

Vapour Treatment Method Against Other Pyro- and Hydrometallurgical Processes Applied to Recover Platinum Form Used Auto Catalytic Converters

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Today more and more cars are produced every year. All of them have to be equipped with catalytic converters, the main role of which is to obtain substances harmless to the environment instead of exhausted gases. Catalytic converters contain platinum group metals (PGM) especially platinum, palladium and rhodium. The price of these metals and their increasing demand are the reasons why today it is necessary to recycle used auto catalytic converters. There are many available methods of recovering PGM metals from them, especially platinum. These methods used mainly hydrometallurgical processes; however pyrometallurgical ones become more and more popular. The article presents results of the research mainly concerning pyrometallurgical processes. Two groups of research were carried out. In the first one different metals such as lead, magnesium and copper were used as a metal collector. During the tests, platinum went to those metals forming an alloy. In other research metal vapours were blown through catalytic converter carrier (grinded or whole). In the tests metals such as calcium, magnesium, cadmium and zinc were applied. As a result white or grey powder (metal plus platinum) was obtained. The tables present results of the research. Processing parameters and conclusions are also shown. To compare efficiency of pyrometallurgical and hydrometallurgical methods catalytic converter carrier and samples of copper with platinum obtained from pyrometallurgical method were solved in aqua regia, mixture of aqua regia and fluoric acid.

KEY WORDS: Used catalytic converters; PGM; Platinum; Recovery; Pyrometallurgy; Hydrometallurgy

1. Introduction

Compounds which are harmful to the environment are emitted when the car engine is working – this is especially connected with the combustion process of the fuel. Every year the number of cars on the market is bigger, thus they increase the amount of emitted exhaust gases. That was the reason why special regulations limiting emission of harmful substances were introduced. Today the catalytic converter is installed in every produced car^[1,2].

The catalytic converter (see Fig. 1) is built mainly from the metallic or ceramic carrier with porous surface, which is covered by PGM, especially platinum,

palladium and rhodium. The catalytic carrier is wrapped with the fibrous material (the main aim is to prevent displacing) and closed in the stainless steel shell. The structure of ceramic carrier is similar to a honeycomb, so consists of the dense net of square holes (see Fig. 2). Such structure increases the active surface (contact zone between catalytic substances like Pt, Pd or Rh and the exhaust gases which flow through the channels). As a result very quick reactions are observed: oxidation of carbon oxides and hydrocarbons and reduction of nitrogen oxides. Finally, compounds such as water, nitrogen and carbon dioxide are obtained which are neutral to the environmental.

The content of PGM in catalytic converters (average 2 g) depends not only on the catalytic converters construction but also on the application of catalytic converters and the car producers. Catalytic convert-

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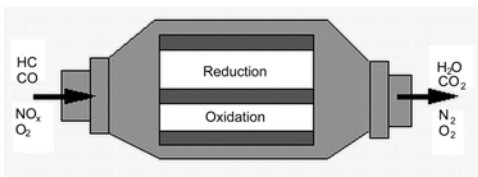


Fig. 1 Schematic diagram of catalytic converter

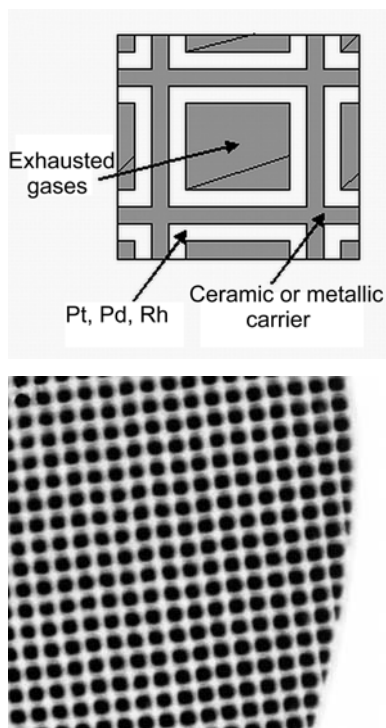


Fig. 2 Schematic diagram of catalytic carrier channels with a honeycomb structure

ers should be periodically regenerated and after some working time, changed. Therefore, more and more used auto catalytic converters (both from exchanged and exploited cars) go to the scrap disposal sites. The necessity of waste management and also high prices of precious metals make the recovery of those metals profitable. Finally, the recovery of precious and other metals is very beneficial because it limits the amount of disposed wastes, saves the natural resources and limits the energy consumption. Additionally, pollution emitted when the obtaining metals from wastes is lower than during their production from primary raw material.

2. Review of Available Methods of PGM Recovery from Used Auto Catalytic Converters

Arguments for the PGM metals recovery are the following: limited PGM resources, scarceness of their occurrence, expensive and energy-consuming process of their output and at last the considerable amount of wastes present during the production process. 1 kg

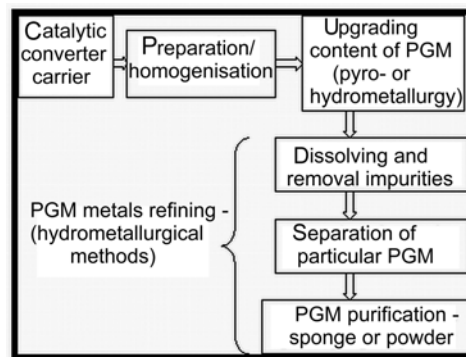


Fig. 3 Main stages of PGM recovery from used auto catalytic converters^[3,5,6]

of platinum can be obtained by outputting 150 tones of ore or by processing 2 tones of used auto catalytic converters^[4]. Fig. 3 presents main stages of catalytic converter treatment during the process of PGM recovery from used auto catalytic converters.

