EXTRACTION AND PURIFICATION OF PGM SOLUTIONS OBTAINED FROM METALLURGICAL TREATMENT OF USED AUTOMOTIVE CATALYTIC CONVERTERS

[1]Mariola SATERNUS, [1]Agnieszka FORNALCZYK, [2]Władysław GĄSIOR, [2]Adam DĘBSKI, [2]Sylwia TERLICKA

[1]Silesian University of Technology, Faculty of Materials Engineering and Metallurgy, Gliwice, Poland, EU, mariola.saternus@polsl.pl

[2]Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Cracow, Poland, EU, w.gasior@imim.pl

https://doi.org/10.37904/metal.2019.759

Abstract

Today, the demand for platinum is constantly growing. It is related to its use as a catalyst mainly in the production of cars. Car production has been increased year by year, consequently the used catalytic converters is the biggest problem. On the one hand, it is a waste, on the other it is also a source of valuable and precious metals. Thus, the automotive catalytic converter is treated hydrometallurgically and pyrometallurgically to recover valuable metals. However, this process is not so easy. After obtaining solutions containing precious metals from hydrometallurgical methods or alloys of the metal collector with PGM (Platinum Group Metals) from pyrometallurgical methods there should be separation and purification of PGM. These processes are difficult and complicated due to their resistance to chemicals attack and the ability to create many chemical compounds. The article presents and discusses the possible methods of separation and purification of platinum and PGM (e.g. liquid-liquid extraction, adsorption, ion exchange).

Keywords: Automotive catalytic converter, platinum recovery, metallurgical treatment, PGM separation

1. INTRODUCTION

Today, the use of precious metals, such as silver, platinum, rhodium, palladium, is constantly growing due to their catalytic properties [1]. Platinum is particularly popular, but the natural resources of platinum group metals (PGM) are limited and shrinking. The availability of PGM in the future is questionable considering their high demand in recent years (see **Table 1**); social, economic, environmental as well as political aspects connected with their production (see **Table 2**).

Table 1 Supply, demand and recycling of platinum, palladium and rhodium [2]

Metal	**Supply** (kg)	**Demand** (kg)	**Recycling** (kg)
Pt	169,400	222,400	56,000
Pd	187,020	287,800	82,950
Rh	21,260	29,710	9,180

Table 2 Primary production of palladium and platinum in 2017 and 2018 [3]

Metal	**Year**	**Production** (kg)						
		Total	USA	Canada	Russia	RSA	Zimbabwe	Other
Pd	2017	225,000	13,600	17,000	85,200	86,800	12,000	10,800
	2018	210,000	14,000	17,000	85,000	68,000	12,000	11,000
Pt	2017	199,000	3,980	9,500	21,800	143,000	14,000	6,510
	2018	160,000	4,100	9,500	21,000	111,000	14,000	6,100

To almost exclusive producers of primary platinum belongs South Africa - nearly 70 %. However, in 2018 the production is decreased compared to 2017 mainly due to the reduction of employment and mine-shaft closures. Over the next two to three years, this production in South Africa is expected to decline as one of the leading PGM companies have announced a 13,000 job reduction in part of its mine [4]. In the case of palladium, the situation is better due to the fact that production takes place not only in South Africa, but also in Russia (40 %), Canada (8 %) and USA (7 %). That is why waste materials are becoming a valuable source of platinum group metals. An important advantage of such materials is the high concentration level compared to the basic sources [4-6], therefore the recycling of PGM from the spent automotive catalytic converters becomes a necessity.

2. METALLURGICAL TREATMENT OF USED AUTOMOTIVE CATALYTIC CONVERTERS

There are many methods used for PGM recycling from used automotive catalytic converters based on pyrometallurgical and hydrometallurgical treatment. In a pyrometallurgical manner, catalytic converter carriers are smelted with various metals (called collector metals), such as copper, iron or lead [7-12]; platinum went to the metal collector, while the alumina carrier formed slag. **Figure 1a** shows a typical pyrometallurgical treatment of used automotive catalytic converters with copper as a metal collector - the produced alloy is then electrorefined to separate platinum group metals. **Figure 1b** presents a diagram of a modified metal collector method using a magneto-hydro-dynamic pump for flushing platinum from a catalytic converters and creating a closed loop. In addition, the whole carriers are used in this method, whereas in the copper collector method the carriers are ground, milled and homogenized. In industry pyrometallurgical methods are used [13] because are effective, but on the other hand, they are slow and energy-consuming.

