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THE IMPORTANCE OF RECOVERY OF PGMS FROM CATALYSTS – A CASE STUDY OF RECYCLING NETWORK IN POLAND

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Abstract

Combustion engines are the main driving force of passenger cars, trucks or buses. Engines burn fuels, and as a side effect, release many pollutions to the atmosphere. Car manufacturers had been aware of a need of lowering the amount of exhaust fumes. This brought on the market the first catalytic converters. Nowadays automobile catalyst manufacturing is the largest sector of demand of PGMs (mainly platinum, palladium and rhodium), and unfortunately consumption and future demand of there critical metals is getting higher.

Over the past two decades, most countries around the world have developed and implement solutions that would minimize the impact of the growing number of cars on the environment. One solution contributing to this is the organisation of an end-of-life car collection and recycling network, which is now an integral part of automotive industry. The main drivers for the development of such network were stricter environmental regulations and economic conditions.

The development of recycling is also becoming more popular in Poland. However, catalyst recycling system is still not transparent to all stakeholders. Due to the huge variety of catalysts and their different structure and composition of elements from the PGMs group, the valuation of their price before they are recycled is not obvious. This raises a lot of controversy and does not inspire trust among those who recycle their catalysts.

The aim of this work is to show how the management of used catalytic converters looks like in Poland and how developed is network of catalysts recycling in Poland. At the same time this will show how important it is in terms of a circular economy and the recovery of valuable raw materials from a group of PGMs.

Keywords: **Catalysts; Recycling; PGMs recovery; Platinum; Palladium; Rhodium.**

1. INTRODUCTION

To neutralize harmful emissions and meet their limits imposed by legislations the automotive catalytic converters (automotive catalysts) started being used in the exhaust system of the car in mid-1970s in the USA and have been used since then [1]. Today, manufacturing of them is the largest sector of demand of platinum group metals due to their stability, activity and selectivity [2]. They are porous, ceramic materials in which PGMs (Platinum Group Metals) are used to decrease the amount of exhaust gases [3]. They convert CO and CHx to CO_2 and H_2O. There is also NO_x in the exhaust gases. The rhodium in the catalyst reduces the NO_x to N_2 [4]. These metals are in automotive catalysts and due to increasing demand for precious metals and that the extraction of them is a costly process, it is worth recovering them during recycling of used catalysts [5]. To make these recovery processes profitable with high cost effectiveness, over 90% of platinum and other PGMs metals needs to be recovered [6]. What is more, the necessity of recycling is forced with the EU end-of-life vehicle legislation. In particular, the Directive on End of Life Vehicles (2000/53/EC) aims both to reduce the total volume of waste at landfills and to increase the share of produced cars made from recovered materials [7]. The directive made the manufactures responsible for the collection and scrapping of cars since January of 2007 and wants for the weigh proportion of the car that is recycled/reused to reach 85% and reused/recovered to reach 95% [8].

Since the automotive catalysts have started to be used, the demand for platinum group metals has dominated the market for platinum and rhodium [9]. In 1989 the USA consumed around 32 094 kg of platinum group metals with 6594 kg recovered. In 1997, annual demand for PGMs in this sector reached level of 120 000kg (52 000kg for platinum, 65 000 kg of palladium and 1000kg of rhodium) [10]. Nowadays, we can talk about the demand for PGMs in this sector of about 422 700 kg (90 600kg for platinum, 301 000 kg for palladium and 31 000 kg for rhodium) (data for 2019) [11]. Spent catalysts from cars have about 1kg of PGMs per 1000 kg of catalyst [12]. Although in first 20 years of using catalysts in cars it consumed more than 568 000kg of PGMs (just in the USA) and legislations there (as well as in many other countries) requires the removal of catalysts before crushing the scrap vehicles, only 56 800kg of PGMs have been recovered. In 2019 the amount of 149 800 kg of PGMs was recovered [13].

Different sizes of automotive catalysts contain different amounts of platinum group metals used for catalytic materials, usually the ranges are: 3–7g of Pt, 1.5–5.0g of Pd and 0.8–1.5g of Rh [14]. However, this consumption corresponds to amounts of 50% of globally produced platinum, 80% of globally produced palladium and 80% globally produced rhodium. This causes that automotive catalytic converters are a very important secondary source of PGMs [15].

