

Review

Platinum Group Metals: Green Recovery from Spent Auto-Catalysts and Reuse in New Catalysts—A Review

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Abstract: This manuscript reviews the current trends in the recovery of Platinum Group Metals (PGMs) from end-of-life autocatalysts and the aims of the recently funded Marie Skłodowska-Curie Project “Chemistry of Platinum Group Metals-CHemPGM” towards the greening of PGMs recovery processes and the reusing of recovered PGMs for preparation of new catalysts. Together with the analysis of the state of the art recovery of PGMs from spent autocatalysts through pyrometallurgical and hydrometallurgical routes and the recent trends in reducing their environmental impact, also emerging sustainable and green technologies are analyzed. Particular focus is given on the mechanochemical processing as a promising sustainable route not only for the pretreatment of waste materials but also for direct PGMs leaching. The present review identifies also the trends in catalysts for carbon neutrality and the few recent efforts in developing PGM-based catalysts starting directly from the liquor of the leach solutions of spent catalysts envisaging therefore a possible key to close PGMs loop in a more efficient and sustainable way.

Keywords: platinum group metals; PGMs recovery; PGMs reuse; mechanochemistry; PGM-based catalysts



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1. Introduction

1.1. Platinum Group Metals

The Platinum group metals (PGMs) consists of six chemically similar elements, sometimes further classified into light (ruthenium (Ru), rhodium (Rh) and palladium (Pd)) and heavy (iridium (Ir), osmium (Os) and platinum (Pt)). The chemistry of these elements is similar being based on 4d electron shells (Ru, Rh, and Pd) or 5d shells (Os, Ir, and Pt) [1]. Most of the world’s PGMs are produced from two types of deposits: PGM-dominated deposits where PGMs are the main product and Ni–Cu sulfide deposits where PGMs are the by-product [2]. In the former case their production is concentrated in South Africa, Zimbabwe and USA while in the latter case in Canada and Russia [3].

Since 2011, PGMs have been included in the list of critical raw materials for the EU [4] because they represent metals which are strategic for the EU economy and at high supply risk.

PGMs supply risk, however, is not only an EU concern. Recently, also the US has been considering PGMs as critical for the energy sector recognizing their strategic role in tomorrow’s decarbonized economy [5]. PGMs are in fact employed as catalysts in many

decarbonization and energy technologies, including catalytic converters, fuel cells, thermal catalytic reactors and electrolyzers [5,6].

Figure 1 reports the flow chart of PGMs prices over the last five years, expressed in USD dollars/troy oz, where 1 troy oz equals 0.0311035 kg [7]. The Pd price increase, starting in 2020, is attributable to the suspension of Nornickel's Taimyrsky and Oktyabrsky mines due to severe flooding [8], resulting in a 28% reduction in palladium output.

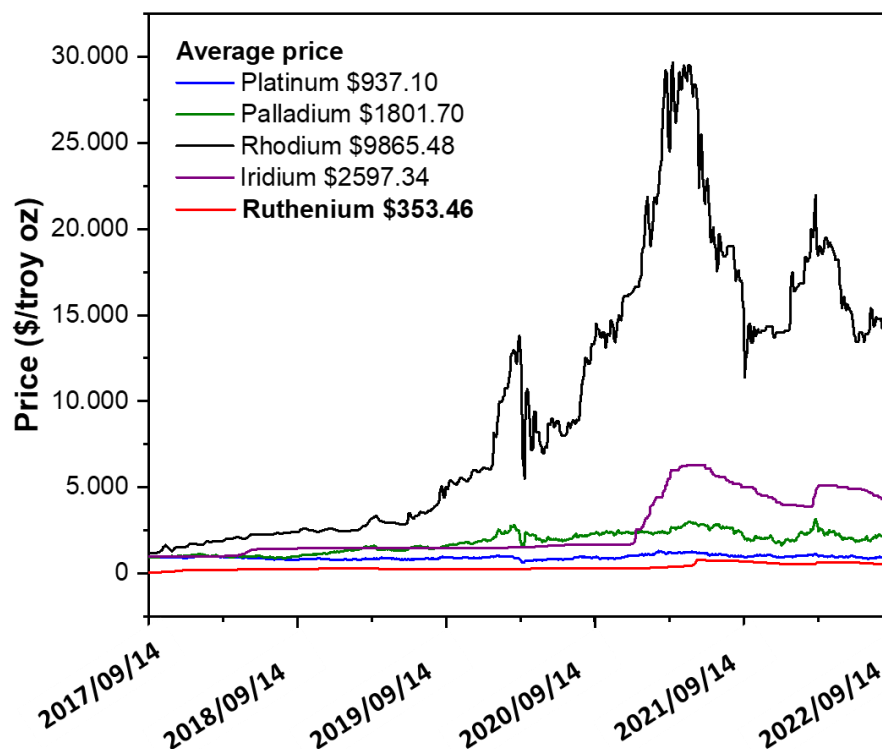


Figure 1. Flow chart of PGMs prices over the last five years. Reprinted with permission from [7].

Rh is the most expensive among PGMs and its price is nowadays about 8 times higher than that of gold. Ru is instead the cheapest one. The high price of PGMs has pushed the development of efficient recycling processes worldwide rendering secondary resources such as spent automotive catalysts, electronic scraps and residues of primary production as valid alternatives to the primary ones. Among secondary resources, spent automotive catalysts (SACs) play a crucial role because they can deliver more than 57% of PGMs' European supply [9]. Processing 2 mg of spent automobile catalysts to recover PGMs can prevent the mining of 150 kg of their ores [10,11]. In addition, recovery of PGMs from secondary sources minimizes also waste disposal, limits power consumption and reduces environmental pollution: according to Fornalczyk and Saturnus, 1 kg of platinum from primary ores is obtained from processing 150 Mg of ores and generates 400 Mg waste, whereas the same amount of platinum can be recovered from recycling 2 Mg of SACs [12]. According to Saidani et al., the estimated required amount of energy and greenhouse gas emissions to produce 1 kg of platinum from primary ores in South African mines are 20 times higher than those used for recycling from secondary resources in European refining plants [13].

