Previous studies [13, 15, 16, 18, 19] indicate that the process of metals bioleaching from electronic waste is a complex process, determined by many factors, including: the type of microorganisms, pH, concentration of Fe$^{2+}$ in the system, qualitative and quantitative composition of waste, toxicity of ingredients and fineness of the material. Temperature and time also play a significant role in the reaction.

We can assume [20] that the mechanism of metals bioleaching from electronic scrap involving bacteria, is the same, as in the case of metal sulfides leaching. In case of Cu: Fe$_2$(SO$_4$)$_3$ created by *Acidithiobacillus ferrooxidans* oxidizes elemental copper contained in the waste to the copper in form of ion, according to reactions:

\[
\text{Cu} + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Cu}^{2+} + 2\text{Fe}^{2+} + 3\text{SO}_4^{2-} \quad (1)
\]

\[
2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + 0.5\text{O}_2 + \text{bacteria} \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \quad (2)
\]

Material heterogeneity of waste, in particular the presence of alkaline particulate components of the solid phase might hinder the bioleaching process and slow down its dynamics [13, 16]. This phenomenon was observed by Brandl and Bosshard [13], who conducted the process of metals microbiological leaching from electronic waste using a mixture of bacterial cultures of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*. Although bacteria of the *Acidithiobacillus* genus are characterized by highly developed adaptability to extreme environmental conditions (e.g. high concentrations of metals [13]), the toxic influence of waste on microorganisms can be observed. It is believed that high Al concentrations (and the alkaline character of the non-metallic components) in the environment inhibits the growth of bacteria. Gradual adaptation of bacteria to the environment and the addition of acidifying agent can improve efficiency of the process. In such conditions nickel, aluminum, zinc and copper were dissolved in solution with effectiveness close to 90%.

The concentration of Fe$^{3+}$ ions, pH and the number of used microorganisms play a crucial role in the leaching process of metals from solid state to solution [16]. Introducing the higher dose of *A. ferrooxidans*, iron ions Fe$^{2+}$ to the system and ensuring pH in the
Extraction of metals from electronic waste by bacterial leaching

range of 1.5 to 2.0 (adjusted H₂SO₄) improved the efficiency of copper extraction from the waste. Bioleaching process may be accompanied by chemical precipitation of metals [13, 18, 20] in the form of sludge, which was observed for Pb and Sn (precipitation probably in the form of PbSO₄ and SnO). Therefore the process should be carried out under controlled conditions, with appropriate selection of input iron ions and complexing agent addition, ensuring optimum conditions for pH suitable for the bacterial growth.

Temperature is an important parameter that guarantees the activity of microorganisms. The optimum temperature of genus *Acidithiobacillus* is 28–35 °C [21]. For the electronic waste, bioleaching experiments were carried out at 30 °C [13, 16]. The effectiveness of process at 22–25°C was also examined [22, 23].

The factor influencing the dynamics of metal dissolution is the particle size of the bioleaching material and the ratio of solid phase to liquid phase. Therefore it is important to prepare electronic waste properly and to identify its material composition. The experimental results indicate [16] that the degree of copper, lead and zinc leaching from the solid phase increases with the decreasing sieve fraction of crushed samples of the waste. Keeping the density of the solid phase at the constant level of 7.8 g/dm³, copper is dissolved in 99.0%, 74.9%, 99.9% for the fraction of 0.5–1.0 mm with *A. ferrooxidans*, *A. thiooxidans* and the mixture of these bacteria, respectively.

In experiments related to the study of biological leaching of metals from electronic waste [13, 15–20], these studies were performed periodically. Experiments of bioleaching metals from electronic scrap by a dynamic, continuous column method were carried out by Ilyas et al. [18]. A consortium of selected strains of acidophilus thermophiles: *Thermosulfidooxidans sulfobacillus* and heterotrophic acidophilus – *Thermoplasma acidophilum* was used. Tolerance of these bacteria cultures on a mixture of metal ions (Ag⁺, Al³⁺, Cu²⁺, Fe³⁺, Ni²⁺, Pb²⁺, Zn²⁺ and Sn²⁺) has been effectively improved by their adaptation to the environment after nearly two years, from 12 g/dm³ to 20 g/dm³. Due to the alkaline nature of the waste, the bioleaching process was preceded by an initial leaching, to stabilize pH to the value of 2. During the bioleaching process for 280 days, ca. 80% Zn, 64% Al, 86% Cu and 74% Ni were leached.