Pyrometallurgical and hydrometallurgical methods are applied for PGM recovery from used auto catalytic converters. In hydrometallurgical method PGM go into the form of chloride complexes (MCl_6^{2-}) as a consequence of dissolution in water solution of chlorides, chlorates, chlorine, hydrogen peroxide, bromates, nitrates and aqua regia. Solution obtained in such a way contains PGM but their concentration is rather small. Therefore the next stage is concentrating this solution and the PGM extraction. During all these processes many liquid wastes are generated which are the potential threat to the natural environment.

When applying pyrometallurgical methods grinded catalytic converter carrier is melted with the addition of other metal which is treated as a metal collector. This process allows PGM to go to the alloy and the carrier, as a slag is separated and becomes a waste. The obtained alloy contains high concentration of platinum and other precious metals so then purification is applied to separate particular precious metals (see Fig. 4).

The following belong to the pyrometallurgical methods^[6,8–11].

(1) RoseTM method – grinded used auto catalytic converter is melted with copper oxide, iron oxide, coke, lime and silica in electric furnace; PGM are extracted from the molten copper, ceramic carriers melted with lime, silica and iron oxide go to the slag; copper is oxidized, PGM metals are separated. As a result the level of Pt concentration in the solution is 75%; solution with Pt is refined and the oxidized copper is reduced in electric furnace and used again.

(2) Melting method – PGM recovery process from used catalytic converters during their melting with iron at the temperature 2000 °C; separation of slag from the metallic phase is done due to the differences in density; obtained metallic phase is leached

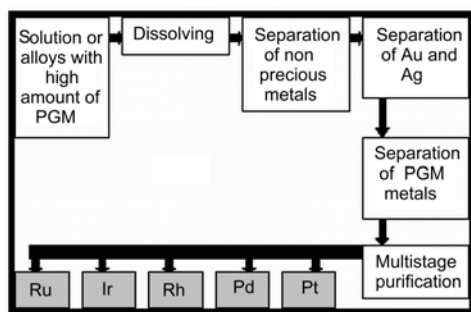


Fig. 4 Schematic diagram of purification (separation) of particular PGM^[3,5,7]

in H_2SO_4 , as a result, iron is precipitated from PGM. It is possible to use other metals as a metal collector for example copper or nickel, then the process is quite similar, but the temperature of the process is considerably lower, slag less aggressive and the condition less reductive.

(3) Method applying used printed circuits – copper, zinc and iron which form printed circuits are treated as a metal collector; used auto catalytic converter carrier and used printed circuits are crushed, incinerated and then melted with the addition of fluxes and carbon.

(4) Method based on blowing metal vapours – metal such calcium or magnesium in the form of gaseous vapour is blown through grinded or whole catalytic converter carrier, as a consequence alloy consisting of metal and PGM is obtained.

The following belong to hydrometallurgical processes^[6,8–15].

(1) Cyanide extraction – method applying cyanide under pressure; in standard condition reaction between sodium cyanide and precious metals is not proceeded—kinetics of this process is too weak; however if the temperature is higher (about 120–180 °C), then the PGM metals can be leached by the sodium cyanide, technique proposed by Chen and Huang^[13] allows to recover 96% of Pt, 97.8% of Pd and 92% of Rh from used auto catalytic converters.

(2) Separation method – used auto catalytic converter carrier is grinded and homogenized, then it is milled with the addition of carbon and the mixture of calcium, sodium and potassium chlorides; such a charge is heated and blown with oxygen (8%–10%); obtained mixture is washed by water and in order to condense the solution heating is applied—part of the solution is evaporated.

(3) Aqua regia extraction – during this method platinum goes to the solution in the form of $PtCl_6^{2-}$, the next stage is extraction with the Al/Zn powder; during this process PGM metals in concentrated solutions are reduced to the metallic form; the last stage is PGM metals separation process.

(4) Chlorination – this method is used by the Tanaka Kikinokoku firm; the process of calcination and reduction by CO in the presence of sodium chloride is

applied; charge obtained in such a way is then blown by air and successively this solution is chlorinated in increased temperature (1200 °C); after this PGM are leached and precipitated by adding SO_2 or TeO_2 and refined.

(5) Method using the system of liquid diaphragms – is used mainly for Pd recovery from used auto catalytic converters; in order to separate and concentrate palladium from water solution of chloride, Cyanex 471 is applied, the process is carried out in two semi-permeable membranes.

3. Experimental

Research concerning the possibility of platinum recovering from used auto catalytic converters was carried out by means of pyro - and hydrometallurgical methods. In the research three different furnaces were used: electric furnace, inductive furnace and chamber vacuum furnace. To analyze the concentration of platinum in the carrier before melting process and in samples after tests the mass spectrometers ASA and ICP were applied. Catalytic converters from motor-cars with petrol engine were used in the tests. Analysis of platinum content in catalytic converters carriers 0.16% to 0.32% showed big differences between carriers. There were even carriers in which platinum content was 0.016%, this could be explained by poisoning the catalytic converter. The probable cause could be too long work of catalytic converter without regeneration.