About 80% of the PGMs demand is in catalytic converters [10] where Pt is used both as an oxidation and as a reduction catalyst, Pd as an oxidation catalyst and Rh as a reduction catalyst [14]. While Pt and Pd can be interchanged, they cannot substitute Rh role in autocatalysts. PGMs are also used in light duty diesel engines. Pd substitution by Pt, which is low-price and abundant relative to Pd, has been investigated recently by many groups [15], especially because of Pd's increased price and the increased fuel quality (less sulfur).

Despite their positive role in controlling exhaust emissions, PGMs are known to be present in the urban environments together with the residual exhaust fumes, polluting therefore biosphere, soil, vegetation, river and marine environments.

This review reports about the most notable research trends in PGM-based catalysts, PGMs recycling from spent autocatalysts and reusing of recovered PGMs in new catalysts. With respect to the many already published papers on the topic, a special focus is given here on new emergent methods and especially on the application of mechanochemistry not only as an efficient pretreatment process of waste materials, but also as a new and green promising route for the leaching of spent autocatalysts. In addition, the few attempts reported in the literature to synthesize PGM-based catalysts directly starting from the liquor of the leach solutions are described. Both of the above mentioned issues are among the scopes of the Marie Curie Project “Chemistry of Platinum Group Metals-CHemPGM” whose efforts are devoted to secure and close the PGMs loop.

1.2. PGM-Based Catalysts

Catalysis is a key component in many industrial applications and PGMs play a fundamental role in many homogeneous and heterogeneous catalytic processes, as summarized in the review from Huges et al. [1]. Homogeneous catalysts offer advantages in terms of reactivity and stability due to their high solubility in reaction media, but they are difficult to recover. On the other hand, heterogeneous catalysts are less efficient but more easily to be recovered [16]. Table 1 reports the main precious metals (PMs) and supports used in heterogeneous catalysts for a wide range of applications.

Table 1. Heterogeneous catalysts: support, precious metal (PM) load and applications [17–19].

Catalyst Type Support	Application	Precious Metals	PM-Loading
Al ₂ O ₃ Al ₂ O ₃ zeolites SiO ₂ zeolites Al ₂ O ₃ (SiO ₂ , TiO ₂)	Oil-refining Reforming Isomerization Hydrocracking Gas to liquid (GTL)	Pt, Pt/Re, Pt/Ir Pt, Pt/Pd Pd, Pt Co+(Pt or Pd or Ru or Re)	0.02–1%
Actives carbon (powder)	Fine Chemicals Hydrogenation Oxidation Debenzylation Hydro-isomerisation Reduction	Pt–Zn Pt–Sn–In/Al ₂ O ₃ –Li Pt/Ni Pt–Cu Pt/C	0.5–10%
Cordierite monolith Ceramic pellet Metallic monolith SiC or cordierite	Automotive Catalysts Diesel particulate filter	Pt/Rh Pt/Pd/Rh Pt Pt/Pt Pt (gauze catalyst)	0.1–0.5%

A broader and more detailed PGMs utilization in various catalytic applications is reported in [1].

A modern three-way auto-catalyst contains a skeleton with a honeycomb structure made of cordierite (2MgO•2Al₂O₃•5SiO₂), which is coated with a thin layer of washcoat (90% γ-Al₂O₃), catalytic metals (PGMs) and other additives (oxides of Ce, Zr, La, Ni, Fe and alkaline earth metals) (Figure 2).

The proportion of PGMs in catalysts is dependent on several factors: the manufacturer, the characteristics of the vehicle, including the engine power, the weight of the vehicle, the type of fuel consumed by the vehicle (gasoline or diesel), as well as the required catalytic functions [15].

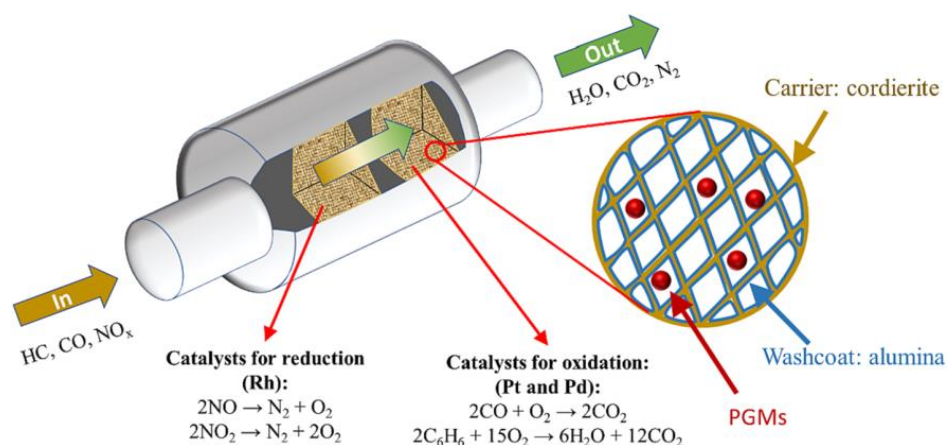


Figure 2. Scheme of automotive catalytic converter. Reprinted from [20], with permission from Elsevier, copyright 2023.

Through a series of oxidation reactions Pt and Pd convert CO and HC to CO₂ and H₂O, and the reduction of NO to N₂ is accomplished by Rh [14,21]. The catalytic efficiency of each element is influenced by several factors such as the engine temperatures, the type of fuel used, the quality of the fuel and the durability of the autocatalyst washcoat [22].

