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REMOVAL OF PLATINUM GROUP METALS FROM THE USED AUTO CATALYTIC CONVERTER

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Recycling of platinum group metals from the used auto catalytic converters is profitable from ecological and also economical point of view. This work presents the analysis of the chances of removing the platinum group metals (PGM) from the used auto catalytic converters applying pyrometallurgical and hydrometallurgical methods. The characteristics of auto catalytic converter is shown as well the available technologies used for processing the auto catalytic converters are also presented.

Key words: auto catalytic converter, PG metals, platinum removal

Izdvajanje metala iz grupe platina iz korištenih automobilskih katalitičkih convertera. Recikliranje metala iz grupe platina od korištenih automobilskih katalitičkih konvertera je profitabilno s ekološkog i također s ekonomskog stajališta. Ovaj rad prezentira analizu mogućnosti izdvajanja metala iz grupe platina od korištenih automobilskih katalitičkih konvertera uz primjenu pirometalurških i hidrometalurških metoda. Prikazane su karakteristike automobilskih katalitičkih konvertera kao i raspoložive tehnologije koje su korištene za obradu automobilskih katalitičkih konvertera.

Ključne riječi: auto katalitički konverter, GP metali, izdvajanje platine

INTRODUCTION

Milions of cars that drive every day on the roads are the source of pollution to the air. This is especially observed in the big cities and urbanized areas. The average family car would emit 15 Mg of the toxic and harmful polluting gases over a 10 year life period [1]. These polluting gases can be reduced by catalytic converters (remove 98 % of pollution).

Therefore, current legislation establishes standards that require the fitting of catalytic converters to all new cars. The first countries that established such standards were USA and Japan. Then this legislation came into force in Europe, Australia and parts of Asia in the 1980s, followed in the 1990s by the developing economies of Brazil, Mexico and India [2].

It is estimated that this regulations have prevented emission of 12 billion Mg of harmful polluting gases to the air [3]. Today over half of the world's 500 million cars are fitted with a catalytic converters.

CHARACTERISTIC OF AUTO CATALYTIC CONVERTERS

An auto catalytic converter (Figure 1) reduces the emission of harmful gases, such as carbon monoxide, hydrocarbons and nitrogen oxides. During the catalytic process these gases are transformed into carbon dioxide, water, and nitrogen. The following chemical reaction can be written:

$$2CO + O_2 = 2CO_2 \quad (1)$$

$$2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O \quad (2)$$

$$2NO + 2CO = N_2 + 2CO_2 \quad (3)$$

Most modern cars are equipped with three-way catalytic converters. This refers to the three regulated emissions it help to reduce their harmfulness.

Large active surface of catalytic converter is a necessary condition for its efficient working. This surface is created by the carrier with a honeycomb structure

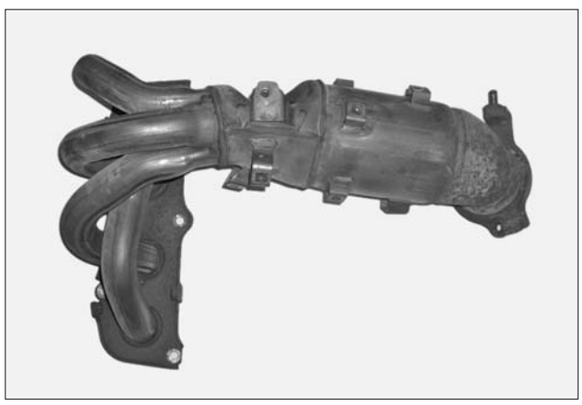

Figure 1. View of an auto catalytic converter

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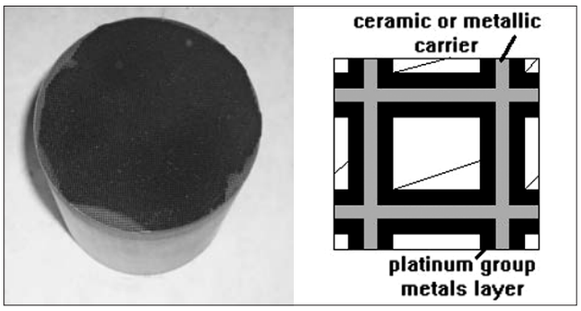

Figure 2. The carrier auto catalytic converter with a honeycomb structure

(Figure 2) and the catalytic system. Carrier consists of a ceramic or metallic substrate coated by an aluminium oxide (Al_2O_3) with other rare earth oxides such as CeO_2, ZrO_2. Platinum group metals (platinum, palladium, rhodium) are responsible for the catalytic function.

