THE RESULTS OF PLATINUM RECOVERY FROM METAL SUBSTRATE CATALYTIC CONVERTERS BY USING MAGNETO-HYDRO-DYNAMIC PUMP

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Abstract

The spent auto catalytic converters are a valuable source of platinum group metals (PGM metals), such as platinum, palladium and rhodium. There are two main types of structures used in construction of catalytic converters -ceramic or metallic carrier. Metal supported auto catalysts have been used in sports and racing cars initially, but nowadays their application systematically increases. World literature describes a number of pyro- or hydrometallurgical methods that are used for recovery of the platinum and other precious metals from used auto catalytic converters. However, all the methods are used to recover platinum and other metals from ceramic carriers. Among auto catalytic converters withdrawn from use, these with metallic carrier constitute quite a big group. This work presents a method of PGM metals recovery from auto catalytic converters in which they are washed out by a liquid metal (metal collector). Liquid metal is put in motion by means of magneto-hydro-dynamic pump, and then the PGM metals are eluted from channels of the used auto catalytic converters. Analysis of platinum content in the carrier before and after the process was performed using atomic absorption spectroscopy. The obtained results were discussed.

Keywords: Recovery, PGM metals, platinum, spent auto catalysts

1. INTRODUCTION

Catalytic converters containing platinum, palladium and rhodium installed in exhaust system of every car enable to limit considerably the emission of harmful substances to the natural environment. In auto catalytic converter platinum, palladium and rhodium play the catalytic role; and they are covered the ceramic or metallic carrier. Catalytic converter with metallic carrier called also Metal Substrate Converters (MSC) was primary used in sport and racing cars - in such cars it is needed the low returnable pressure of exhaust gases and the operational reliability at the high continuous load. Metallic carriers are not so commonly used (4% of all produced catalytic converters), however, due to the numerous advantages, their application has systematically increased [1].

The metallic carriers are built from the heat-resisting foil (Fe-Cr-Al) covered by the platinum group metals (PGM metals) - this foil is wrapped in such way that it enables to increase maximally the contact area with catalytic substances. The amount of PGM metals in metallic carriers are similar like in ceramic carriers (mostly not more than 2-3 grams); although the metallic material of the carrier causes that it is not possible to use the typical technologies to recover PGM metals from that type of carrier. There is scarcity of information about the way of PGM metals recovery from metallic carriers in the literature. **Table 1** presents the list of chosen available patents (and the name of applicants) used for the PGM metals recovery from auto catalytic carriers with metallic carrier. The only firm that concerns on a mass scale with this problem in the world is Umicore Precious Metals Refining. This is one of the biggest plant dealing with precious metal recovery - it is the owner of the highly-automated lines of grinding the catalytic converters with metallic carriers in Maxton (USA) [2]. The first stage of PGM metals recovery is mechanical separation of the particular parts of the catalytic converters (including PGM metals) from the base [2]. Then the appropriate selection to fraction is made; afterwards fraction containing PGM metals is also homogenized.

Table 1 Patents describing methods of platinum and other PGM metals recovery from spent auto catalytic converters with metallic carriers [4-19]