### 2.2. BIOLEACHING OF PRECIOUS METALS

Apart from the basic and associated metals (e.g. Cu, Fe, Ni, Al, Sn, Zn, Pb) contained in electronic waste materials, precious metals (Ag, Au, Pt) should be taken to consideration. Presence of these metals has decisive influence on the value of electronic scrap and cost of its processing. Some of the earliest works on the possibility of extracting gold from printed electronic circuits by bioleaching were done by Faramarzi et al. [15]. In the experiments, cut pieces of printed circuit boards (5 mm × 10 mm) were used. In the presence of *Chromobacterium violaceum* gold was microbiologically dissolved to the form of dicyanoaurate [Au(CN)₂⁻]. The maximum concentration of dicyanoaurate corresponds to dissolution of initially added gold at the level of 14.9%.
Apart from using \textit{C. violaceum} bacteria, the ability of Au bioleaching from electronic scrap shredded by the microorganism \textit{Pseudomonas fluorescens} was also evaluated \cite{12}. \textit{C. violaceum} proved to be more efficient in the mobilization of gold, and allowed one to achieve higher concentration of dicyanoaurate. Maximum dicyanoaurate concentration corresponded to 68.5\% dissolution of the total gold added. In the case of \textit{P. fluorescens}, [Au(CN)\(_2\)] does not remain stable in the solution. It may be due to the sorption processes occurring in biomass or biodegradation because the metal cyanides can be used as a source of carbon or nitrogen. The presence of copper cyanide complexes was also observed. In addition to dicyanoaurate, cyanide-complexed copper was detected during the treatment of electronic scrap. It was probably possible due to the high copper content of the scrap and its rapid reaction with cyanide. Pham et al. \cite{24} proposed the use as a first stage of gold recovery, electrowaste bioleaching by \textit{A. ferrooxidans} bacteria. It allowed one to remove more than 80\% copper from the waste and significantly improved Au recovery, especially with the participation of \textit{C. violaceum}.

3. EXPERIMENTAL

The experimental studies including initial testing of biological leaching of electronic waste involving bacteria of the genus \textit{Acidithiobacillus} were carried out. Various doses of bacteria cultures in leaching solutions were used in the experiments.

\textit{Waste material}. Electronic waste in the form of printed circuit boards (PCB) from cell phones were tested. The waste was grounded in the cutting mill to a particle size fraction <0.5 mm. The metal content in the sample was determined by the atomic adsorption spectrometry (AAS). Its composition is shown in Table 3.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Cu</th>
<th>Fe</th>
<th>Zn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content, %</td>
<td>35.9074</td>
<td>0.6293</td>
<td>0.2074</td>
<td>0.6763</td>
</tr>
</tbody>
</table>

\textit{Applied microorganisms}. Bacteria of the \textit{Acidithiobacillus ferrooxidans} species, the strain isolated from ferruginous mineral waters was used in the study \cite{25}. In order to increase the activity of the cells before the inoculation of waste samples, cultures were transferred several times with fresh Silverman/Lundgren medium (9K), containing ions of Fe(II) (9 g/dm\(^3\)) with an initial pH of 2.5. To provide favourable conditions for microorganisms, pH of samples was corrected using H\(_2\)SO\(_4\).

\textit{Bioleaching}. Bioleaching experiments were carried out in Erlenmeyer flasks of 300 cm\(^3\) capacity, by using a rotary shaker (130 rpm) at 20–22 °C. 9K medium was used in all biological experiments as a leaching solution. Samples used had the volume
of 100 cm³. *A. ferrooxidans* bacteria were inoculated into 9K medium at volume doses of 10%, 20%, 50% and 100% (v/v). Mass of waste was constant equal to 1 g. The changes of copper concentration in solution, the oxidation-reduction potential (ORP) and pH were analyzed. Experiments were carried out for 21 days, in two measurements series. The control tests under sterile conditions using solutions of 9K were carried out without adjusting their acidity and with adjustment of pH to 2.5.

4. RESULTS AND DISCUSSION

4.1. EFFECT OF ADDING BACTERIA IN LEACHING SOLUTIONS ON pH AND OXIDATION-REDUCTION POTENTIAL (ORP)

The changes of pH observed during biolcheating are presented in Fig. 1. All biological samples show a gradual trend to decrease this parameter (the effect of sulfuric acid).
In the presence of bacteria, the initial pH value 2.7–3.0 decreases to 2.2, after 21 days of the process. Electronic waste has alkaline nature what has been observed by Brandl et al. [13]. The increase of pH is observed for control tests (Fig. 1a) and for all biological samples in the initial phase of the process (Fig. 1b). Samples inoculated with a lower dose of bacteria (10% and 20%) reaching pH about 3.0 after 24 h of bioleaching showed the highest pH. Increasing pH values of these samples were adjusted several times to the value of 2.5, providing optimum conditions for bacterial growth. The optimum pH of *Acidithiobacillus ferrooxidans* bacteria is 1.8–2.5 [26]. Exceeding the upper limit of pH can significantly reduce the activity of these microorganisms, and thus slow down the kinetics of bioleaching. In sterile solutions (9K), for both samples with and without pH adjustment a continuous increase in pH has been observed (Fig. 1a). In samples without adjustment of the acidity within 21 days of bioleaching pH systematically increased from initial 2.3 to 3.0 in the final stage of the process. Systems with controlled pH required constant readjustments to pH 2.5.

