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CATALYTIC CONVERTERS AS A SOURCE OF PLATINUM

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Preliminary Note – Prethodno priopćenje

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 hyrdometallurgical 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

Katalitički konverteri kao izvor platine. Porast zahtjeva za materijalima iz grupe platina u automobilskoj industriji je povezan s povećanim brojem automobila opremeljenim katalitičkim konverterima. Rad prezentira pregled dostupnih tehnologija tijekom procesa recikliranja. Također je istražena mogućnost izdvajanja platine iz korištenih katalitičkih konvertera primjenom pirometalurških i hidrometalurških metoda. Metali kao Cu, Pb, Ca, Mg, Cd su korišteni pri pirometalurgijskom istraživanju (katalitički konverter je rastaljen s Cu, Pb i Ca ili s Mg i Cd parama koje se ispuhavaju kroz cijeli nosač). Kod hidrometalurgijskog istraživanja katalitički konverter je otopljen u carskoj vodici. Analiza sadržaja Pt u nosaču prije i nakon procesa je izvedena pomoću spektroskopije atomskom apsorpcijom. Dobiveni rezultati su obrazloženi.

Ključne riječi: auto katalitički konverter, postupak recikliranja, izdvajanje platine

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 dioxides, 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 metallurgical process of obtaining platinum on the natural environment platinum recovery in the recycling way is very advantageous. Recycling gives such benefits as limiting the number of waste disposal, saving of natural resource, limiting the electricity consumption and diminishing pollutant emission. To get 1 kg of platinum for example it is necessary to output 150 Mg of ores from 1 000 meters depth. During this process 400 Mg of waste is obtained. The same amount of platinum can be obtained from the recycling process of 2 Mg of used auto catalytic converters [1-3].

RECYCLING OF THE USED AUTO CATALYTIC CONVERTERS

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

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Figure 1 View of the used auto catalytic converter

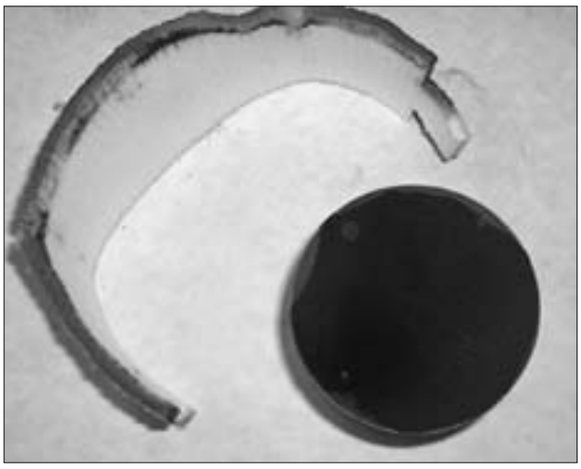

Figure 2 View of the carrier with honeycomb structure covered with the fibrous material

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]**

Hydrometallurgical processes used in PGM recovery from the used auto catalytic converters	
Process	Specification
segregation	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.
aqua regia	Catalytic converter is dissolved in aqua regia (mixture of HNO_3 and HCl in the ratio 3:1). As a result H_2PtCl_6 is obtained, then this solution is precipated, by the Al/Zn powder. The last stage is platinum refining process.
chlorination	Used auto catalytic converters are chlorinated in the high temperature. The temperature must be higer than 1 200 °C to evaporate the metallic fraction.

Table 2 **Available pyrometallurgical processes used in PGM recovery from the used auto catalytic converters [4,7]**

Pyrometallurgical processes used in PGM recovery from the used auto catalytic converters	
Process	Specification
Rose method	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 oxidaizing furnace where copper is oxidized and platinum (does not react with oxygen) is separated. Obtained product contains 75 % of metal and go to refinning section.
Melting method	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_2SO_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.