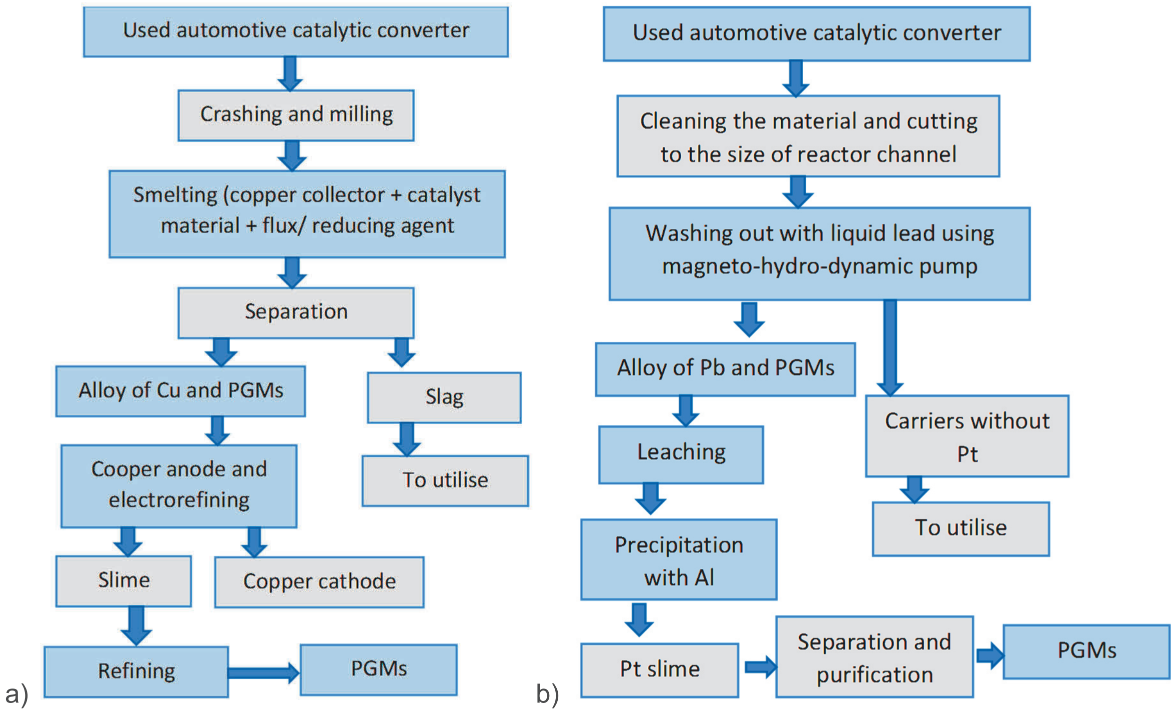

Figure 1 Pyrometallurgical treatment of used automotive catalytic converters: a) copper as metal collector, b) modified method with magneto-hydro-dynamic pump and lead as metal collector [7-9]

The second method is hydrometallurgical treatment (commonly used for the recovery of non-ferrous metals from waste materials, such as catalyst or printed circuit boards [14-16]). They are divided into two groups:

- used directly (feed digestion) - leaching in various media, such as chlorine, chlorides, aqua regia, with addition of H_2O_2, H_2O_2 and sulphuric acid, cupric ions [17-20] - see **Figure 2a,**
- used after pretreatment methods (e.g. thermal pretreatment) or pyrometallurgical methods and leaching - solution purification with metals separation using solvent extraction.

Hydrometallurgical methods in comparison with pyrometallurgical methods consume less energy, but the recycling efficiency is not so high and a large amount of waste solutions is also generated. In both cases it is necessary to further process the product obtained: pyrometallurgical alloy of a metal collector with platinum group metals and hydrometallurgical solutions with PGM. The platinum-copper alloy may be electrorefined for platinum recycling; whereas precipitation, extraction methods or ion-exchange can be applied for separation and purification of PGM from solutions [21-25].

3. SEPARATION AND PURIFICATION OF PGM SOLUTION

As mentioned earlier, many researchers have investigated the extraction and separation of platinum group metal from aqueous solutions, but this process is still difficult and complicated due to the similarity of physical and chemical properties of PGM. Therefore, they are resistant to chemical attack and at the same time have the ability to create many chemical compounds in chloride solutions. Various methods are applied as precipitation, ion-exchange and adsorption or solvent extraction (liquid-liquid extraction - an aqueous solution of PGM ions and organic solution of an extractant). Solvent extraction is one of the most important and often proposed techniques for the selective recovery of PGM ions from various solutions. **Figure 2b** shows the solvent extraction scheme used for metal recovery. **Table 3** shows the main characteristics of the various methods used to extract and separate PGM, while **Table 4** presents typical commercial extractants used for the recovery of platinum group metals from catalyst leaching solutions. **Figure 3** shows a scheme of Pt(IV), Pd(II), Rh(III) and Ir(IV) separation from hydrochloric acid solutions by solvent extractions.