Figure 2 summarizes the changes in ORP (oxidation-reduction potential). On the 3rd day of bioleaching, pH of the samples containing 50% and 100% inoculum was 2.4 and during next days steadily decreased. Decrease in pH (on the 3rd day) was accompanied by visible increase in ORP (Fig. 2) which proved the growth in activity of microorganisms. This indicates that leaching takes place in a biological way and there is a bacterial oxidation and regeneration of Fe$^{2+}$ to Fe$^{3+}$ [9, 27]. Slightly different situa-
tion is visible for samples inoculated with 10% and 20% of bacteria. In this case, in the initial phase of the process (respectively to 6th and 4th day) it seems to be the dominant chemical process (ORP growth is slower). The second phase of bioleaching with a visible increase in ORP (and high value of this parameter 602–610 mV during next days) suggests intensification of the biological process. Increased concentration of microorganisms results in higher initial value of ORP parameter, contributing to the intensification of copper bioleaching reaction (Fig. 3).

4.2. INFLUENCE OF BACTERIA DOSE ON THE EFFICIENCY OF COPPER LEACHING

The effect of dose of microorganisms on the degree of Cu leaching is shown in Fig. 3. Higher dose of bacteria cultures accelerates the copper extraction process, which results in higher concentration of Fe^{3+} ions present in solution oxidizing elemental copper to copper ion according to the reaction (2) [16, 20].

![Fig. 3. Time dependences of the efficiencies of copper leaching from electronic waste with various doses of \textit{A. ferrooxidans} and in the control tests](image)

Within three days, over 60% (66.4% and 61.8%) of copper from samples inoculated with 50% and 100% of bacteria have been leached. Whereas in the tests with low concentrations of bacteria (about 10% and 20%), 19.7 % and 25.4% Cu have been leached, respectively. Full transfer of Cu from solutions (99.3%) was observed after 17 days of the process (after 21 days – 99.8%) in the presence of 100% of the bacteria. For samples inoculated with a lower dose of \textit{A. ferrooxidans} (20%, 50%), copper was leached in more than 99% after 21 days. The sample containing 10% of bacteria
showed the lowest efficiency – 73.7% Cu. Comparable efficiency of Cu bioleaching (98–99%) was achieved for samples 20%, 50% and 100%. This suggests the possibility of an effective process in the presence of a lower initial dose of microorganisms. The exception was the sample inoculated with 10% dose of bacteria. Despite the high value of ORP, the degree of copper leaching, compared to other samples, was slightly lower. This can result from the delayed growth of bacteria in environment and insufficient concentration of Fe(III) compounds in solution, which had influence on slow Cu dissolution. However, taken into consideration the material complexity of leached electronic waste, the explanation of this trend is difficult and requires further study.

Comparative results of control leaching conducted under sterile conditions without correction and with adjustment of pH to 2.5 showed that the extraction of Cu (with respect to the bacterial samples) was much slower – within 21 days 23.8% and 27.0% of Cu were transferred into solution, respectively.

5. CONCLUSIONS

Apart from traditional methods of electronic waste processing (pyro- and hydrometallurgical methods), new solutions for efficient recovery of metals are being searched for. Biohydrometallurgical processes with the use of microorganisms have been recently the subject of particular interest and may become long-term and developmental methods for metal recovery.

Based on preliminary examination on biological leaching of electronic waste involving bacteria of the genus Acidithiobacillus, it was found that variable initial doses of microorganisms (in the range of 10–100% v/v) used in experiments do not significantly affect the final efficiency of copper transition into solution. Higher quantity of bacteria enhances the process of copper dissolution only in its initial stage. Within 21 days, comparable high efficiencies of Cu dissolution (98–99%) both at higher (100%) as well as at lower (20%) doses of bacteria were achieved. For the sample with the lowest quantity of bacteria (10%), a slower transition of Cu was observed. The biological leaching of electronic material and extraction of copper from waste was higher than in control tests. There was no significant difference in the effectiveness of chemical leaching carried out in conditions without correction and pH adjustment to 2.5. Further studies are needed to optimize the bioleaching from electronic waste not only copper but also other useful metals.

ACKNOWLEDGEMENTS

Financial support from the Ministry of Science and Higher Education is acknowledged: Project N N508 6225 40 and BK-377(RM1) 2011.
REFERENCES