With the development of the car industry, catalysts for automobiles cover the largest market share of platinum group metals with the consumption of Pt, Pd and Rh over 45%, 67% and 85% of their global demand in 2016, respectively [16]. The world reserves of PGMs are very rare and scarce (only about 69 000 Mg) and 99% of them are in South Africa, Canada, Russia, America and Zimbabwe. The concentration of PGMs in these sources is very low, usually in the range between 2 and 10 ppm (g/t) and usually are obtained as coproducts. In South Africa, for example, there have been many challenges facing the mining industry. Current exploitation decreased worldwide. In the Bushveld Complex, it has been noted that the ore grade has decreased from 2.8 g/t to 0.7 g/t–1.4 g/t [17]. With the increase of car industry needs, in the long-term, these resources will not meet them. It is especially because of their rapid depletion of high-grade and low-grade ores and that remaining ones have low concentration what makes mining process unprofitable from both economic and environmental perspectives [18]. What is more, other countries suffer from lack of PGMs and have to overcome serious supply risk. Recently, the number of discarded cars has increased and what follows, more than 80 000 Mg of spent auto-catalysts are available in the world to be recycled, and in addition, these secondary sources have a higher concentration of PGMs, that can be extracted, than natural ores. The change between The Euro 1 and Euro 4 standards shows, that the average PGMs loading in a 1.4–2 l gasoline vehicle rise from the level of 2.04 g/car to 3.99 g/car [19]. It illustrates the importance of recycling of catalytic converters and its impact on PGM market. These aspects make the primary producers economically disruptive. Together with catalysts' limited lifetime, it caused that spent catalysts has become the most significant source of secondary PGMs but to estimate the efficiency and profitability of a extraction procedure of metal from catalytic converters substrates, it is obligatory to know their concentration in the original sample. Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) is widely used to determine the PGMs in samples [20].

There are many secondary sources for PGMs, e.g. jewelry and refinery sweeps and cuttings, but recycling from autocatalytic converters is the most effective, taking under consideration the global production of auto-catalysts compared with other sectors. Their economic viability depends, however, on several factors. They include sample homogeneity, PGMs and the rest of metals loading content, supporting material, and pre-concentration. The most commonly used techniques for recovery precious metals are pyrometallurgical and hydrometallurgical processes and the combination of these methods allows to make a closed production cycle and get a high concentration of PGMs for further refining so they can be considered as environmentally friendly and economically profitable [21].

The development of recycling is becoming more and more popular. However, catalyst recycling system is still not transparent to all stakeholders especially in Poland. Due to the huge variety of catalysts and their different structure and composition of elements from the PGM group, the valuation of their value before they are recycled is not obvious. This raises a lot of controversy and does not inspire trust among those who recycle catalysts. Therefore, apart from the recycling technology itself, it is important for the company to have a transparent way of testing the catalysts, which will determine the value of the product in an equal way [22].

Novelty of the paper is first of all the analysis of the Polish catalytic converters market, which is still developing and its subject is poorly described in the literature. The Polish catalytic converters recycling market has still a great chance to develop in many regions of Poland. Moreover, the subject of recycling catalysts from secondary sources perfectly fits the model of Circular Economy which is being developed nowadays. Such a policy of catalyst management from spend vehicles is something that will be required in the near future. Also Platinum Group Metals are on the list of Critical Raw Materials which means that they are strategic for functioning and economic development of the EU. That's why recovery of PGMs and development of catalysts recycling market is so important.

2. LCA ANALYSIS

In 2020, the International Platinum Group Metals association prepared the Life Cycle Assessment study on platinum, palladium, and rhodium metals, which are the most relevant for catalytic converters. The analysis was conducted based on 2017 and concerned primary and secondary production of PGMs.

The LCA quantified the environmental impact of primary and secondary production of platinum group metals (PGMs) and is based on the "cradle-to-gate" approach which covers processes within the life cycle of the product from the extraction of the raw materials to the finished product.

The study focused on quantifying the environmental impact of the average production of PGMs, the fabrication of catalysts using PGMs as well as the use of these catalytic converters in a EURO 5 vehicle system over a lifetime of 160,000 km. This enabled the evaluation of the benefits of PGMs during the vehicle's lifetime.

The results of the analysis are presented in the table 1 and table 2. Table 1 shows the results for primary production of platinum group metals (Platinum, Palladium and Rhodium), and the Table 2 presents secondary production results [23].

The impact potentials for the primary production of 1 g of platinum, 1 g of palladium and 1 g of rhodium are presented in six categories (Global Warming Potential, Primary Energy Demand, Acidification Potential, Eutropication Potential, Photochemical Ozon Creation Potential, Blue Water Consumption).

The results show that the production of secondary PGM causes a much lower environmental impact in all 6 analyzed impact categories. It is because the power consumption during mining and ore beneficiation has been identified as the major impact of the production of PGMs on the environment. The main reason is the low grade of ore, difficult mining conditions as well as the power energy mix which was assumed to be largely based on fossil fuels.