A three-way automotive catalytic converter it is considered to have between 3–7 g Pt, 1.5–5.0 g Pd and 0.8–1.5 g Rh [23].

The automotive catalyst industry in Europe had a large growth both due to the implementation of emission standards such as Euro 5 and Euro 6 and the adoption of a regulation in 2017 in which more reliable emission tests have been implemented such as Real driving Emissions (RDE) and World Harmonized Light Vehicle Test Procedure (WLTP) for the light motor vehicles [24–26].

Also, an increase in the demand for catalysts is expected due to the strict emission standards implemented by governments around the world. As an example, in China the regulations regarding emission control limits implemented by the State Environmental Protection Administration (SEPA) have become recently more stringent to reduce pollution [24].

Autocatalysts global market had a size of USD 12.45 billion in 2022 with a prevision of USD 18.98 billion by 2030 at a compound annual growth rate (CAGR) of 5.4% [24].

Auto market is actually dominated by internal combustion engine vehicles (ICEs) powered by fossil fuels, but to achieve carbon neutrality by 2050 there is the need of substituting the conventional fossil fuels across the different segments of the economy. To meet the goal of CO₂-neutral by 2050, starting from 2035 in Europe all the new cars that come on the market cannot emit any CO₂. Given that the life span of a car is about 15 years, we may predict that the source of PGMs from catalytic converters will last at least until 2050 for gasoline powered car. Catalytic converter, however, will continue to be on the marked for application in plug-in hybrid cars and even if automotive industry will move away from fossil fuels, the ICEs imprint will last still for decades.

To achieve carbon neutrality and realize the so-called “double-carbon” goal, two strategies to reach CO₂ emissions reduction can be adopted. The excess CO₂ may be removed by the atmosphere and converted into reusable value-added chemicals through an efficient transformation technology. The other strategy is to develop a clean and efficient energy conversion technology to produce green and environmentally friendly renewable energy, such as hydrogen, to effectively replace traditional fossil fuels and reduce CO₂ emissions. A recent review from Whang et al. deals with the description of the challenges and outlooks for future applications of single-atom catalysts in contributing toward carbon neutrality [27].

According to the International Energy Agency (IEA), about 6.6 million electric vehicles (EVs) were sold in 2021, and the trend is expected to increase in the next years towards a final transition from ICEs to EVs powered by batteries or H₂ (fuel cells.)

The near future trend for light vehicles is mostly towards battery-electric vehicles, because the total cost of ownership is lower than the hydrogen and e-fuels alternatives. However, because batteries are heavy, ships, planes or heavy-duty vehicles cannot easily be battery-powered and therefore hydrogen or e-fuels can be good alternative solutions [28].

Some EVs based on polymer electrolyte membrane fuel cells (PEMFC), phosphoric acid fuel cells (PAFC), direct methanol fuel cells (DMFC) and alkaline fuel cells (AFC) rely on the use of PGMs.

Despite Pt and Pd are not key components in a battery, next-generation lithium-ion battery technologies will probably need platinum and palladium to enhance overall battery performance [1,19,27,29]. Instead, the technologies for the production of green hydrogen by using water electrolysis powered by renewable energy sources, at present the most promising way to produce green hydrogen potentially free of greenhouse gas emissions, mainly rely on PGMs. Presently, there are two low-temperature water electrolysis technologies commercially available, the alkaline water electrolysis (AWE) and the proton exchange membrane water electrolysis (PEMWE) [30], while up-scaling of the high temperature solid oxide electrolysis (SOE) technology is hindered presently by the high degradation and the thermal variations that cause thermomechanical stress in the cell.

AWE is a mature technology with low investment costs, but its major limitations lie in the low operational current density and low conversion energy efficiency. AWE does not rely necessary on PGMs, being able to utilize non-noble-metal electrodes and, despite the low efficiency, it has been established as the technology closest to large-scale industrial realization [31–33]. On the other hand, PEMWE relies on Pt, Ir and Ru supply as catalysts to promote the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER). According to the study from Minke et al. [34] two necessary preconditions have been identified to meet the immense future iridium demand: first, the dramatic reduction of iridium catalyst loading in PEM electrolysis cells and second, the development of an efficient recycling infrastructure for iridium catalysts. The global availability of the mainly South African supplied iridium is, in fact, insufficient to meet the targets of the EU Commission which has a strategy demanding for 40 GW of electrolyser capacity by 2030, if conventional Ir based catalysts are used [35].

Both commercial PEMFCs and AFCs use Pt-based catalysts. Despite the advantages of fast response, low operating temperature, high energy conversion efficiency and high power density, PEMFCs have as drawback the low catalytic activity and the low stability. Improving the catalytic activity and the stability of the electrodes by using Pt nanoparticles with particular morphologies and reducing the Pt loading by alloying with other metals, together with the search of innovative catalysts supports are the current strategies to improve the PEMFCs performances [36].

DMFCs are a subcategory of PEMFCs in which methanol rather than hydrogen is consumed in the fuel cells. Instead of hydrogen oxidation reaction (HOR), the methanol oxidation reaction (MOR) occurs at the anode material. DMFCs use mainly Pt-Ru or Pt-Co or Pt-Ni based catalysts. DMFC is considered one of the most likely fuel cells to be commercialized due to its advantages of low operating temperature and high energy density, but still has the disadvantages of stability and the methanol crossover through the Nafion membrane [37].

According to the recent study about DMFCs from Zuo et al. [38], more than 97% research works are concerning on precious-metal-based catalysts, of which Pt- and Pd-based electrocatalysts mainly, while only about 3% refer to nonprecious metal catalysts for sustainable energy applications.

