PRELIMINARY STUDIES ON SIMULTANEOUS RECOVERY OF PRECIOUS METALS FROM DIFFERENT WASTE MATERIALS BY PYROMETALLURGICAL METHOD

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Automotive catalytic converters have a limited life time, after which the catalyst must be replaced or regenerated. The spent catalytic converters contain small amount of precious metals. Recovery of these metals is essential for environmental and economic reasons. The waste electronic equipment is also an attractive source for recovery of precious metals. The waste electronic equipment is also an attractive source for recovery of precious metals. Precious metals in electronic scraps are concentrated mainly in printed circuits and integrated circuits – so generally in elements that are the most diverse in their composition. Material heterogeneity of these elements is the reason why there is no universal method for processing this type of scrap. Methods used in the world for recovery of precious metals from spent automotive catalysts and electronic wastes by pyrometallurgical and hydrometallurgical methods were mentioned in this paper. The results of simultaneous melting of electronic waste with spent automotive catalysts were presented. The printed circuit boards were used as the carrier and as a source of copper. The precious metals present in the catalyst were collected in copper.

Keywords: electronic waste, copper, platinum, metal collector, pyrometallurgical methods

1. Introduction

Today almost half of the produced platinum, the majority of palladium and 80% of rhodium is used for the production of auto catalytic converters. Catalytic converters have a limited life time (about 80 000 km), after which the catalyst must be replaced or regenerated. Large quantities of used catalytic converters give possibility to recover the considerable amount of platinum. Possibility of reusing the material, that is platinum group metals recovery from used auto catalytic converters, becomes very important, taking into consideration the economical management of natural resources and energy.

Catalytic converter is built from stainless steel shell with a ceramic or metallic carrier inside it. Ceramic carrier is made from alumina with a small addition of cerium oxide. The ceramic carrier is then covered by a thin layer of precious metals such as: platinum, palladium and rhodium (PGMs – Platinum Group Metals). These metals play a catalytic role [1]. To recover precious metals from spent catalysts many hydro- and pyrometallurgical methods are used [2]. None of these methods however, is perfect and can be used to recover metals from all types of spent catalysts. In the hydrometallurgical methods PGMs contained in the used auto catalytic converters are dissolved in an aqueous solution of chlorate, perchloric acid, Cl₂, H₂O₂, bromate, nitrate, aqua regia or cyanide solution [3-5]. The obtained solutions contain PGMs, but their concentration is low. So the next stage is to concentrate the solutions and extract metals from these solutions [6]. The hydrometallurgical methods also require to solve the problem of harmful waste solutions generated during the process.

In pyrometallurgical methods grinded carriers covered by the PGMs are melted with the addition of other metal
which has a special function – a metal collector. The main advantages of applying metal collector is to decrease the temperature of the process, and in the same time to reduce the cost of the PGMs recovery. Melting of typical ceramic carrier (silicon-aluminium-magnesium oxide) requires high temperature and addition of fluxes. The operating temperature of common processes is between 1500°C and 1900°C [5,7]. Obtained alloy is rich in PGMs, so the next stage is the PGMs purification. Different metals such as calcium, zinc, magnesium, cadmium, lead, nickel and copper can be used as a metal collector. These metals are selected taking into account the solubility of platinum [1,6,7]. Unfortunately there are some disadvantages: pyrometallurgical methods require special equipment which allows to reach the desired temperature; it is not only expensive but also highly energy consuming as well. The methods used in the world for the recovery of PGMs from spent auto catalytic converters are shown in Fig. 1.

![Fig. 1. Applied methods of PGMs recovery from spent auto catalysts](image)

2. Experimental method

Research was conducted on the waste material in the form of:
- carriers of spent auto catalysts (AC) coming from different cars and
- printed circuit boards (PCBs) obtained from used mobile phones.

The scraps of PCBs and auto catalyst were ground to powder by using cutting mill. Then they were melted in electric inductive furnace (type St 5/40) for one hour in 1700°C. The samples in the amount of 100 g (ratio of 4:1 PCBs:AC) were melted with addition of fluxes. The main aim of this stage was to collect platinum in copper derived from PCBs. The analysis of metals content in the samples were carried out by means of the atomic adsorption spectrophotometer (SOLAAR M6-UNICAM Atomic Absorption). The platinum average content in ceramic carriers was between 0.11% and 0.13% whereas PCBs contained Cu 30.22%, Fe 1.91%, Au 0.12%, Zn 0.24%, Sn 0.94%.