Table 1.
Result for the LCA of the primary production of 1g of Platinium Group Metals

Impact Category	Unit	Platinum	Palladium	Rhodium
Global Warming Potential	kg CO_2-eq/g	41.8	25.3	36.9
Primary Energy Demand	MJ/g	464.6	318.9	414.2
Acidification Potential	kg SO_2-eq/g	0.934	1,595	0.412
Eutrophication Potential	kg PO_4-eq/g	0.025	0.013	0.020
Photochemical Ozone Creation Potential	kg Ethene-eq/g	0.041	0.066	0.02
Blue Water Consumption	kg/g	265.1	172.5	242.8

Table 2.
Result for the LCA for the secondary production of 1g of Platinium Group Metals

Impact Category	Unit	Platinum	Palladium	Rhodium
Global Warming Potential	kg CO_2-eq/g	0.63	0.72	0.84
Primary Energy Demand	MJ/g	10.1	11.7	12.6
Acidification Potential	kg SO_2-eq/g	0.0029	0.0035	0.0043
Eutrophication Potential	kg PO_4-eq/g	0.00035	0.00039	0.00046
Photochemical Ozone Creation Potential	kg Ethene-eq/g	0.00013	0.00016	0.00018
Blue Water Consumption	kg/g	6.039	7.035	8.622

That is why, secondary production has a much lower impact than primary production. This is expected for various reasons, including the vast difference in the concentration of PGMs between primary and secondary sources.

3. METHODS FOR RECYCLING THE AUTOMOTIVE CATALYSTS

Auto-catalysts recycling has raised great attention for the consideration of environmental and economic benefits. It has been widely explored via different ways to recover PGMs using pyro and hydrometallurgical methods [24]. Hydrometallurgical processes are inefficient, connected with formation of new wastes and involve PGMs leaching, precipitation, solvent extraction, ion exchange and electrolysis [25]. Some of the leaching systems like aqua regia and cyanide have been forbidden, some of them like application of chlorination leaching has been limited. It has been done because of generating harmful pollutants and low efficiency in case of chlorination leaching (especially for Pt and Rh, mainly because of their low concentration) [26]. In the pyrometallurgical process, which is a simple and efficient way for the high enrichment of PGMs from spent automotive catalysts with degree of extraction up to 99%, metals including lead, copper, nickel and iron are used [27]. Other than PGMs like aluminum, magnesium and cerium are transferred to the slag. They do not produce harmful compounds [28]. Nevertheless, there are huge redistribution costs which influence cost-effectiveness of this technology reducing it, along with high energy consumption and gaseous emissions that stay questionable [29]. Improving the technology to make it optimal and energy-saving is still very important from the economic point of view [30]. Table 3 shows the recovery efficiencies of PGMs by different kinds of melting methods.

Table 3.
The recovery efficiencies of PGMs by different kinds of melting methods

Collector	Temperature	Recovery Efficiencies	Scale
Lead	1 130°C	Pt/Pd>98%, Rh>95%	Industrial
Copper	1 130°C	PGMs>95%	Industrial
Copper	1 150°C	Pt 90%, Pd, Rh 82%	Lab
Copper	1 150°C	PGMs>84%	Lab
Copper	1 150°C	Pd>97%	Lab
Iron plasma melting	>1 600°C	Pt, Pd>98%, Rh>97%	Industrial
Iron	1 560°C	PGMs>90%	Industrial
Ni_2S_3-CuS	1 200°C	Rh 94%	Lab
Ni_2S_3-CuS	1 050°C	Pt 90%, Pd 93%, Rh 88%	Lab

Source: own work based on [13]

An iron plasma melting is a very promising and economical collector for concentrating PGMs from spent auto-catalysts. The recovery efficiencies are high, however, the operation temperature is between 1600°C and 2000°C and it is difficult to keep the properties of materials in such high temperatures. What is more, it reduces Si and helps the formation of Fe-Si alloy, which are hard to dissolve.

While using these methods (pyro and hydro), recovery of other than platinum group metals has never attracted enough attention, even though they cover over 90% of volume of spent material. Aluminum and magnesium are not that valuable as the rare metals like cerium, but they are important due to their common applicability. Their recycling and recovering can be profitable if it is done properly. In other case it may cause environmental problems with landfill disposal.

4. CASE STUDY OF CATALYSTS RECYCLING NETWORK IN POLAND – COMPARISION WITH CHOSEN COMPANIES IN THE WORLD

According to Statistical Central Office in Poland there were 30 million of cars on Polish roads in 2018. Data base form June 2018 indicates, that 29 656 238 all kinds of vehicles have been registered (of which 3 338 166 trucks and 1 428 299 motorcycles registered). To compare a decade ago, total number of cars in Poland was estimated on 22 024 697. The largest group was passenger car. The same year, over 1 000 000 used cars were imported, additionally 523 000 new cars have been sold. At the end of the first half of 2018, the amount of population in Poland was estimated at 38 413 thousand people. Taking under consideration those numbers, it is easy to estimate, that we have 1.7 car per person in Poland [31].