Recently, PGM-doped lanthanum ferrites have been proposed as a viable solution for intermediate temperature solid oxide fuel cells (IT-SOFCs) electrodes in substitution of Co-based ferrites, due to the increase in Co cost. Pt was found to increase the number

of oxygen vacancies, thus promoting the oxygen reduction reaction (ORR) and reducing the lanthanum strontium ferrite (LSF) polarization resistance by 12.9%, while Ru was found to improve LSF stability in reducing conditions promoting the exsolution of metal nanoparticles [39]. The same authors have also investigated the effect of a small Pd doping on the properties of a lanthanum strontium ferrite in a IT-SOFC. Pd was found to positively affect the oxidation properties toward H₂ and CH₄ oxidation. In addition, the potential presence of PdO on the perovskite surface was found to promote the ORR [40].

Pt-based catalysts are also quite demanding for CO₂ capture and valorization. For CO₂ utilization, various transformative catalytic or non-catalytic reactions have been developed [41].

As an example, CH₄ and CO₂ may be used as feedstock in the production of syngas, a mixture of H₂ and CO known as a building block to produce value-added compounds like alcohols and olefins through the Fischer-Tropsch process [42,43]. The main players in the dry reforming of methane (DRM) (Equation (1) and Figure 3) are Ni-supported catalysts which suffer from both coking and sintering. PGMs are very active for DRM because they limit the deactivation of Ni catalysts by carbon residues thus preserving the catalysts stability over time. Many studies have reported on the superior catalytic properties of Ni when promoted by PGMs such as Pt, Rh, Ru, or Pd, both because of the increased activity and coke resistance compared to the non-promoted Ni catalysts [44–46]. Different types of supported metal catalysts such as Pt, Rh, Ir, Ni and Co-based have displayed promising catalytic properties in the DRM process [42,47,48]:

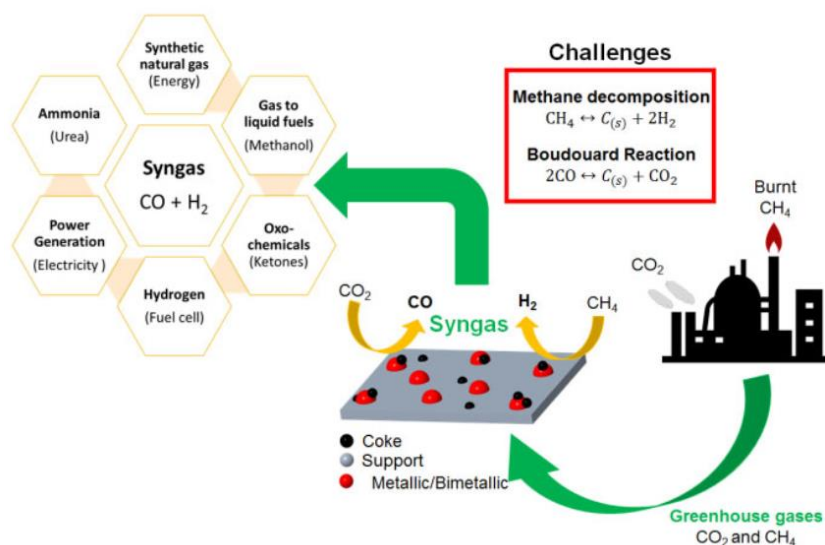


Figure 3. Schematics of the DRM reaction and of syngas utilization. Reprinted from [44].

From what above mentioned, it is therefore clear that the recovery of PGM from spent catalysts is not only an actual urgent demand, but will continue to be essential also in the future to meet the growing PGMs demand and close the PGMs loop until PGM-free green power technologies will be consolidated.

2. Recycling of PGMs

According to data provided by Johnson Matthey's PGM market report [49] and represented in Figures 4a, 5a and 6a, the Southern African region holds the largest market share for PGMs, with almost half of the global supply.

For platinum main applications are those related to automotive and jewelry (Figure 4b). In the case of palladium, the automotive sector and that of electronics are applications that represent a major share of the total consumption (Figure 5b).

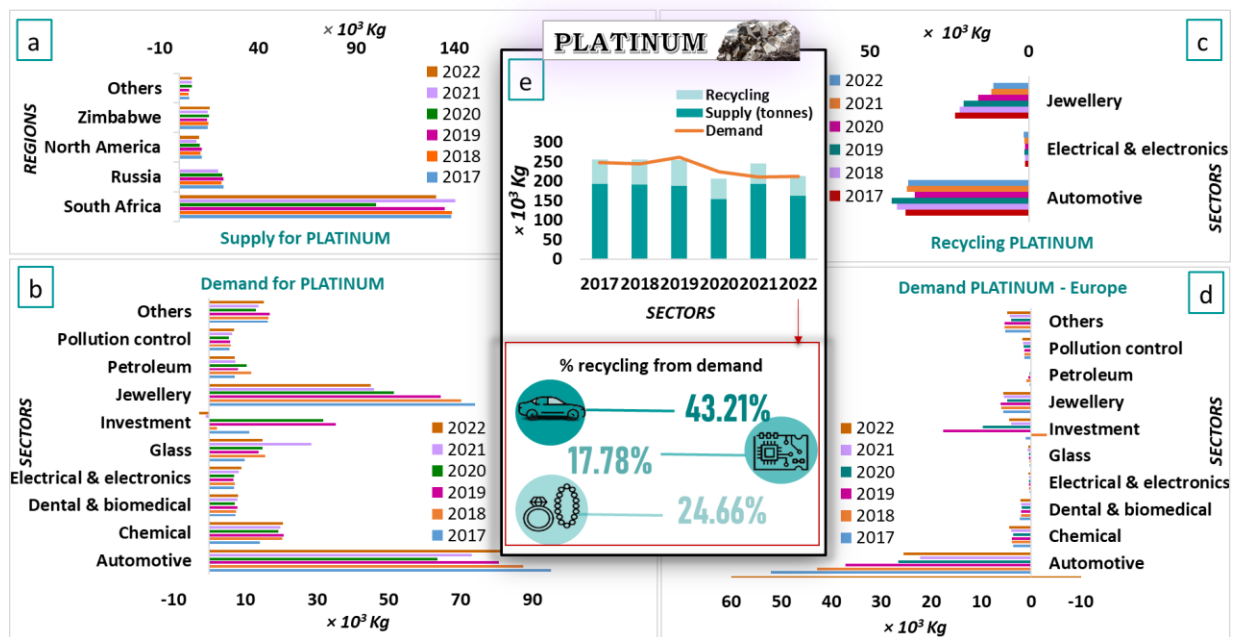


Figure 4. (a) Platinum supply by region from 2017–2022; (b) Platinum demand by sectors from 2017–2022; (c) Platinum Recycling by sectors from 2017–2022; (d) Platinum demand in Europe from 2017–2022; (e) Global platinum recycling, supply and demand from 2017–2022 (according to the data from [49]).