Preparing catalytic converters to the further research include the following stages: (1) dismantling catalytic converter; (2) separating metallic part from the ceramic one (removing the stainless steel shell); (3) removing fibrous wrapping; (4) for some test whole catalytic carrier was taken, for others the catalytic converter was disintegrated and homogenized (to obtain high initial level of platinum).

4. Results

Three different experimental kinds of research were carried out. The first was concerning the metal collector – so grinded catalytic converters were melted with different metals the function of which was to collect platinum. Other tests were conducted taking into account the whole carrier and metal vapours were blown through it. Some tests taking into consideration hydrometallurgical way were also carried out – ceramic carrier was dissolved in different acids or mixture of acids.

4.1 Platinum recovery by means of metal collector method

This kind of research was based on the melting process of used grinded auto catalytic converter carrier with chosen metals which function was to capture platinum. Metals were selected taking into account the solubility of platinum in them. Therefore calcium,

Table 1 Results of research concerning melting process of grinded catalytic converters carrier with calcium as a metal collector

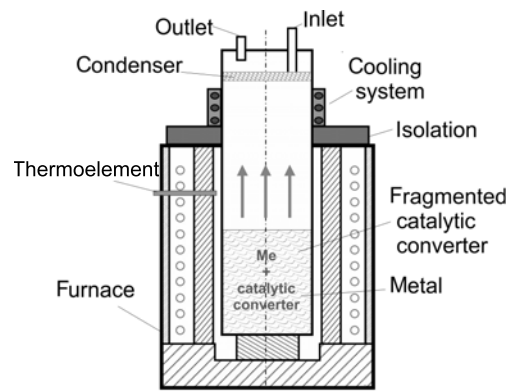
No.	Temp. (°C)	Mass of metal and carrier			Platinum analysis		
		Before test		After test Carrier melted with Ca (g)	Pt content		Pt recovery (%)
		Carrier (g)	Ca (g)		Initial (wt.%)	Final (wt.%)	
I	1000	250	200	440.0	0.28	0.11	69
II	1000	250	200	402.5	0.282	0.12	70
III	1200	200	100	295.0	0.11	0.061	82
IV	1200	200	150	348.0	0.28	0.13	81
V	1350	200	100	205.0	0.16	top: 0.11 bottom: 0.042 dust: 0.21	62% of Pt goes to dust
VI	1350	150	100	–	0.19	top: 0.17 middle: 0.12 bottom: 0.10	converter with Ca melted with crucible

copper and lead played the role of a metal collector in the research. During melting process the ceramic parts of the carrier should go to the slag. Platinum, as its melting temperature is higher than melting temperature of metal collector, should be collected in liquid metal and create an alloy with it after solidification. For the research at that stage, the inductive, electric and vacuum furnaces were used. The neutral atmosphere in the furnace can be kept by applying argon blow. Fig. 5 shows the scheme of this process. Temperature in each test was selected taking into consideration melting temperature of the metal collector. The time of melting process was adjusted to the chosen metal and lasted from 1 to 2 h.

In first tests calcium was used as a metal collector. Parameters of the tests were the following: (1) furnace chamber: electric furnace; (2) temperature: 1000 °C, 1200 °C and 1350 °C; (3) time of the process: 3600 s; (4) argon blow: 50 L/h; (5) sample was cooled together with the furnace.

Table 1 presents results of this kind of research. Using calcium as a metal collector better results were obtained in the temperature 1200 °C, however the research had to be carried out very carefully (applying the neutral atmosphere) due to the high reactivity of calcium. Test No.V gave the possibility to recover 62% of platinum. It went to the white powder in the upper part of the crucible. The gradation loss of platinum from the bottom of the crucible (from 0.160% to 0.042%) could be also observed. In tests the white powder was observed on the wall of the furnace – it was really hard to remove.

In other tests lead was used as a metal collector. Parameters of the tests were the following: (1) furnace: chamber vacuum furnace; (2) temperature: 1200 °C; (3) time of the process: 4400 s; (4) melted lead was mixed with the grinded ceramic carrier by means of a stirrer; (5) mass of metal and carrier: in tests (50+50+60+50) g of carrier was used, total 210 g, in every test it was necessary to add extra portion of lead – this was caused by the fact that lead was oxidized (in the atmosphere occurring in the furnace), so it disappeared during every test; therefore during the

**Fig. 5** Schematic diagram of a test stand for platinum removal using the method of metal collector

test 707 g of Pb was used and as a consequence 16.4 g of lead was obtained and 802 g of melting losses; then melting losses were reduced by carbon, and as a result 7 g of lead was obtained and 850 g of melting losses.

Table 2 presents results of this kind of research. Research using lead as a metal collector did not give satisfactory results because almost all metal was oxidized (the favourable in this case was the furnace atmosphere). There were also problems with capturing and obtaining lead for the second time. All platinum in presented samples went to the melting losses.

