INTRODUCTION

Catalytic converters are widely applied in industry. They are so popular because they give possibility to accelerate and increase the yield of processes, for example the combustion process. The auto catalytic converters consist of the stainless steel shell and metallic or ceramic carrier with a honeycomb structure and the catalytic system. The honeycomb structure means that there is a dense net of squares holes through which the combustion gas flows. Platinum group metals (Pt, Pd, Rh) are responsible for the catalytic function. Combustion gases due to the contact with the platinum group metals undergo much faster oxidation in case of hydrocarbons and carbon monoxides and reduction in case nitrogen oxides. Products such as: carbon dioxide, water and nitrogen obtained after catalyzed combustion process are not harmful to the natural environment.

Today almost half of produced platinum, the majority of palladium and 80 % of rhodium is used for the production of auto catalytic converters. The used auto catalytic converters give possibility to recover the considerable amount of platinum. Taking into account the price of platinum and the harmful influence of the metal-

The increase of Platinum Group Metals demand in automotive industry is connected with growing amount of cars equipped with the catalytic converters. The paper presents the review of available technologies during recycling process. The possibility of removing platinum from the used catalytic converters applying pyrometallurgical and hydrometallurgical methods were also investigated. Metals such as Cu, Pb, Ca, Mg, Cd were used in the pyrometallurgical research (catalytic converter was melted with Cu, Pb and Ca or Mg and Cd vapours were blown through the whole carrier). In hydrometallurgical research catalytic converters was dissolved in aqua regia. Analysis of Pt contents in the carrier before and after the process was performed by means of atomic absorption spectroscopy. Obtained result were discussed.

Key words: auto catalytic converter, recycling process, platinum removal

CATALYTIC CONVERTERS AS A SOURCE OF PLATINUM

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The technology of the recycling process is rather complex and consist of many technological stages such as:

- preparation and homogenisation of carrier, Figure 1 presents picture of the catalytic converter that is installed in car, Figure 2 present picture of the catalytic converter carrier with the honeycomb structure,
- upgrading of PGM content by the pyro- or hydrometallurgical methods,
- PGM concentrate refining which consists of the following operations: dissolving and removal of
non PGM elements, separation of PGM from one another, PGM purification giving the high grade sponge or powder.

PGM purification let to obtain very high purity metal, but the process is still very expensive.

In hydrometallurgical methods in the first stage the chloro- complexes of PGM (for example PtCl$_6^{2-}$, PdCl$_4^{2-}$, RhCl$_6^{3-}$) are obtained. This is because the catalytic converters are dissolved in the liquid solutions of chlorides, chlorans, hydrogen peroxide and the aqua regia. Such solutions have rather low level of Pt concentration, so must be concentrated and then the extraction of platinum is done. The advantage of this method is the low need of energy. The average efficiency of platinum recovery is about 90 %.

In pyrometallurgical method the most important stage is melting the grinded catalytic carrier with some metal, for example copper. Platinum goes to alloy, ceramic carrier is removed and scraped. Obtained alloy which is rich in platinum is later refined [4]. The average efficiency of recovery equals 90-95 % [4,5].

Table 1 and Table 2 show the available processes used for platinum and other precious metals recovery from the used auto catalytic converters taking into account the hydrometallurgical and pyrometallurgical method respectively.

Table 1 Available hydrometallurgical processes used in PGM recovery from the used auto catalytic converters [1,4]

<table>
<thead>
<tr>
<th>Process</th>
<th>Specification</th>
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<tbody>
<tr>
<td>segregation</td>
<td>During the grinding process the small addition of KCl and NaCl is used, heating is applied to concentrate the solution; as a consequence a part of solution is evaporated; during the platinum extraction the oxygen blow is used.</td>
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<tr>
<td>aqua regia</td>
<td>Catalytic converter is dissolved in aqua regia (mixture of HNO$_3$ and HCl in the ratio 3:1). As a result H$_2$PtCl$_6$ is obtained, then this solution is precipitated, by the Al/Zn powder. The last stage is platinum refining process.</td>
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<tr>
<td>chlorination</td>
<td>Used auto catalytic converters are chlorinated in the high temperature. The temperature must be higher than 1 200 °C to evaporate the metallic fraction.</td>
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Table 2 Available pyrometallurgical processes used in PGM recovery from the used auto catalytic converters [4,7]