Applicant	Patent no/date	Characteristics
FOSHAN BRUNP CYCLE TECHNOLOGY CO LTD	CN102732728 (A) 2012-10-17	Metal carrier of spent auto catalyst is crushed into particles; they are dissolved in aqua regia; solution is filtered, a leachate is obtained, which is extracted by using a mixed liquid of 2-hydroxyl-5-nonyl acetophenone oxime and kerosene (Pd-containing extract is obtained) or extracted by using a mixed liquid of 3-(trimethoxysilyl)propylamine and kerosene (Pt and Fe-containing extract is obtained); dilute HCl is added for extracting Pt and Fe. The method provided high recovery rate and high purity of Pt and Pd.
KUNMING INST OF PRECIOUS METAL	CN101509077 (A) 2009-08-19	1. mixing the spent auto catalyst with reducing and trapping agent; 2. putting the mixed materials into an electric or electric arc furnace for smelting; obtaining a noble metal phase; 3. selectively leaching base metals from the noble metal phase, refining the enrichment of the noble metal to produce Pt, Pd, Rh products - process is characterized by recovery rates of noble metals.
TANAKA PRECIOUS METAL IND	JPH02209435 (A)1990-08-20	To recover a PGM metals from spentcatalystwithmetallic carrier it is treated with a solution prepared by adding an oxidizing agent(H_2O_2 and HNO_3) to a solution containing 15% thiocyanogen; Na_2S is added to the resulting leach liquor, PGM metals are precipitated in the form of sulfides and recovered.
CATALER IND CO	JPH0834619 (A) 1996-02-06	To recover precious metals from spent metallic carrier catalyst, at first, it is immersed in a solution of sulfuric acid (30%) and/or phosphoric acid, catalyst is separated into metallic carrier material and catalyst layer by heating to dissolve catalyst layer of the metallic carrier. Then, conventional methods are used.
NIPPON STEEL CORP	JPH08266911 (A) 1996-10-15	Metal carrier is crushed by an inexpensive, simple device without using an acid or other chemical liquid to recover the precious metals. The separation and recovery of a precious metal after crushing are easy, and the recovery efficiency is good to reduce the recovery cost (energy- saving method).
EAR GMBH	US5279464 (A) 1994-01-18	Spent catalysts with metallic carrier are recycled by admitting them into an impact pulverizer (mixture of particles: first fraction - dust-like particles of wash coats and catalyst, second fraction - nonmagnetizable and magnetizable particles of carriers. A high percentage of the first fraction is withdrawn from the pulverizer with an air stream. The remainders of the first and second fractions are evacuated from the pulverizer by gravity flow, the mixture of first and second fractions is classified by pneumatical conveying and by magnetical separating the remaining particles of the carriers.
R.O. PROCESSING, INC	US2008282842 (A1) 2008-11-20	Process for recovering catalyst coating material from metal carrier catalyst, including contacting the catalytic coating material with sodium; potassium or ammonium hydroxide-containing compound at an elevated temperature; rinsing with a liquid and filtering the solid catalyst coating material from the solution.
CALSONIC KANSEI CORP NAKANISHI YUKIO CALSONIC KANSE	EP1594610 (A1) 2005-11-16	The metal carrier catalyst recovery system includes: a container into which materials are thrown; impact blades which destroy the materials by impact to make the materials have a size to fall by its own weight, and separate powder including the metal catalyst from the destroyed pieces of the materials, a floating (separated powder floats higher upward inside the container), powder collector (sucks in and recovers the powder floating inside the container).
CATALER CORP	JP2015098619 (A) 2015-05-28	Metal carrier catalystis dissolved into a solution containing more than 5% nitric acid, and 10% or more phosphoric acid. Then, conventional methods are used.
NIPPON STEEL CORP	JPH11158563 (A) 1999-06-15	A metal carrier catalystis heated to the high temperature (800-1400 °C) and then rapidly cooled by water cooling - injecting water the gas passage of the honeycomb body (10 to 50 dm^3/min per cm^2) - a wash coat layer containing precious metals is peeled off from the metal carrier.
DOWA MINING; TA-NAKA KIKI-NZOKU KOG-YO KK; NIP-PON PGM:KK	JP3516604 (B2) 2004-04-05	In this method, the auto catalyst with metallic carrier is subjected to oxidizing treatment together with metal copper within a furnace. By this method, the metal-substrate catalyst can be separated into a molten oxide layer containing the oxides of the metallic components of the substrate and a molten metal copper layer containing the platinum group metals.

Continue **Table 1**

CATALER CORP; WATA-NABE TUNE-YUKI; HAYASHI KIYOTAKA	WO2014038048 (A1) 2014-03-13	A method for recovering precious metal held in a metal carrier catalyst that includes first step in which the catalyst is heated in a nitric acid solution, and a second step in which the first post-step catalyst is heat treated in a sulfuric acid solution.
LOTTERMOSER MANFRED	DE19715981 (A1) 1998-10-22	Recovery of platinum metal compounds from catalysts with metallic carriers by initiating chemical reactions on the surface of the carriers.
RHONE POULENC CHIMIE	EP0871787 (B1) 1999-10-20	A method for the recovery of precious metals(Pt, Pd, Rh) from a metal carrier by electrochemically separation; the composition to be processed forming one of the electrodes used, or directly contacting one of the electrodes used.
DEGUSSA	EP0648848 (A1) 1995-04-19	Separation of the platinum metals from auto catalysts with metal supported by ultrasound treatment in a liquid bath. The platinum metal/oxide mixture detached from the support is worked up by known methods.
ISHIFUKU METAL IND; NAKATSU SHIGERU; YOKOTA TOMONAO	WO2005087375 (A1) 2005-09-22	A method for recovering platinum group metals from auto catalyst with metallic carrier, which comprises treating the catalyst device having a metal carrier provided with a wash coat and, carried thereon, a catalyst component containing a precious metal with an aqueous mixed acid solution containing sulfuric acid and nitric acid. The method can be employed for separating and recovering a wash coat containing a precious metal from the metal carrier without substantially crashing or dissolving metal carrier with good efficiency.

Metallic carrier is crushed using one or even more kinds of grinders. During the crushing process the dust rich in precious metals is created - such dust should be precisely collected due to avoiding the additional losses during the process [3]. Almost 100% of precious metals, which can be found in catalytic converters, are recovered from the collected dusts. Whereas the fragments of catalytic converters stainless steel shell and the metallic foils are practically without the precious metals and returned to the reusing, e.g. in steel production processes [3].