In the last tests of this series copper was used as a metal collector. Parameters of the tests were the following: (1) furnace: inductive furnace (ELKON); (2) temperature: 1450 °C, 1550 °C and 1700 °C; (3) time of the process: 5400 s; (4) argon blow: 50 L/h; (5) sample was cooled with the furnace.

Table 3 presents results of this kind of research. The highest platinum recovery was observed for tests No.IV and No.VI. Both tests were carried out in the temperature equal 1550 °C. The higher mass of catalytic converter (test No. VI) with the similar mass of copper decreased the efficiency of platinum recovery about 5%. It could be also marked that the ceramic carrier of catalytic converters in test No.VI contained 0.04% more platinum than in test No.IV. The higher

Table 2 Results of the research concerning melting process of grinded catalytic converters carrier with lead as a metal collector

No.	Temp. (°C)	Pt content		Pt recovery (%)
		Initial (wt.%)	Final (wt.%)	
I	1200	0.129	0.03	88 (Pt in PbO)
II		0.26	0.04	90 (Pt in PbO)
III		0.26	0.05	93 (Pt in PbO)

Table 3 Results of the research concerning melting process of grinded catalytic converters carrier with copper as a metal collector

No.	Temp. (°C)	Mass of metal and carrier			Platinum analysis			
		Before test		After test carrier with Cu (g)	Initial (wt.%)	Final (wt.%)	In slag (wt.%)	Pt recovery (%)
		Carrier (g)	Copper (g)					
I	1450	210.0	569.7	567.8	0.290	0.036	0.024	34.4
II	1450	210.0	704.5	704.1	0.290	0.023	Lack	26.6
III	1450	210.4	756.2	754.1	0.280	0.014	Lack	18.6
IV	1550	225.0	1050.0	1000.0	0.281	0.080	0.001	95.2
V	1700	393.0	1044.0	967.0	0.281	0.060	0.004	70.1
VI	1550	707.0	980.0	978.0	0.320	0.210	0.008	90.7
VII	1700	413.0	1087.0	1003.0	0.196	0.050	0.001	62.8
VIII	1550	245.0	1030.0	975.0	0.196	0.036	0.007	77.1

temperature (1700 °C) the lower efficiency of platinum recovery (in test No.V and No.VII platinum recovery was at the level of 70%). In the higher temperature the ceramic carrier was highly more melted and there were problems with the separation metal from ceramics. Fig. 6 presents typical sample obtained from this kind of research – two layers can be seen: (1) upper one – slag with residue of ceramic carrier; (2) bottom one – copper with platinum.

4.2 Platinum recovery based on blowing metal vapours

In this kind of research metals vapours which were blown through the catalytic converter carrier picked platinum and were settled inside the furnace in the form of dust which was then easy to collect. In this research two kinds of tests were carried out: (1) magnesium vapours were blown through grinded used auto catalytic converter carrier – Fig. 7 presents the scheme of this process; (2) metals vapours such as magnesium, zinc, cadmium and calcium were blown through the whole catalytic converter carrier – Fig. 8 presents the scheme of this process.

In the first tests magnesium was used to blow through grinded carrier, so parameters of the tests were following:

- (1) furnace: chamber electric furnace;
- (2) temperature: 1150 °C, 1170 °C, 1200 °C, 1350 °C;
- (3) time of the process: 3600 s;
- (4) argon blow: primary for tests No.I, No.II, No.V, No.VII, No.VIII; continuous of 50 L/h for tests No.III, No.IV, No.VI, No.IX; continuous of 150 L/h for test No.X;
- (5) sample was cooled together with the furnace, except test No.V. During the test No.V, sample was additionally cooled with water.

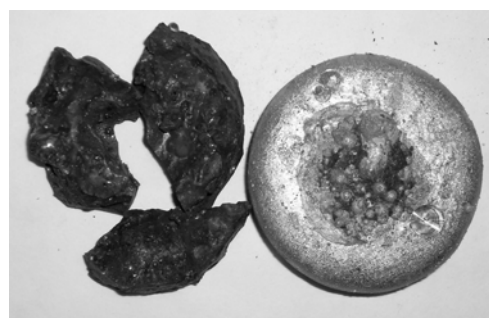
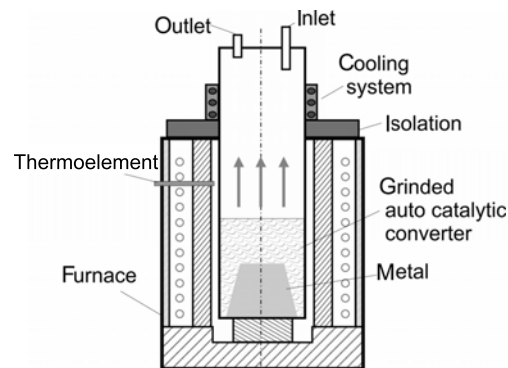
**Fig. 6** Sample obtained after melting the grinded catalytic converter with copper, it is easy to separate slag from alloy: copper with platinum**Fig. 7** Schematic diagram of the test stand to blow metals/magnesium vapours through grinded used auto catalytic converter carrier

Table 4 presents results of such a research. In test No. I and No. IX the high residue of platinum in the carrier could be caused by the lack of magnesium boiling. It could be testified by the high concentration of platinum in residue of melted catalytic converters with magnesium and also small amount of material