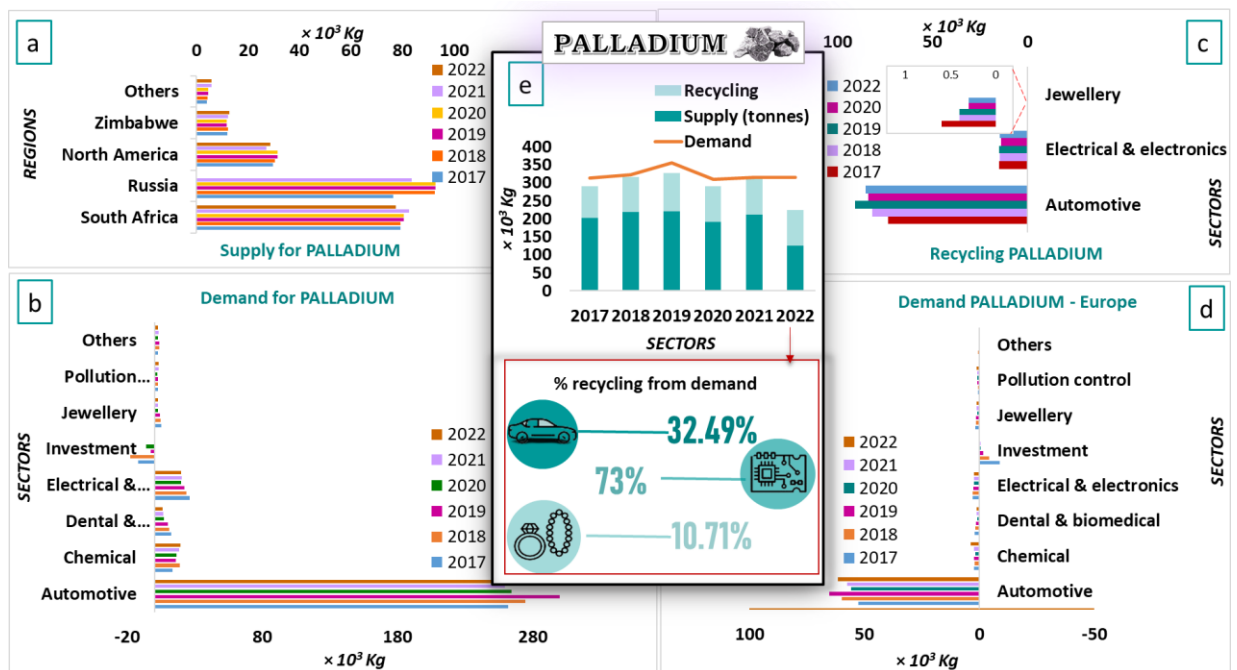


Figure 5. (a) Palladium supply by region from 2017–2022; (b) Palladium demand by sectors from 2017–2022; (c) Palladium recycling by sectors from 2017–2022; (d) Palladium demand in Europe from 2017–2022; (e) Global palladium recycling, supply and demand from 2017–2022 (according to the data from [49]).

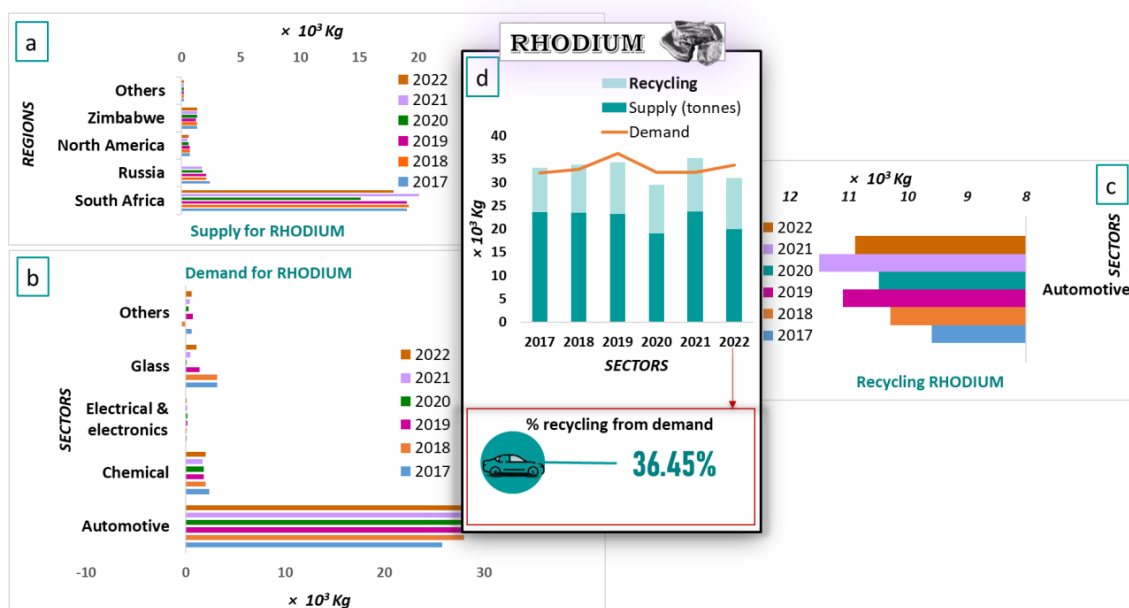


Figure 6. (a) Rhodium supply by region from 2017–2022; (b) Rhodium demand by sectors from 2017–2022; (c) Rhodium recycling by sectors from 2017–2022; (d) Global rhodium recycling, supply and demand from 2017–2022 (according to the data from [49]).