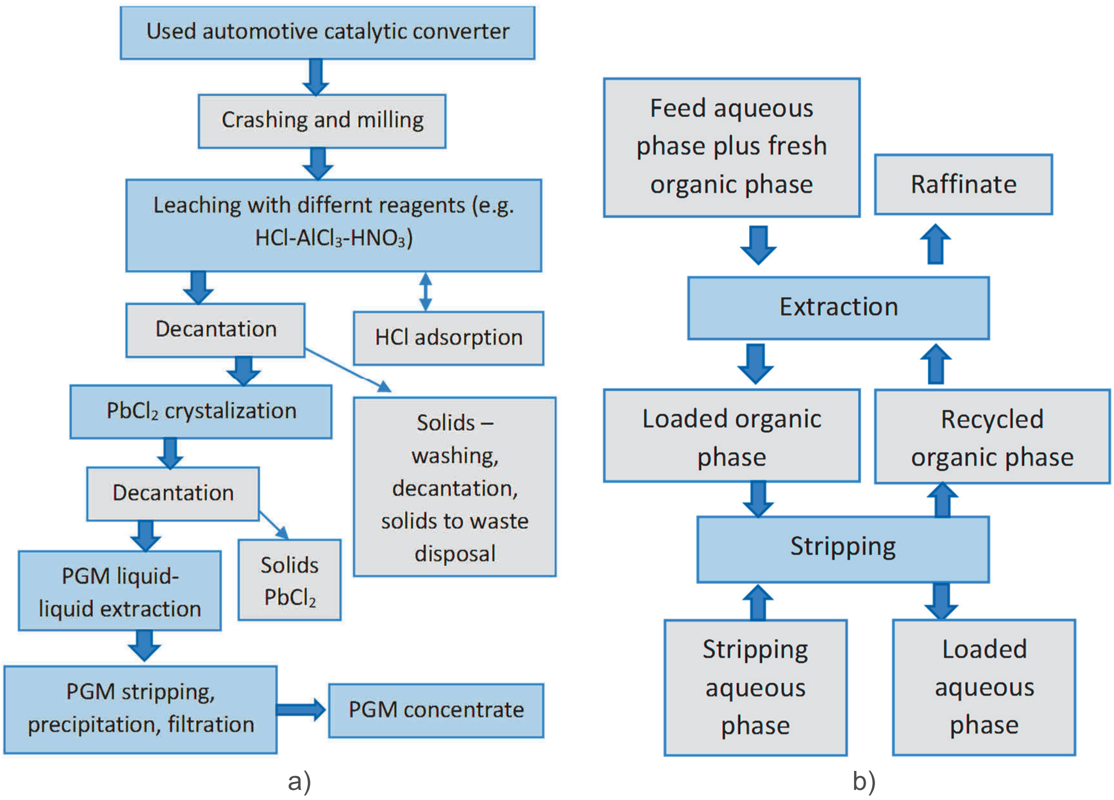

Figure 2 a) Hydrometallurgical treatment of used automotive catalytic converters, b) solvent extraction scheme applied for platinum group metals recovery [22,23]

Table 3 Characteristics of methods used for extraction and separation of PGMs from aqueous solutions [20,22,23]

Method	Characteristics
Precipitation	Addition of different chemical reagents such as zinc or aluminium powder, ammonium chloride which gives Pt precipitate, leaving the accompanying platinum group metals in solution.
Adsorption and ion-exchange	Anion-exchange process took place only on the surface of the adsorbent, therefore the loading or the exchange capacity of adsorbents is relatively smaller when compared with ion-exchange resins; in adsorption the most important parameters are the characteristics of surface and the pores of adsorbents; ion-exchange relies on passing a metal ion-containing solution through bed of solid ion-exchange resin: metal ions are exchanged with the ions of the resin carrying accessible cations, anions or amphoteric ions, then the pregnant resin is washed with another aqueous solution to elute the adsorbed metal ions and to regenerate resin; typical adsorbents and resins used for removal Pd(II) and Pt(IV): Lewatit TP 214, Amberlite IRA-478RF, Amberlite XAD-1180, Amberlite XAD-7, Dowex MSA-1, Purolite S-984, Purolite A-830, MP-102, TAPEHA, activated C, alumina nanopowder.
Solvent extraction	Includes an extraction and a stripping stage, in extraction the feed aqueous phase contacts with an efficient and selective extractants, the loaded solvent is then equilibrated with a stripping aqueous medium, which causes the transfer of the metal to the new aqueous solution.