Table 4 Results of the research concerning metal vapour (magnesium) blown through grinded catalytic converter carrier placed on this metal in alundum crucible

No.	Temp. (°C)	Mass of metal and carrier					Platinum analysis				
		Before test		After test			Pt content				R (%)
		1 (g)	Mg (g)	2 (g)	3 (g)	4 (g)	I (%)	T (%)	B (%)	C (%)	
I	1200	174.4	308.2	225.9	39.5	15.5	0.320	0.004	0.0039	0.2200	89.3
II	1150	252.8	278.8	297.4	235.7	17.2	0.320	0.056	0.0038	0.0037	6.3
III	1150	254.1	302.4	227.0	284.0	12.0	0.320	0.040	0.0040	0.0035	7.5
IV	1200	246.0	336.4	237.0	306.0	19.0	0.320	0.060	0.0036	0.0040	3.8
V	1200	254.2	309.1	327.8	211.2	8.7	0.320	0.071	0.0040	0.0035	2.5
VI	1150	258.0	303.1	212.0	302.0	24.0	0.320	0.041	0.0037	0.0040	8.5
VII	1200	362.0	409.0	422.0	255.0	60.0	0.170	0.037	0.0020	0.0650	49.2
VIII	1200	351.1	295.5	328.8	198.1	15.7	0.095	0.065	0.0040	0.0037	6.1
IX	1170	785.0	390.0	804.0	137.0	78.0	0.160	0.026	0.0003	0.1500	99.2
X	1350	142.0	76.5			M	0.180	0.120*	0.0810	0.1500	M

Note: 1–carrier; 2–carrier melted with magnesium; 3–powder from the top of furnace; 4–dust from bottom and side walls of furnace; I–initial; T–top of the furnace, B–bottom and the side walls of the furnace; C–carrier with magnesium; R–residue in carrier; M–carrier melted with crucible, *–dust from crucible.

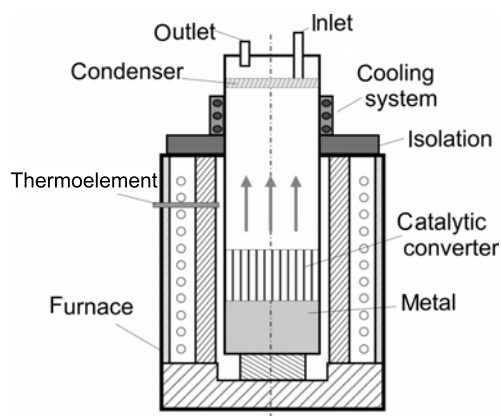


Fig. 8 Schematic diagram of the test stand to blow metals vapours (magnesium, zinc, calcium, cadmium) through the whole used auto catalytic converter carrier

which was vapour deposited in the side walls of the crucible and also on the crucible cover. It is also probable that the leakage of the system caused the additional losses of platinum – from initial contents 0.32% in ceramic carrier to about 0.22% of platinum which was placed in charge after the tests. In test No VII it was possible to evaporate 50.8% Pt which was introduced in the charge, in the remaining tests the residue of platinum in the carrier was rather small, that means the majority of platinum went to the dust/powder.

In the following tests calcium was used to blow through whole catalytic converter carrier, parameters of these tests were the following:

- (1) furnace: chamber electric furnace;
- (2) temperature: 1200 °C, 1300 °C, 1350 °C, 1450 °C;
- (3) time of the process: 3600 s apart from test No.X (18000 s);
- (4) argon blow: 150 L/h for tests No.I, No.II and 200 L/h for test No.III–No.X;

(5) sample was cooled with furnace.

Table 5 presents results of such a research. In all tests calcium completely decomposed into powder. The loss of platinum in the carrier after the test was observed. The biggest problem was calcium dust which settled everywhere in the furnace.

In other tests cadmium was used to blow through whole catalytic converter carrier, parameters of these tests were the following:

- (1) furnace: pit furnace;
- (2) temperature: 800°C;
- (3) time of the process: 3600 s;
- (4) argon blow: to 50 L/h;
- (5) sample was cooled with furnace;
- (6) two tests were carried out: with open and closed outlet of gases.

Table 6 presents results of such a research. In both tests the loss of platinum from ceramic carrier was observed. However, the tests did not balance – the high loss of cadmium was stated. These differences were probably caused by the leakage of the apparatus. It is also possible that in the test with an open outlet of gases, cadmium vapours did not condensed and when leaving the furnace oxidized, and went to the filter.

In further tests magnesium was used to blow through whole catalytic converter carrier, parameters of these tests were the following:

- (1) furnace: electric chamber furnace;
- (2) temperature: 1200 °C, 1350 °C;
- (3) time of the process: 3600 s and 7200 s (test No. VIII);
- (4) argon blow: 150 L/h, for test No. VIII: 200 L/h;
- (5) sample was cooled with furnace.