Platinium is responsible for transforming hydrocarbons and carbon monoxide to water and carbon dioxide, while rhodium is most efficient in reducing nitrogen oxides to nitrogen. Palladium can handle all three pollutants, but less efficiently than platinium or rhodium. Diesel oxidation catalytic converters contain no rhodium.

Today's exhaust systems are characterized by an increased complexity, as one distinguishes oxidation catalysts and three-way catalysts for gasoline engines, NO_x adsorbers for lean-burn engines, particulate filters and oxidation catalysts for diesel engines, aside from selective catalytic reduction units and NO_x adsorbers for diesel and many others [4].

PGM DEMANDS AND SUPPLIES

PGM (Pt, Pd, Rh) are used in auto catalytic converters due to their remarkable resistance to high temperature corrosion and oxidation. The quantity of platinum, palladium and rhodium used in auto catalysts may vary greatly by vehicle type, manufacturer, country, year and additional factors. For example depending on the engine capacity the auto catalytic converters can contain about 1,5 g of platinum, 0,3 g of rhodium and small amounts of palladium [5, 6]. In three-way catalytic converters the ratio of platinum and rhodium is 5 to 1 and the ratio of palladium and rhodium is 7 to 1. The contents of PGM ranges from 1,42 to 1,76 g for 1 dm^3 of carrier capacity [5, 6].

The demand for auto catalytic converters is still increasing [6], therefore the demand for PGM is expected to grow in the nearest future. The driving force behind this is the use of platinum in catalytic converters, particularly those fitted to diesel vehicles. Tighter restrictions on the permissible levels of NO_x in automotive exhaust continue to drive the demand for rhodium. Auto catalytic converters now account for over 87 % of the rhodium used [6]. Table 1 presents primary PGM (Pt, Pd, Rh) production, whereas Table 2 presents demand for PGM with special focus on using this PGM in auto catalytic converters.

Table 2 also presents the value of recycled PGM. It can be observed that this value is getting higher every year.

Table 1. **Primary production of palladium, platinum and rhodium in the years 2001 – 2007 [7]**

Year	Primary production / Mg		
	Pd	Pt	Rh
2001	227,7	182,3	18,8
2002	163,3	185,7	19,1
2003	200,6	192,8	22,5
2004	265,9	201,9	22,4
2005	261,4	206,5	23,5
2006	250,7	211,3	25,6
2007	258,8	207,1	25,0

About 15 - 20 % of the world demand for platinum comes recycling especially from the used auto catalytic converters. However, this amount of platinum is not enough to meet the growing demand for this material (Table 1 and 2) [8]. All these makes platinum reserves shrink and in consequence platinum prices increase (Table 3). For palladium and rhodium present situation is more comfortable, production is, respectively, sufficient or nearly sufficient to meet the demands.

The high value of PGM (Table 3) encourages recycling from scrap material especially coming from auto catalytic converters and is already successfully practised. Table 4 shows the values of Pt and Pd recovery from the used auto catalytic converters in different geographical regions in the years 2001 - 2007. The North America is the undisputed leader in this recovery.

RECYCLING OF AUTO CATALYTIC CONVERTERS

Recycling of PGM is very important because it provides a supplementary source to the mining of these metals, therefore protecting environment by limiting the number of waste disposal, savings of natural resources exploitation, limiting the electricity consumption, diminishing pollutant emission.

At present in Poland there is no plant where PGM can be recovered. The used auto catalytic converters are purchased, collected and then imported to other countries especially Germany. In the world there are some firms which recover PGM metals from the used auto converters. Umicore Autocatalyst Recycling is a good example of them. Its plants are presented in Table 5.