2. METHOD OF METAL COLLECTOR WITH THE USE OF MAGNETO-HYDRO-DYNAMIC PUMP FOR MSC CATALYST

To the research method of metal collector was used; it is typical method applied commonly for PGM metals recovery from spent auto catalytic converters with ceramic carriers. The main advantage of this method is lower temperature of the process and the lower aggressivity of the slag; whereas there is also less reductive condition of the process. Such method was intensified by using magneto-hydro-dynamic pump to intensify the process. In that solution liquid lead (which plays the role of metal collector) is put into rotary motion using the mentioned pump. External inductor generates the vortex field with the axis according to the axis of the channel ring. Rotating electromagnetic field creates in the liquid metal rotary current, which influences with the electromagnetic field of the inductor generating the electrodynamic force causing rotary motion of the metal. Application of the electromagnetic field to move the liquid metal enables to simplify the construction of the reactor and to avoid the necessity of applying the mechanical pumping the liquid metal. The metallic carriers of the spent auto catalytic converters are placed inside the channel of the reactor using to the research. Lead flowing through the catalytic converters channels collects platinum and other precious metals because it is possible to wash out the platinum, palladium and rhodium from channels and then solving them into the lead bath. The continuous motion of the lead considerably intensifies the process of washing out. Using the same metal to wash out the big amount of catalytic converters causes that PGM metals appears in the liquid metal bath and then there is increase of their concentration to the level guaranteeing that the process of PGM metals extraction from the liquid bath if profitable. Using the closed cycle of the liquid metal limits the unfavourable influence of this process on the environment. **Figure 1** shows the scheme of test stand using to the research.

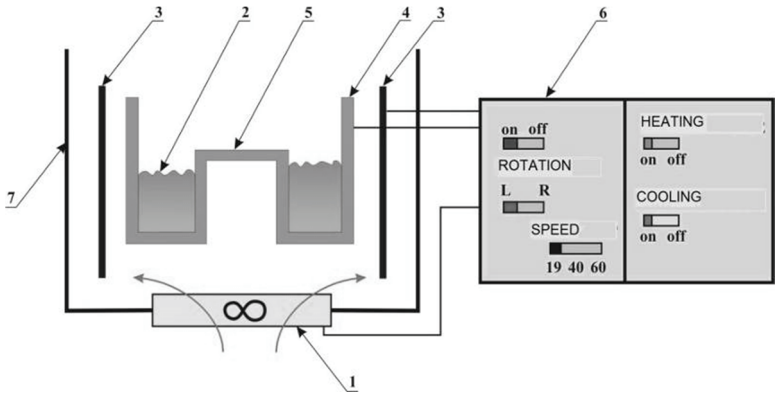
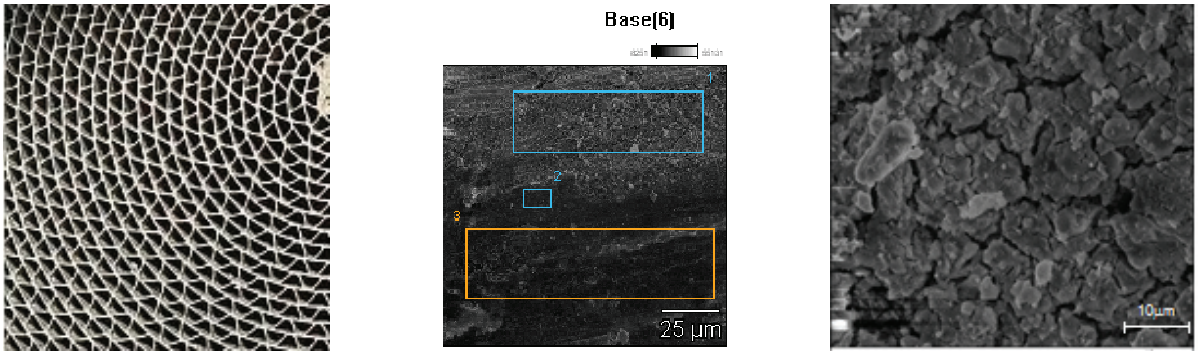


Figure 1 Device for PGM metals recovery from spent catalytic converter using electromagnetic field: 1 - cooling, 2 - liquid metal, 3 - winding stirrer, 4 - boundary of the liquid metal, 5 - thermal insulation, 6 - controller, 7 - casing

3. RESEARCH METHODOLOGY AND RESULTS

The research was carried out in the laboratory of the Institute of Metals Technology at the Silesian University of Technology. Metallic carriers used in the research came from different cars. Analysis of PGM contents in the carrier before and after melting process was performed by means of atomic absorption spectroscopy. The analysis indicated the difference in platinum contents in different catalytic carriers. 50 kg of lead (99.99% purity) was used to the research as a metal collector. During tests it was carried out the influence of process time on platinum recovery from spent auto catalytic converters.