Table 7 presents results of such a research. In all cases the loss of platinum from the carrier was observed. As a result magnesium powder with platinum was obtained. There were also parts of the carrier mixed with magnesium powder. Magnesium powder was very hard to collect because it settled everywhere

Table 5 Results of the research concerning metal vapor (calcium) blowing through the whole catalytic converter carrier

No.	Temp. (°C)	Mass of metal and carrier				Platinum analysis			
		Before test		After test		Pt content			R (%)
		C (g)	Ca (g)	B (g)	RM	I (%)	A (%)	Other (%)	
I	1200	209.8	54.0	182.0	*	0.11	0.088	P: 0.100 ML: <0.004	70
II	1200	250.0	60.0	230.0		0.15	0.095	P: 0.120 ML: <0.004	58.3
III	1300	160.0	50.0	185.2		0.19	0.160	P: 0.240 DM: 0.091	95.4
IV	1300	250.0	50.0	244.0		0.19	0.140	P: 0.21 DM: 0.082	71.9
V	1350	441.0	50.0	408.6		0.16	0.120	DT: 0.062	69.5
VI	1350	350.0	50.0	329.0		0.19	0.130	DT: 0.085	64.3
VII	1350	300.0	50.0	289.1		0.16	0.110	DT: 0.075	70.7
VIII	1350	400.0	136.4		**	0.19	0.007	powder: 0.065	***
IX	1400	320.8	112.0			0.19	0.008	powder: 0.062	
X	1450	362.4	181.2			0.11	<0.004	powder: 0.058	

Note: C – carrier, B – carrier melted with calcium, I – initial, A – carrier after the process, RM – remarks, R – residue in carrier, * – calcium completely decomposed into powder, ** – carrier melted with the crucible-there is no possible to weight it, P – dust from alundum crucible, ML – powder from melting loss, DM – dust from the middle, DT – dust from the top, *** – not possible to calculate

Table 6 Results of the research concerning metal vapour (cadmium) blowing through the whole catalytic converter carrier

No.	Mass of metal and carrier (g)		Pt content in carrier (%)	
	Before test	After test	Before test	After test
I	774	198	0.22	0.11
II	862	333	0.22	0.10

Table 7 Results of the research concerning metal vapour (magnesium) blowing through the whole catalytic converter carrier

No.	Temp. (°C)	Mass of metal and carrier (g)				Pt contents					R (%)
		Before test		After test		Initial (%)	Dust (cover) (%)	Crucible (%)	Carrier+Mg (%)		
		Carrier	Mg	CM	MCC				Top	Bottom	
I	1200	205.71	256.85	186.4	162.8	0.18	<0.002	<0.002	0.180	0.120	60.4
II	1200	250.00	250.00	195.2	172.6	0.18	<0.002	<0.002	0.180	0.130	49.9
III	1200	250.00	280.50	201.1	196.5	0.18	<0.002	<0.002	0.180	0.110	48.0
IV	1200	150.00	200.00	110.2	149.8	0.18	<0.002	<0.002	0.180	0.120	66.6
V	1200	205.80	200.00	175.3	168.2	0.18	<0.003	<0.002	0.180	0.100	45.4
VI	1200	220.00	200.00	198.5	169.9	0.16	<0.002	<0.003	0.180	0.120	57.9
VII	1350	200.20	54.65	518.0 ¹⁾		0.18	<0.003	<0.002	0.260	0.150	83.0
		518.48 *									
VIII	1200	170.00	169.80	879.2 ²⁾		0.16	<0.004	0.006	0.150	0.077	48.0
		882.48 *									

Note: * – total with crucible, CM – carrier melted with magnesium, MCC – mass of metallic magnesium with the catalytic converters inclusions, ¹⁾ – problems with separation, ²⁾ – problems with separation too big carrier, R – residue in carrier.

Table 8 Results of the research concerning metal vapour (zinc) blowing through the whole catalytic converter carrier

No.	Mass of metals and carrier (g)					Platinum analysis			R (%)
	Before test		After test			Pt content (%)			
	Carrier	Zn	Condensed Zn	Carrier	Melting losses	Initial	Condensed Zn	Carrier with Zn	
I	811.0	1000.0	301.4	842.0	188	0.16	–	0.0837	52
II	805.0	838.4	102.0	899.0	16	0.29	0.027	0.1300	45
III	438.0	775.0	95.0	456.2	309	0.23	0.020	0.0820	36

Note: R – residue in carrier

in the furnace (not only in crucible).

At 1350 °C catalytic converter carrier melted with the crucible and it was difficult to separate these materials. In tests No. I to No. IV residue of platinum in

the carrier was between 45% and 65%. It was really hard to determine platinum recovery in magnesium dust because it was almost everywhere.

In the last tests zinc was used to blow through

Table 9 Results and parameters of the research concerning solution of the used auto catalytic converter carrier in aqua regia (No.I, No.II, No.III, No.IV) and mixture of aqua regia and fluoric acid (No.V, No.VI, No.VII)

No.	Time of heating (s)	Platinum analysis		
		Initial (%)	Final (%)	Pt content (average), which went to solution (%)
I	1800	0.230	0.207 0.221 0.203	91.3
II	1500	0.230	0.191 0.180 0.201	82.7
III	1200	0.230	0.163 0.187 0.153	73.0
IV	0	0.230	0.154 0.152 0.162	68.0
V	0	0.015	0.010	48.0
VI	0	0.016	0.012	53.0
VII	0	0.020	0.013	49.0

Table 10 Results and parameters of the research concerning dissolving copper with platinum and slag from the process in which copper was used as a metal collector in aqua regia