The surface of the samples (before and after melting process) was analysed by using a scanning electron microscope (SEM), equipped with a Hitachi S 4200. Microanalysis of the chemical composition was performed by EDS method (Energy Dispersive Spectrum) [19]. Observation of the surface and the X-ray microanalysis were carried out at an accelerating voltage of 15kV. Results of AC and PCBs microanalysis and their chemical composition were shown respectively in Fig. 2 and Fig. 3.
3. Results

As a result of melting, the alloy of Cu-Fe-Au-Pt and slag were obtained. Table 1 shows the chemical composition of such alloy. Definitely the dominant metal is copper with the addition of platinum and gold. The alloy contains about 5% of iron and about 2% of tin. The results of microscope observations and chemical composition analysis by SEM are shown in Figure 4 and 5 and summarized in Table 2. Microscope studies indicate the complex structure of the alloy. Copper and platinum are present in the microregions in significant different mass ratio. These metals were accompanied by metals derived particularly from the PCBs (Ni, Sn). Carbon and silicon (components of spent catalysts as well as partially of PCBs) were also present in the surface of alloy. The average recovery level of metals is following: Pt 78.3%, Cu 81.2%, Au 83.7% Fe 60.6%. During melting process average – 37% loss of weight was observed, mostly related to the incineration of organic and plastics components in PCBs. Formed slag, next to typical oxide constituents, contained also copper (from 0.31% to 0.66%). In case of properly conducted process, there should not be any copper and precious metals in the slag. For greater efficiency and purity of the alloy, it is necessary to correct the process conditions. Proposed procedure that improves its purity may be refining, adapted to local conditions [20,21].

### Table 1
Chemical composition of received Cu-Fe-Au-Pt alloy

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alloy mass, g</th>
<th>Concentration, %</th>
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<tr>
<td></td>
<td>Cu</td>
<td>Pt</td>
</tr>
<tr>
<td>1</td>
<td>14.74</td>
<td>75.461</td>
</tr>
<tr>
<td>2</td>
<td>12.98</td>
<td>69.198</td>
</tr>
<tr>
<td>3</td>
<td>12.34</td>
<td>70.766</td>
</tr>
</tbody>
</table>

### Table 2
Chemical composition of Cu-Fe-Au-Pt alloy in places marked in Fig. 4

<table>
<thead>
<tr>
<th>Analysis, No.</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>Ca</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Sn</th>
<th>Pt</th>
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<tr>
<td>pt1</td>
<td>3.62</td>
<td>-</td>
<td>2.43</td>
<td>-</td>
<td>-</td>
<td>0.97</td>
<td>2.64</td>
<td>76.51</td>
<td>6.63</td>
<td>0.01</td>
</tr>
<tr>
<td>pt2</td>
<td>1.52</td>
<td>-</td>
<td>1.47</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>80.37</td>
<td>16.27</td>
<td>0.37</td>
</tr>
<tr>
<td>pt3</td>
<td>22.80</td>
<td>-</td>
<td>3.42</td>
<td>0.34</td>
<td>0.34</td>
<td>0.97</td>
<td>2.64</td>
<td>52.91</td>
<td>4.27</td>
<td>0.31</td>
</tr>
<tr>
<td>pt4</td>
<td>6.39</td>
<td>0.31</td>
<td>0.59</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>89.30</td>
<td>6.63</td>
<td>0.13</td>
</tr>
</tbody>
</table>

4. Conclusion

Spent automotive catalysts and printed circuit boards are a rich source of PGMs. Due to high value of PGMs, the recycling of the spent catalysts or e-waste at the end of their life...
is crucial for economic or environmental reasons. Such an approach gives considerable benefits such as limiting the number of waste disposal, saving natural resources, limiting the electricity consumption and diminishing pollutant emission. As a result of simultaneous melting of spent catalysts with PCBs, Cu-Fe-Pt-Au alloy was obtained. As a metal-collector, copper derived from PCBs was used and additionally Fe played the role of a collector. During the melting process about 78% of platinum went to copper. Organic and plastics components of PCBs were incinerated during melting process and ceramic carrier created the slag. The efficiency of recovering platinum is promising. However, it is necessary to improve process conditions.

REFERENCES