Palladium, platinum and rhodium are widely used in the automotive sector, more precisely for catalytic converters because these elements do not form volatile oxides like the other PGM elements [50,51]. The automotive sector is the most important in the case of rhodium (Figure 6b).

For ruthenium, the main markets are represented by the electrical & electronics and chemical sectors (Figure 7a), while for iridium, the main markets are the electrochemical and electrical & electronics sectors (Figure 7b).

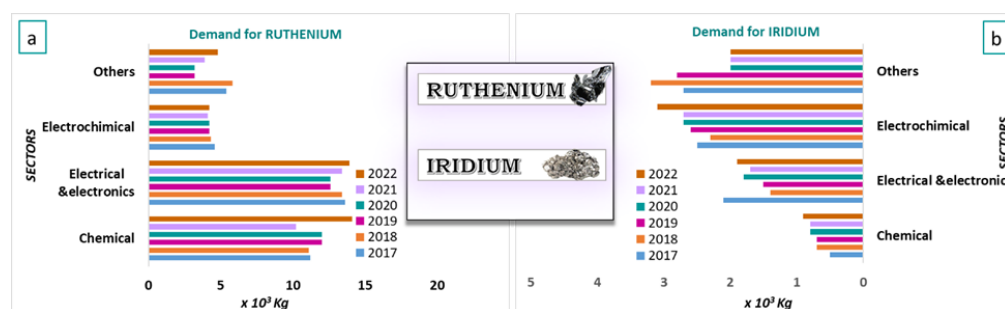


Figure 7. (a) Ruthenium demand by sectors from 2017–2022; (b) Iridium demand by sectors from 2017 (according to the data from [49]).

In recent years there has been an increasing interest in recycling PGMs from secondary sources such as spent catalysts, electronic scrap and membrane electrode assemblies, used equipment and jewelry [52,53].

In 2022, the recycling of platinum from the automotive field contributed with 43.21% of the demand for the same field; recycling from the electrical and electronic field with 17.78% of the platinum demand for the same field; recycling from the jewelry field with 24.66% for recycling from the same field (Figure 4e).

Regarding palladium, in 2022, recycling from the automotive field contributed to the demand for the same field by 32.49%, for the electrical & electronics field with 73%, and for jewelry with 10.71% (Figure 5e). The recycling of rhodium from the automotive field contributed to the demand for the same field with 36.45% (Figure 6d).

The primary production of PGMs must be intertwined with the recycling of PGMs to support sustainable development, reducing the environmental footprint of PGMs production.

With the data reported so far, in 2022 the recycling of PGMs was approximately 160 Mg. The largest contribution to the global demand for elements from the PGM group was Rh with 36.45% of the global demand for Rh, followed by Pd with 31.65% of the global demand for Pd and Pt with 23.91% of the global demand for Pt, as shown in Figure 8.

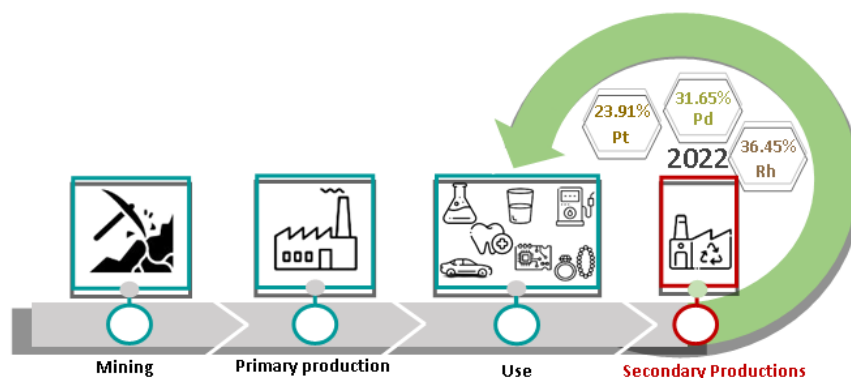


Figure 8. Contribution of PGM recycling to global demand for PGMs in 2022 (According to data from [49]).

As the main end-use sector of PGMs, the automotive industry, i.e., spent automotive catalysts, represents the major recycling potential. It should be noted that a SAC contains a higher amount of PGMs than natural ores, 2000–15,000 g/Mg compared to 2–10 g/Mg [9,54–56]. Moreover, spent catalysts contain as critical elements also rare earth oxides (REOs).

Article 7 of the End-of Life Vehicles (ELVs) Directive 2000/53/EC targets for each country the reuse and recovery of ELVs (95% by an average weight per vehicle and year). These targets were due to be met by the Member States by 1 January 2015. According to data in 2017, 15 of the 28 Member States had met the minimum reuse and recovery target of 95% by an average weight per vehicle and year. The average reuse and recovery rate for the EU28 as a whole was 94%, just below the target [57,58].

PGMs recovery consists of several steps as follows: pretreatment, PGMs enrichment, PGMs extraction, PGMs separation and purification and reduction to metal products [56,59,60]. In Figure 9 the overall process for recovering PGMs is presented.