No.	Time of heating (min)	Pt content in solution (%)							
		1 st series		2 nd series		3 rd series		Average	
		A	B	A	B	A	B	A	B
I	30	0.0288	0.0096	0.0230	0.0093	0.0291	0.0094	0.02697	0.00943
II	25	0.0249	0.0085	0.0257	0.0081	0.0259	0.0086	0.02550	0.00840
III	20	0.0239	0.0084	0.0246	0.0079	0.0241	0.0084	0.02420	0.00823
IV	–	0.0236	0.0076	0.0240	0.0075	0.0442	0.0079	0.03060	0.00767

Note: A–copper with platinum obtained in pyrometallurgical method solved in aqua regia; B–slag obtained in pyrometallurgical method (copper used as a metal collector) solved in aqua regia

whole catalytic converter carrier, parameters of these tests were the following:

- (1) furnace: pit furnace,
- (2) temperature: 900 °C,
- (3) time of the process: 3600 s,
- (4) argon blow: 150 L/h,
- (5) sample was cooled with furnace.

Table 8 presents results of the research. Platinum residue in the carrier was in the range from 36% to 52%. Parts of platinum went to condensed dust, the rest to melting losses. It seems that Ca and Mg are much better for this kind of experiments.

4.3 Platinum recovery by means of hydrometallurgical method

Research of platinum recovery from used auto catalytic converters carrier by solving them in acid was carried out to compare efficiency of pyro- and hydrometallurgical methods. Two different tests were conducted:

(1) 3 g of grinded catalytic converter carrier was dissolved in aqua regia (10 cm³ HNO_{3conc} and 30 cm³ HCl_{conc}), some solutions were heated;

(2) 3 g of grinded catalytic converter carrier was dissolved in mixture of acids 10 cm³ HNO_{3conc}, 30 cm³ HCl_{conc}, and 10 cm³ HF_{conc}, all solutions were

heated.

After such treatment solutions were filtrated to separate clear solution from non-soluble parts of ceramic carrier. Table 9 presents parameters of the process and results of the research. Platinum content increased insignificantly with the longer time of heating the solutions. Addition of fluoride acid to aqua regia did not improve platinum recovery from the carrier.

Samples obtained by pyrometallurgical method (using copper as a metal collector in temperature 1500 °C) were also solved in aqua regia. Both copper with platinum and also slag were solved and then analyzed for platinum content.

Table 10 presents results obtained from this process. Slag which was a waste in pyrometallurgical method contained lower amount of platinum than copper with platinum.

5. Discussion and Conclusions

Environmental protection, limitation of produced wastes and the use of valuable secondary materials belongs to requirements industry faces nowadays. Recovery of valuable materials such as PGM especially platinum is very important. Demand of the car industry for these metals is very big, while prices very

high.

Research concerning platinum recovery from used auto catalytic converters by means of pyro- and hydrometallurgical methods were carried out. Both methods have advantages and disadvantages. The content of platinum in different industrial catalytic converters was done and placed in Tables 1–8. Choosing the method of platinum recovery taking into account the initial content of platinum in catalytic converter is not practical and economical. Each car has different catalytic converter. Some of them have high level of platinum (*e.g.* German cars) and some really low level. So even if the catalytic converters are grinded, homogenization should be made. The problem appears when the whole catalytic converter carrier is applied, then the primary analysis of such material should be made. So in that case the determined types of catalytic carriers should be used to make the process cost effective.

Pyrometallurgical methods need an application of appropriate aggregates which can reach high temperature. Furnaces ensuring such temperature and required processing conditions are not only expensive, but also energy-consuming. If the metal collector with platinum is obtained, hydrometallurgical methods (*e.g.* precipitation) must be used to separate platinum from this metal collector. The other possibility is to find application for such alloy.

On the other hand, if hydrometallurgical methods are applied many dangerous wastes solution can be created which are harmful to natural environment. These methods need to be very carefully proceeded because cyanides, concentrated acids and solutions of chlorine are used.

Three different furnaces was used because different metals and methods of recovery were applied. Such parameters as temperature, ensuring inert atmosphere, possibility of blowing metals vapours and even the dimensions of working space of furnace chamber decided which furnace was the most optimal for given metals and the way of catalytic converters treatment.

Both methods of platinum recovery are multistage and complex processes which require the catalytic converters to be appropriately grinded and homogenized. After many operations the obtained alloy or solution also need platinum separation.

Results of the research applying metals as a platinum collector were different. When lead played the role of metal collector, results were not so satisfactory and promising. Lead oxidation was observed which was caused by the oxidative atmosphere of the furnace. The best results were observed for copper. At 1500 °C even 95% of platinum could be recovered from catalytic converter carrier. However, higher temperature caused problems in separating slag from copper and platinum alloys. It is also possible to obtain platinum from alloys of copper with platinum – cast alloy for anode and treated electrowinning process. When

the copper was used as a metal collector the possibility of creating slag and easiness of its dividing form metal collector was considered. The obtained slag in which mainly alumina carrier is melted can be used to recover pure Al_2O_3 . This is really important from ecological point of view, because today's production of this material is connected with great amount of waste (red mud) obtained in Bayer's method. As we know red mud is really danger to environment, thus obtaining alumina in optional way could be really promising.