<table>
<thead>
<tr>
<th>Process</th>
<th>Specification</th>
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<tr>
<td>Rose method</td>
<td>Grinded (milled) catalytic converter is melted in the electric furnace with the copper oxide, coke, calcium, iron oxide and silica. After melting copper with platinum and slag are obtained. Slag consists of ceramic carrier, calcium, silica and iron oxide. The alloy is proceeded in oxidizing furnace where copper is oxidized and platinum (does not react with oxygen) is separated. Obtained product contains 75 % of metal and go to refinng section.</td>
</tr>
<tr>
<td>Melting method</td>
<td>The catalytic converters are melted with iron in temperature higher than 2 000 °C. Slag from the metallic phase is separated due to the difference between its density. Obtained metallic phase is leached in the H$_2$SO$_4$. As a result iron is removed from the platinum solution. In the lower temperature other metal can be also used for collecting platinum. The obtained slag is less aggressive and the condition are less reactive.</td>
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RESULTS OF RESEARCH

Research of platinum recovery from used auto catalytic converters by means of hydro- and pyrometallurgical method were carried out. First, the catalytic converters were grinded and milled.

In pyrometallurgical tests catalytic converter was melted with chosen metals such as Pb, Cu, Ca - the reactor used in this test is presented in Figure 3. There were also tests in which metal vapours (Mg, Cd) were blown
through the whole carrier. Figure 4 presents the reactor used in this test.

Used metals were chosen taking into accounts the system of platinum solubility in these metals or melting temperature of these metals. Analysis of PGM contents in the carrier before and after melting/blowing process was performed by means of atomic absorption spectroscoopy.

Table 3 presents parameters of pyrometallurgical treatment of catalytic converter and the results obtained from the these tests.

In hydrometallurgical tests, grinded catalytic converter was dissolved in aqua regia or in mixture of aqua regia with fluoric acid. Some of the test probes were heated. Than these probes were filtrated to separate the solution from the insoluble remains of the carrier. Analysis of PGM contents in the carrier before and after dissolving process was performed by means of atomic absorption spectroscoopy.

Table 4 shows parameters of this research and their results.
SUMMARY

1. In the research three metals were used as a material which can dissolve platinum and decrease its melting temperature: lead, copper and cadmium. Test with lead did not give satisfactory results because almost all lead oxidized in the furnace atmosphere, so the kinetic conditions were not good enough to use lead in this kind of tests (Pb very easily oxidized during the melting process and we obtained alloy Pt+PbO instead of Pt+Pb). The second metal, cooper gave better results. The calculated yields were very promising. However, there can be a problem with removing platinum from cooper, so the other tests are planned.

Calcium as a collector metal is better than lead. However, the best results are obtained in the temperature of 1 200 °C. In this case the process have to be lead very carefully, especially in argon atmosphere because of high reactivity of calcium.

2. The tests with magnesium and cadmium as a metal which can dissolve platinum and decrease its melting temperature are being done. The initial results are promising. The loss of platinum content in the carrier after the cadmium vapour treatment (Table 3) can be observed. However no success has been reached in improving the concentration of Mg/Cd vapours with platinum.

3. Hydrometallurgical method of platinum recovery from the used auto catalytic converters gives 85% of metal recovery. Heating test probe slightly increases the concentration of platinum in the solution. The addition of fluoric acid to aqua regia does not influence the increase of platinum recovery.

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REFERENCES


Note: Responsible for English language is M. Kingsford, Katowice, Poland.