Table 4 Typical commercial extractants applied for platinum group metals recovery from catalyst leaching solutions [20,22-30]

Extractants	Comments
Alamine 300	Separation of Pt(IV) and Pd(II) from chloride solution using Alamine 300 at 0.001 - 0.01M in presence of 0.5M HCl in the aqueous phase, 99.99 % Pt and 98 % Pd can be separated.
Alamine 308	Typical for Pd(II), poorly selective over Pt(IV) and other metals.
Alamine 336	Extraction of ruthenium about 72 %, 5 % solution of Alamine 336 in kerosene was used for co-extraction of Pt(IV) and Fe(III), 0.5M thiourea and 0.1 M HCl solution were used for stripping of these metals, purity of Pd (II) and Pt(IV) were 99.7 %.
LIX841	Selective for Pd(II) for leaches at pH 2; separation of Pt(IV) and Pd(II) from associated metals such as Fe(III), Cu(II), Ni(II), Zn(II), Al(III) by 0.5 % LIX841 in kerosene.
Cyanex 921	Pd(II), Pt(IV) and Rh(III) co-extracted, but separated in the presence of tin(II) chloride, rapid for the separation of Pt, Pd and Rh with the recovery efficiency about 99.8 %.
Cyanex 923	Extraction of Pt(IV) from HCl: 70-100 %, from sulfuric or nitric acid: 55 %, extraction of Pd(II) from HNO_3: 70 %, extraction of Rh(III) from HNO_3: 35 %.
Cyanex 471x	Selective Pd(II) separation from low concentrated HCl; extraction of Pd(II) decreases with increasing HNO_3 concentration up to 2M then becomes constant from 92 % to 80 %.
TBP and Aliquat 336	Pd(II) and Pt(IV) co-extracted; selective and quantitative Pd(II) extraction even at the lowest extractant concentration, 99.95 % Pd (II) separation from raffinate; in second stage 99.7 % Pt(IV) extraction from Pd-Fe free raffinate at 0.011M Aliquat 336; TBP in kerosene gives extraction of Pt(IV) about 80 %, Rh(III) and Ir(III) remain in raffinate.
Cyphos 101 IL (ionic liquid)	Selective Pd(II) separation from low concentrated HCl, in pure form able to extract Pd(II) from 1-8M HCl; extraction of Pd(II) from 45 % to 97 % depending on HCl concentration.
Cyphos 102 IL	Able to extract Pd(II) from 1-8M HCl, with Pt(IV) co-extraction.

4. CONCLUSION

Methods for recovering PGM from used automotive catalytic converters can be based on pyro- or hydrometallurgical processes. Both have advantages or disadvantages, pyrometallurgical processes depend on energy consumption; however, it can give large-scale industrial production. Hydrometallurgical methods are more effective, but generate a lot of waste. On the other hand, it is still more ecological than pyrometallurgy and more flexible in terms of composition and grade of the processed materials. Both processes, however, give products that should be further separated, purified or concentrated. Solvent extraction is a conventional operation for the treatment of leaching solutions when hydrometallurgical recycling is considered. In the case of pyrometallurgical treatment, the obtained alloy should be directly applicable (it will be the best solution) or hydrometallurgically treated to separate the platinum and other precious metals.

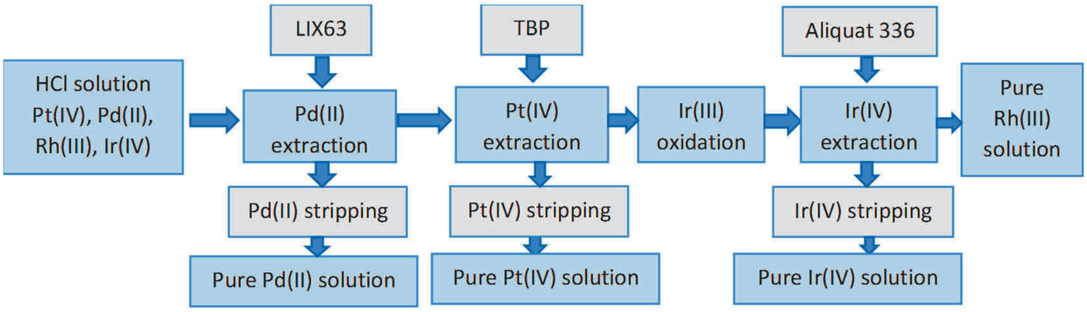

Figure 3 Diagram of the separation of Pt(IV), Pd(II), Rh(III) and Ir(IV) ions from hydrochloric acid solutions by solvent extractions [28]

ACKNOWLEDGEMENTS

The authors gratefully acknowledged the support from the National Science Centre Poland (NCN) within the research project 2017/27/B/ST8/01464.

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