When the lead was used as metal collector the problems connected with this metal was considered. Lead oxidizes, so the inert gases have to be used. More, the further research have to focus on using some equipment (*e.g.* pump that ensure the constant flow of such metal). Fulfilling of those both conditions allow to capture alloy of lead and platinum without lead losses.

Calcium as a metal collector is not bad, but gives worse results than copper. It is possible to recover 82% of platinum. Too high temperature can cause fusion of the carrier and calcium in crucible. Then the separation is impossible. What is more, calcium as a reactive metal can be appropriately stored and also the research should be carried out in accompany of inert atmosphere, especially argon. During experimental tests white dust (alloy of calcium and platinum) settled on the crucible cover and side walls of the furnace. Then it should be very precisely removed from these places and collected. It causes considerable losses of metal and platinum. So further research needs to take into consideration the improvement of leaktightness of the system (crucible put into the furnace) or develop a method of metal condensation in special crucible or container. The metal collector method was conducted to check the process parameters and the behavior of applied metal.

Results of the research applying metal vapours blown through grinded or whole catalytic converter carrier gave promising results. In case of blowing magnesium vapours through grinded catalytic converter carrier only in two tests residue of platinum in the carrier was high. This was probably caused by the lack of boiling magnesium. This could be also confirmed by the little amount of dust/powder condensed on the side walls and cover of the furnace. Platinum in all tests with magnesium (including grinded and whole catalytic converter carrier) and calcium went to dust/powder. This powder was collected from the whole chamber of the furnace, sometimes there were problems with scrapping it from the walls or cover. So, further research like in case of calcium as a metal collector should improve the leaktightness of the system. The solution of such problem for future in industrial application could be some kind of vapour condenser and also cooling system.

Tests concerning blowing zinc vapours through the carrier did not give satisfactory results. During the process too big melting losses were created and the

amount of condensed zinc and platinum contained in it was too small. Therefore, calcium and magnesium seem to be the best ones for blowing in the form of vapours catalytic converter carrier. However, the experiment test should be in both cases carried out very carefully due to high reactivity of those metals.

Obtained powder which is the mixture of Pt-Ca or Pt-Mg could find an application in removing NO_x in power boiler or from combustion gases produced from firing process of coke oven (the catalytic converter of this process is platinum).

Powder Pt-Mg can be also applied in magnesium machining. At present the common application of magnesium alloys is limited by the problems with magnesium casting and also magnesium nature. The low normal potential influences negatively on the protective features of this metal. If magnesium is in contact with other metals, magnesium plays a role of an anode which is very quickly devastated. Admittedly in contact with atmosphere magnesium surface is covered by grey colour oxide layer. However, this layer does not protect the material base from corrosion. This is why the layer has not such a strict structure as aluminium oxide layer present on aluminium. So to prevent magnesium alloys, finishing is used. It is based on removing unfavorable oxide layer and replacing it by protective coating which is more attractive and more mechanical and corrosive resistant. To produce such galvanic metallic coatings platinum is used, so it could be replaced by Mg-Pt powder obtained during the tests.

In case of the research concerning hydrometallurgical methods (dissolving carrier in aqua regia and mixture of aqua regia with fluoric acid) many solid and solution wastes were obtained. It is the main disadvantages of this method. Therefore more effective and less harmful for the environment methods of platinum recovery are being searched for. The tests showed that sample heating could improve the recovery process insignificantly. Addition of fluoric acid to aqua regia did not influence platinum recovery.

Adequate combination of pyro- and hydrometallurgical methods allow to increase the efficiency of platinum recovery from used auto catalytic converters.

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REFERENCES

- [1] A. Fornalczyk and M. Saternus, *Metalurgija* **50** (2011) 261.
- [2] A. Fornalczyk and M. Saternus, TMS Annual Meeting, International Symposium LMPC Santa Fe, USA ISBN 978-0-87339-743-8, 2009, p.381.
- [3] A. Fornalczyk and M. Saternus, *Ores Metals*. **52** (2007) 326. (in Polish)
- [4] J. Merksiz and A. Merksiz-Guranowska, *Recycling* **4** (2006) 18. (in Polish)
- [5] C. Hagelüken, *Chem. Today* **24** (2006) 14.
- [6] Y. Kayanuma, T. Okabe and M. Maeda, *Metall. Mater. Trans. B* **35** (2004) 817.
- [7] C. Hagelüken, M. Buchert and H. Stahl, *Erzmetall* **9** (2003) 529.
- [8] R. Rao, *Resource Recovery and Recycling from Metallurgical Wastes*, Oxford University Press, Elsevier Publisher, 2006, p.
- [9] J.S. Yoo, *Catalyst Today* **44** (1998) 27.
- [10] M. Benson, C.R. Bennett and J.E. Harry, *Resources, Conservation and Recycling* **31** (2000) 1.
- [11] K. Byung-Su, L. Jae-Chun and S. Seung-Pil, *JOM* **12** (2004) 55.
- [12] C. Fontás, V. Salvad and M. Hidalgo, *J. Membrane Sci.* **223** (2003) 39.
- [13] J. Chen and K. Huang, *Hydrometallurgy* **82** (2006) 164.
- [14] T.N. Angelidis, *Topics in Catalysis* **16/17** (2001) 419.
- [15] B. Pospiech, *Physicochem. Probl. Miner. Process* **48** (2012) 239.