Analysis of chemical composition of catalytic converters is shown in **Figure 2** and **3**. The surface of the sample catalysts was analyzed with the use of scanning electron microscope (SEM) equipped with a Hitachi S 4200 the X-ray detector. Accelerating voltage applied during the observation and X-ray microanalysis was 15 kV. Microanalysis of the chemical composition was performed by means of EDS method (Energy Dispersive Spectrum).



a) b) c)

Figure 2 Structure of catalytic converter: a) real view; b) and c) sample with marked selected areas for X-ray energy spectra

Unfortunately, such a structure makes it difficult to recover the precious metal contained in these kind of catalysts. **Table 2** presents parameters of research and the test results obtained in different time of process and for different secondary voltage (V_s).

The desired research result of platinum recovery from used auto catalytic converters using magneto-hydro-dynamic pump is the depletion of platinum content in the catalytic converters, thus the effect was achieved

The growth of platinum content in the metal collector (lead) was not analyzed yet because enormous amount of washed out catalysts would have to be used to notice the real growth of platinum content.

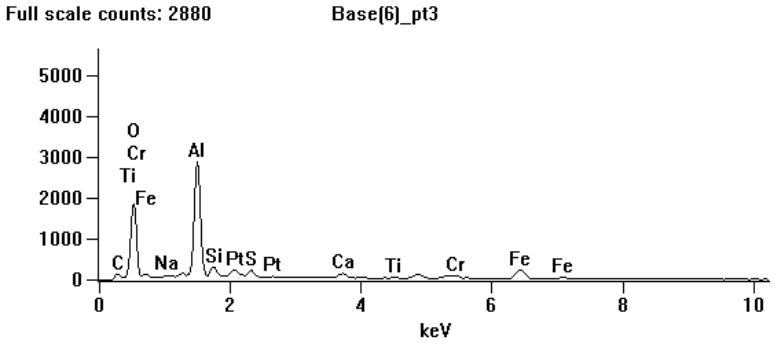


Figure 3 X-ray energy spectra (EDS) for sample of catalytic converters

Table 2 Parameters of the process and the results of the research Pt recover from used autocatalytic converters with metallic carriers

Temp. (K)	Time (s)	Frequency (Hz)	Mass of catalyst (g)		Platinum analysis (wt.%)		Content of Pt removed from catalysts (wt.%)
			Initial	Final	Initial	Final	
673	600	300	86.41	238.90	0.12	0.01	76
			105.77	238.92	0.12	-	100
			96.12	279.06	0.12	0.0026	87
	1200		92.36	253.09	0.12	0.0074	83
			115.90	260.29	0.12	-	100
			95.50	249.93	0.12	0.005	89
673	600	200	113.28	239.49	0.44	0.07	67
			103.45	238.85	0.44	0.01	94
			102.13	182.97	0.44	0.0275	89
	1200		96.39	281.75	0.44	0.019	87
			88.86	295.00	0.44	0.035	80
			82.47	276.67	0.44	0.036	81
673	600	100	93.97	291.42	0.31	0.0087	92
			94.40	241.60	0.31	0.008	93
			75.37	229.14	0.31	0.006	94
	1200		119.90	291.71	0.31	0.021	81
			97.22	296.23	0.31	0.0017	92
			91.67	177.15	0.31	-	100

The frequency that generates a high rate of liquid metal in the duct (higher) is disadvantageous because of the difficulty in wetting the capillary catalyst and problems with splashing of liquid lead. The main aim of the experiments was to remove the platinum from catalyst, which must still be obtained from this alloy. It will probably reduce the efficiency of the process.

4. CONCLUSIONS

In the nearest future the demand for precious metals in the industry will be constantly increasing because of the successive development of automotive industry, which mostly bases on using platinum group metals. Recycling of precious metals is very profitable both ecologically (reduction of energy, reduction of environmental pollution, saving natural resources) and economically (stabilization of metals prices on the market) [20]. The most of precious metals are recovered during recycling process of spent auto catalytic reactor. Majority of them consist of ceramic carrier, only 4% of total catalytic converters have metallic carriers, but in the future this group of catalyst should be increased and will need to reclaimed. In that case the

technologies using for recovering platinum from auto catalyst with ceramic carrier are not applied. Thus, there is need to find simple and efficient method of recovery precious metals from that kind of waste. Presented technology enables to recovery platinum group metals from catalyst with metallic carriers by means of collecting them in the liquid lead. In the process are used magneto-hydro-dynamic phenomena to intensify the process.

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