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

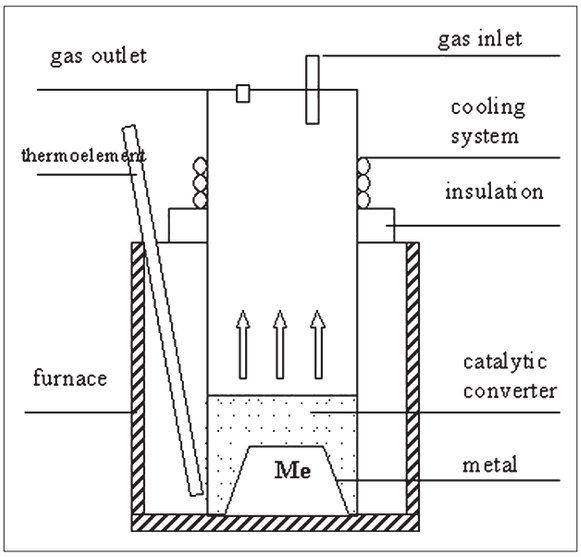

Figure 3 Scheme of reactor used during melting the catalytic converters with Cu, Pb or Ca

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 spectroscopy.

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 spectroscopy.

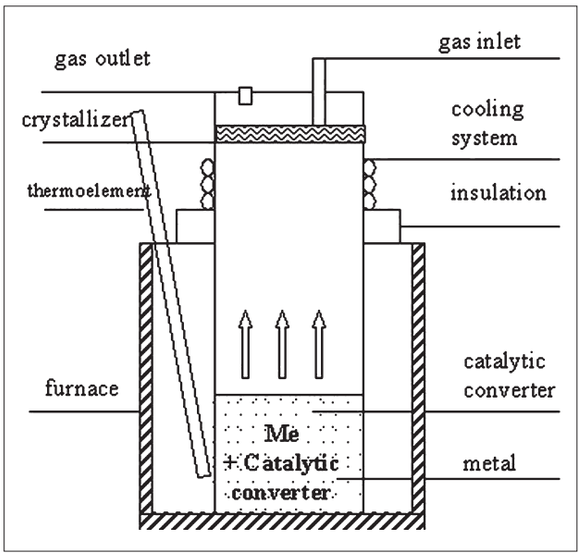

Figure 4 Scheme of reactor used during Cd and Mg vapours treatment of catalytic converters.

Table 3 **Pyrometallurgical treatment of catalytic converter – processing parameters and results**

Metal	T/°C *	Contents of Pt		R/% **
		after %	before %	
Test with metal as a collector				
Platinum is collected in obtained Cu alloy after melting the grinded catalytic converter with the molten pure Cu.				
Cu	1 550	0,196	0,036	85.2
	1 700	0,196	0,050	62,8
	1 550	0,281	0,08	95,2
	1 700	0,281	0,06	70,1
Platinum is collected in obtained Pb alloy after melting the grinded catalytic converter with the molten pure Pb.				
Pb	1 150	0,129	0,031	88
	1 200	0,26	0,05	93
Platinum is collected in obtained Ca alloy after melting the grinded catalytic converter with the molten pure Ca.				
Ca	1 000	0,28	0,11	69
	1 200	0,11	0,061	82
Test with metal vapour				
The tests was carried out with Mg and Cd as a metal which can dissolve Pt and decrease its melting temperature. The loss of Pt content in the carrier after the Cd vapour treatment was observed but there was no success in the concentration of Mg/Cd vapours with Pt.				
Mg	1 150	0,160	0,074	11,1
	1 200	0,220	0,121	12,5
Cd	1 150	0,220	0,097	17,0
	1 200	0,192	0,084	16,8

* - temperature, ** - recovery of platinum

Table 4 shows parameters of this research and their results.

Table 4 **Hydrometallurgical treatment of catalytic converter – processing parameters and results**

Solution	t/s *	Contents of platinum		R /% **
		after %	before %	
Test with aqua regia. Platinum is disolved in mixture of acid HCl and HNO_3 in the ratio 3:1.				
HCl: HNO_3	0	0,230	0,154	86,6
	1 200	0,230	0,163	90,1
	1 500	0,230	0,191	93,3
	1 800	0,230	0,207	94,2
Test with solution of aqua regia and fluoric acid. Platinum is solved in mixture of acid HCl and HNO_3 in the ratio 3:1 and HF.				
HCl: HNO_3:HF	0	0,015	0,010	48

* - time of heating, ** - recovery of platinum

SUMMARY

1. In the research thee 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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Note: Responsible for English language is M. Kingsford, Katowice, Poland.