At first the used auto catalytic converter for recycling must be prepared and homogenized. Then the representative sample is taken and analysis is done. If PGM contents is below 30 %, pre-concentration is necessary. This can be done by incineration, by pyrometallurgical concentration or hydrometallurgical processes. The fol-

Table 2. **Demand for palladium, platinum and rhodium and the value of recycled PGM from auto catalytic converters [7]**

Year	Demand / Mg	Recycled PGM (3)	
	1)	2)	
Palladium			
2001	210,3	158,3	8,7
2002	150,5	94,9	11,5
2003	168,9	107,3	12,8
2004	204,0	117,9	16,5
2005	228,8	120,2	19,4
2006	201,2	125,7	24,9
2007	205,4	136,2	29,4
Platinum			
2001	193,8	78,4	16,5
2002	201,2	80,6	17,6
2003	203,1	101,7	20,1
2004	203,4	108,6	21,5
2005	208,2	118,0	23,9
2006	209,3	128,8	26,6
2007	215,4	131,7	27,5
Rhodium			
2001	18,0	17,6	2,7
2002	18,4	18,6	3,1
2003	19,3	20,5	3,9
2004	22,7	23,6	4,4
2005	25,7	25,8	4,3
2006	26,2	27,0	5,3
2007	25,1	26,8	5,6

1) amount of primary metal that is acquired by the industry
2) amount of metal for manufacturing auto catalytic converters
3) PGM recovered from the used auto catalytic converters

Table 3. **Average values of Pt, Pd and Rh prices in the years 2001 - 2008 [9]**

Year	Price / $/kg		
	Pd	Pt	Rh
2001	19,69	17,13	51,54
2002	10,91	17,42	26,95
2003	6,52	22,31	17,05
2004	7,47	27,27	31,50
2005	6,53	28,90	66,02
2006	10,36	36,76	146,44
2007	11,46	42,03	199,24
2008*	14,39	61,47	272,03

* - average value from 4 months (01 – 04)

lowing stages are dissolution and PGM isolation and finally PGM purification.

PGM purification let to obtain very high purity metal, but after all it is very expensive. It consumes large quantities of energy and can create dangerous solutions. Processes applied for PGM purification are the following: calcinations, ion exchange, (solvent)-extraction, hydrolysis, reduction and oxidation processes, precipitation [10].

Table 4. **Pt, Pd and Rh recovery from the used auto catalytic converters [7]**

Year	Recovery / Mg			
	E	J	A	O
Platinum				
2001	2,18	1,71	11,51	1,09
2003	3,58	1,87	13,06	1,55
2005	5,29	1,09	15,71	1,87
2007	6,69	1,09	17,88	1,87
Palladium				
2001	0,93	1,24	6,22	0,31
2003	2,18	1,24	8,40	0,93
2005	5,13	0,93	12,13	1,24
2007	9,18	1,09	17,42	1,71

E – Europe, J – Japan, A – North America, O – others

Table 5. **Plants working for Umicore Autocatalyst Recycling [4]**

Name of plant	Place
Umicore Precious Metals Refining N.V.	Hoboken
Umicore AG&Co KG	Hanau
Umicore Brazil Ltd	Sao Paulo
Cycleon SASU	Paris
Umicore Autocatalyst Recycling Belgium NV	Hoboken
Umicore Autocatalyst Recycling GmbH	Alzenau
Umicore Autocatalyst Recycling USA	Covington

Figure 3 presents the main steps in PGM recovery from the used auto catalytic converters, while Table 6 shows some processes used to PGM recovery from auto catalytic converters

In the hydrometallurgical methods PGM contained in the used auto catalytic converters were dissolved in an

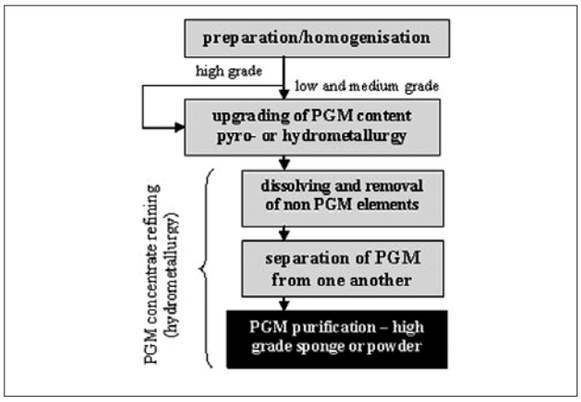

Figure 3. Main steps in PGM recovery from the used catalytic converters [10]