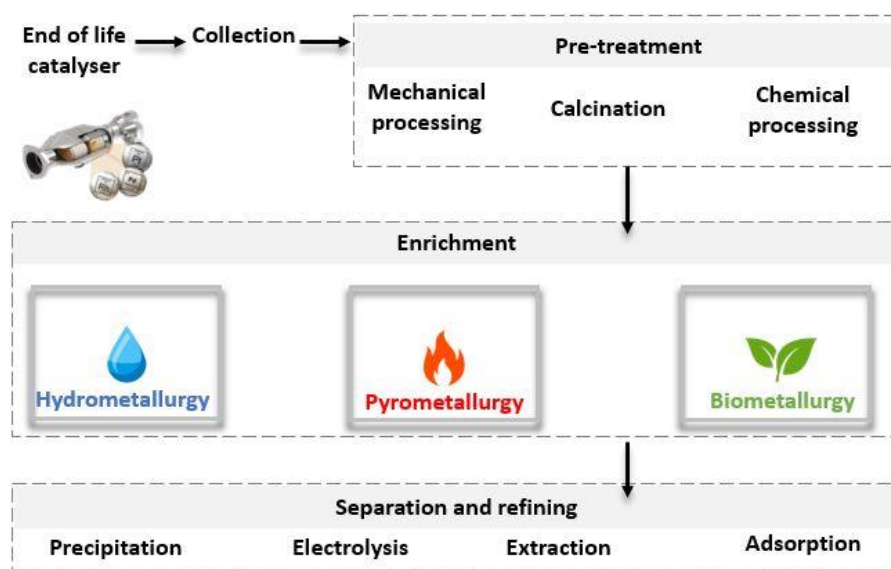


Figure 9. PGMs recycling scheme.

Regardless of the PGMs recovery route adopted, generally a pretreatment stage is necessary. This stage involves mechanical treatment (collection, decanning of the PGMs ceramic monolith carrier, which is crushed and cleaned to remove residues), calcination and chemical treatment aimed at particle size reduction, removal of impurities or activation [61].

The enrichment of PGMs can be carried out by pyrometallurgical, hydrometallurgical or biometallurgical processes.

Table 2 reports about characteristics of the above mentioned processes.

Table 2. Characteristics of metallurgical extraction methods.

Type of Process	Advantages	Disadvantages	Recovery PGM		
			Recovery Yield of the PGMs	Conditions	Ref.
Pyrometallurgical processes	used for upscaling recovery of PGMs, offers promising recovery yields [9].	special equipment, high temperatures, high energy consumption, cost of continuous furnace operation, production of significant waste (e.g., volatile waste, slag) [9,62]	99% Pt, 99% Pd, 97% Rh.	T = 950 °C, T = 75 min, addition of 3 times flux (0.72 wt/wt, B ₂ O ₃ /Na ₂ O) of spent catalytic converters and 10 g of FeS ₂ with a corresponding enrichment factor of around 6.0.	[63]
			98.59% Pt, 97.91% Pd, 97.16% Rh.	T = 1250 °C, t = 2 h, and N ₂ atmosphere (microwave smelting), using nickel matte as collector and sodium salts as fluxes.	[64]
			>97% Pd	T = 1350 °C adding 15 wt% CuO, 5 wt% C, 2 of SiO ₂ /CaO, 2.2 of SiO ₂ /Al ₂ O ₃ and heating time t = 2 h.	[65]
Hydrometallurgical processes	milder process temperatures than pyrometallurgy, process control, high selectivity, minimal energy consumption, ability to be used at both small and large scale [9,61].	attention to waste management (liquid waste, gas emissions), process duration, cost and nature of reagents [9,61]	90–98% Pt, 99% Pd, 70–96% Rh.	11.6 mol L ^{−1} HCl, 1%vol H ₂ O ₂ , T = 60 °C, L/S = 2 L kg ^{−1} and t = 3 h	[61]
			>89% Pt, 100% Pd.	5 M HCl, 1.96 M H ₂ O ₂ , 1.67 M of C ₂ H ₄ O ₂ , 250 rpm of stirring for 3 h, room temperature; 10% of solid concentration.	[66]
			90% Pt, 94% Pd	3 vol% H ₂ O ₂ with 8.0 mol/L HCl solution, T = 55 °C and leach time t = 180 min.	[67]
			97% Pt, 97% Pd, 97% Rh.	Substrate dissolution: NaOH roasting with mole ratio 1:17, T = 600 °C, t = 60 min and dissolution in 1.0 M H ₂ SO ₄ , T = 90 °C, t = 1 h Cementation: AlO-powder 0.5 g/L at T = 90 °C, t = 15 min Oxidation leaching: 6.0 M HCl, 2.0 M NaClO ₃ , T = 90 °C, t = 2 h. Pre-reduction: 15 vol% HCOOH, pulp density 10%, T = 60 °C, t = 1 h,	[68]
			95.1% Pt, 94.9% Pd, 95.2% Rh.	Post-leaching: 2.0 M HCl, 2M NaClO ₃ , T = 90 °C, t = 2 h	[69]
			99.6% Pt, 65% Rh.	Leaching using electro-generated Cl ₂ in 8.0 M HCl, T = 80 °C, pulp density 100 g/L, t = 4 h.	[70]
Biotechnological processes	lower carbon footprint, low energy consumption, the use of more ecological solvents than in hydrometallurgy, the absence of dangerous gases [9].	extensive PGM extraction methodology	>95% Pt, >95% Pd.	biogenic cyanide produced by <i>Chromobacterium violaceum</i> 2 h under 150 °C and 14 bar, <i>Pseudomonas fluorescens</i> (that produce cyanide as a secondary metabolite)	[71]
			58% Pt, 65%Pd, 97% Rh.	0.5% (w/v) pulp density and initial pH 10.	[72]
			38% Pt, 44% Pd, 91% Rh.	<i>Pseudomonas fluorescens</i> were used to bioleach PGMs from pretreated SAC (by Ultrasound-assisted nitric acid), pulp density of 1% (w/v) at pH 9.	[73]
			92.1% Pt, 99.5% Pd, 96.5% Rh	1000 mg/L biogenic cyanide solution, T = 150 °C.	[74]

In the pyrometallurgical process, PGMs are separated from the nonmetal fractions by smelting, fluxes and reductants [65,75]. In hydrometallurgical processes, oxidizing leaching systems (e.g., hydrogen peroxide and ferric iron) acid (e.g., hydrochloric acid, sulfuric acid, nitric acid) and/or bases (e.g., sodium hydroxide and sodium hypochlorite), and complexing agents (e.g., cyanide and thiosulfate) are used to extract PGMs [76]. In the case of biohydrometallurgy, the same similar principles apply, but the leachates are biological products. The leaching rates of biohydrometallurgical processes are slower than those of hydrometallurgical ones, however, they are more environmentally friendly and have a low cost [77].