Before PGMs can be recoved from catalysts, the car has to be recycled and taken apart in car's disassembly stations. Based on market research and interview with companies most of car's disassembly stations handle over used catalysts to D.S AUTO form Chrzanów, which deliver it for further processing to Unimetal Recycling one of the largest processing company of catalyst in Poland.

After disassembly catalysts are going to recycling companies to separate parts of catalysts and take out the monolith containing PGMs. Figure 1 shows the map with catalyst recycling companies in Poland. These are companies which deal mainly with buying catalysts from spent vehicles and recovery of monolith from catalysts from which PGMs are then recovered.

The area of analysis shows that we can identify 10 recycling companies and they are mainly located in the southern part of Poland and still there are a lot of opportunities to develop recycling of catalysts in northern part. Also in-depth review with this companies showed that they have a poorly developed suppliers network and lack sophisticated facilities to analyze catalysts during purchase like for example laboratories and own software. Only Unimetal Recycling have such equipment and thanks to this they become the best developed company in Poland.

Figure 1.
Location of catalyst recycling companies in Poland

4.1 Overview of chosen catalyst recyclers worldwide

After analysing the way foreign companies work, it is easy to see that catalyst recycling is mainly just a part of their recycling activities. That is why on the worldwide market there are some global companies like for example Elemental Holding dealing with urban mining and recycling. Whereas, Unimetal Recycling is focused strictly on automotive catalyst recycling. Activities of Polish companies were compared with chosen recycling companies from abroad (Table 4).

Table 4.
The profile of chosen recycling companies

	Company name	Scope	Range	Source
1	Elemental Holding	Elemental Holding S.A. invests in entities dealing with urban mining and recycling. Companies belonging to the company operate within the framework of four business areas: recycling of spent automotive catalysts (SAC), recycling of waste electrical and electronic equipment (WEEE), recycling of printed circuit boards (PCB), recycling of non-ferrous metal scrap (non- ferrous).	Worldwide	https://elemental.biz/en/
2	Umicore	It is a global materials technology and recycling Group. Activities are organized in three business groups: Catalysis, Energy and Surface Technologies and Recycling.	Worldwide	https://www.umicore.com/
3	Johnson Matthey	They are organized into four areas, aligned to the needs of customers and the global challenges. They are structured into the groups of Clean Air, Efficient Natural Resources, Health, New Markets.	Worldwide	www.matthey.com
4	Remondis PMR B.V.	It is divided into three main groups – recycling, services and water. Many of REMONDIS' companies, therefore, provide services from two or even all three areas.	Worldwide	https://www.remondis-katalysator-recycling.de/en/
5	MONOLITHOS	In addition to recycling, the company deals with the production of catalysts.	Greece	https://www.monolithos-catalysts.gr/en/

5. CONCLUSIONS

The paper discusses the polish market of catalysts recycling and the importance of recovery of PGMs from them. The analysis of this topic allowed for the specification of aspects, which are summarized below.

Challenges standing in front of the catalyst recycling market in Poland include:

1] Most studies and expert opinions predict that future demand for PGMs will increase.

2] This will result in a supply deficiency of these metals if there is no recycling from secondary sources.

3] The main factors that affect the development of recycling network design are regulations and economic determinants, but also the decreasing number of primary sources.

4] In Poland, the catalyst recycling system is on development stage, but there is a significant upward trend, mainly due to the EU circular economy policy.

5] There is no official network or association in Poland, but certain companies are members of the Waste Recycling and Management Cluster.

6] Due to frequent legal and technological changes, the market is not transparent and prices of used catalytic converters vary significantly.

7] It is important for companies to have a transparent catalyst analysis method that clearly and fairly indicates the value of the products

Some opportunities that can be helpful for the development of catalyst recycling market in Poland are summarized below:

1] Since catalysts mainly contain a combination of three metals, which are Pt, Pd and Rh, the production of automotive catalysts is the largest sector of PGM demand and consumption.

2] It is possible that the financial pressure caused by the COVID-19 crisis will push car companies to rethink possibilities for reducing the cost of their aftertreatment systems.

3] Good cooperation in the value chain between disassembly stations and recycling companies also creates a demand for joint R&D projects, close cooperation with universities and enables an increase in economic and resource efficiency.

4] Development of recycling of catalysts in Poland perfectly fits into the circular economy. Such initiatives may be supported in the future by the European Commission within different research and development projects.

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