Table 6. **Some processes of PGM recovery from the auto catalytic converters [11,12]**

Process	Specification
CN extraction	Hydrometallurgy, US Bureau of Mining
Segregation	N.E. ChemCat
Aqua regia	Hydrometallurgy
Chlorination	Tanaka Kikinzoku
Melting method-1	Pyrometallurgy
ROSE^{TM} method	Pyrometallurgy, Nippon PGM
Metal Vapour Treatment	Pyrometallurgy, MatsudaSangyo Ltd

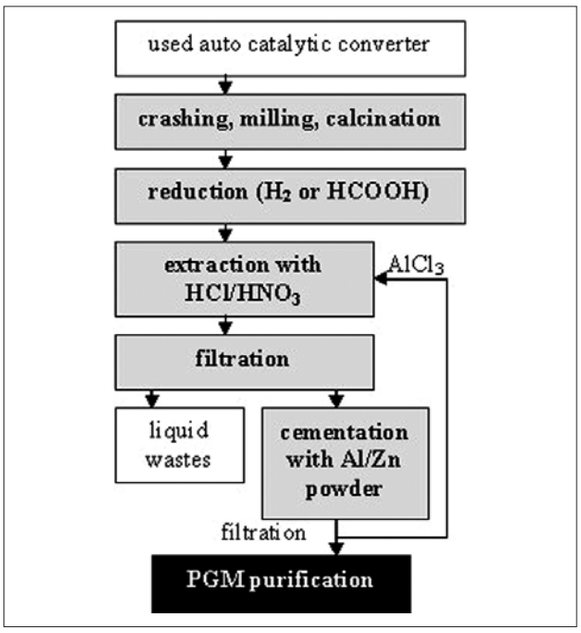

Figure 4. Scheme of hydrometallargical method [11]

aqueous solution of chlorate, perchloric acid, Cl_2, H_2O_2, bromate, nitrate, and aqua regia. As a result PGM are mostly in the form of chloro-complex (MCl_6^{2-}). The obtained solution contains PGM, but their concentration is low. So the next stage is to concentrate the solution and extract them from this solution. However, in hydrometallurgical methods liquid wastes can be created in large numbers. This wastes might be very dangerous to the natural environment. Figure 4 presents the example of hydrometallurgical method.

In pyrometallurgical methods broken-up carriers covered by the PGM are melted with the addition of other metal which has a special function - to be a liquid matrix. PGM pass into the alloy, while carriers are separated and scrapped. Obtained metal is rich in PGM, so the next stage is the PGM purification [11,12].

Both methods are very effective. Using them it is possible to recover 95 % of platinum and 70 % of rhodium. These two methods can be combined. As a result the high level of PGM recovery can be obtained [11].

SUMMARY

The main requirements that the industry has to meet nowadays are the following: the environmental protection, limiting the amount of wastes, reusing the secondary material. So to protect natural environment against harmful polluting gases catalytic converters are installed in cars. Life time of these converters is limited. Thus the recycling of end-of-life catalytic converters is crucial in order to economise on valuable resources and to minimise the environmental pollution connected with PGM production. Processing 2 Mg of the used auto catalytic converters can avoid mining 150 kg of ores and all the following stages which are necessary to obtain pure metal.

Today it is estimated that almost 30 % of all PGM ever mined have been used for auto catalytic converters and more than 2 000 Mg of these is still globally "on the road". So taking into account the prices of Pt, Pd and Rh it is profitable to recover these metals from catalytic converters. Commonly hydrometallurgical methods are used in this recovery. However they also give some dangerous by-products.

Taking into consideration the cost of the used auto catalytic converters and the cost of available technologies it seems appropriate not only to export catalytic converters but to start recycling them in Poland.

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Note: The responsible translator for English language are the Authors.