Table 3 lists some major PGM recycling companies in the world.

Table 3. Companies involved in PGM recycling.

Company	Waste Type	Process	Ref.
Umicore	large variety of complex, precious metals containing materials (E-scrap, spent automotive catalysts, spent industrial catalysts)	smelter, the copper leaching and electrowinning plant and the precious metals refinery.	[78]
BASF	Spent catalyst	process of smelting and refining	[79]
Multimetco	spent automotive and industrial catalyst.	process of smelting and refining	[80]
Johnson Matthey	spent process catalysts, autocatalysts, fuel cell catalysts, secondary mine residues and jewellery or scrap metal.	pyrometallurgy, advanced hydrometallurgy processing	[81]
Hensel recycling	catalytic converters, e-scrap or other materials containing precious metals	smelting	[82]

As can be seen, the existing industry for the recycling of PGMs is based on pyrometallurgical processing operations. Although the hydrometallurgical route represents an innovative and promising method for PGMs recycling, its adoption in the industry is rather slow.

2.1. Pyrometallurgical Processes

Pyrometallurgical processes are used to recover PGMs from both SACs and electronic waste. These techniques involve the physical or chemical transformation of PGMs at high temperatures with or without additives (collectors and fluxes) and include smelting, chlorination, metal vapor treatment, heating-quenching processes, sintering and then recovery through refining technologies [83].

2.1.1. Smelting

Classic smelting refers to the mixing of catalytic converter powder with flux, collector and reducing agent and then melted in a furnace (e.g., plasma, plasma arc and induction) and maintained at approximately 1500–2000 °C. The extraction of PGMs is done in the alloy phase, with the collector (e.g., iron, copper, lead and nickel). The flux agent (e.g., cryolite, borax, lime, and soda ash) has the role of dissolving the impurities in the catalytic converters to generate slag that will easily separate from the metallic phase due to density differences. The PGM alloy undergoes chemical treatment to dissolve and separate the PGMs [18,84].

The most important parameters of the capture process are the choice of collector and flow agent. For example, several factors such as melting point, crystal structure, density, mutual solubility and chemical reactivity will be considered when choosing the collector.

The flow agent must ensure a low viscosity. The oldest collector used to recover PGMs from spent autocatalysts is lead. Although its use is associated with a number of advantages such as simplicity of operation, low melting temperature, easy oxidation to separate lead from PGMs, this process presents environmental problems due to the formation of toxic lead oxide. Besides, Rh recovery is 70–80%, considered to be relatively low [85].

With a lower environmental impact and a higher recovery rate, iron and copper capture technologies have been applied industrially following various studies [14].

When recovering PGMs using copper as a collector, an electric arc furnace is used in which temperatures reach 1450–1600 °C, in which the raw material is introduced accompanied by flows of e.g., SiO₂ or CaO, Cu collector (CuO, CuCO₃) and reductants [86].

Due to the chemical affinity with PGMs to form solid solutions and to the low cost, iron is one of the most promising collectors used. PGM-based waste is crushed and mixed with iron or iron oxide, reductant and fluxes (CaO) in order to melt at a temperature of approximately 1500–2000 °C, thus forming a PGM-Fe alloy. This alloy is easily separated from the slag due to the large difference in density, 6.0–7.0 g/cm³ versus 3.0–3.5 g/cm³ [87,88].

Chuan Liu et al. [89] have recently proposed a new technology for the extraction of PGMs from SACs. By using the vitrification process combined with the melting-collecting process, they obtained a recovery rate of over 99% of PGMs. They mixed SAC waste with cyanide tailings (CT) and subjected it to the thermal carbon reduction-melting process with the addition of CaO flux and Na₂B₄O₇. The Fe-PGM alloy was formed by attaching the PGMs from SAC to Fe from CT. Addition of 30 wt% CT resulted in over 99% recovery of PGMs. The residual slag produced by vitrification could efficiently immobilize heavy metals such as Pb, Cr, Zn and As. Their proposed method of simultaneous treatment of hazardous waste by SAC and CT offers a practical strategy for the recovery of PGMs and Fe from hazardous waste, with a process cost lower than the costs of traditional processes.

2.1.2. Chlorination

The chlorination method, also called the carbochlorination process, is the process involving the volatilization of PGMs under high temperature conditions with the aim of forming chlorine salts in the gas phase, followed by condensation at lower temperatures to allow separation from the carrier, achieving the enrichment of PGMs [90,91].

Kim et al. [90] recovered approximately 95.9% platinum and 92.9% rhodium from unroasted spent autocatalyst samples using a mixture of chlorine and carbon monoxide, at a temperature of 550 °C. However, this technique is still approached at the laboratory level, due to the fact that it presents a series of disadvantages such as high temperature, strong corrosion, high equipment requirements and toxic gases (CO, Cl₂) [18].

The chlorination reactions of PGMs are expressed by the following equations:



2.1.3. Metal Vapor Treatment

Metal vapor treatment involves the reaction between PGMs and vapors of active metals at a high temperature, in order to form a metal-PGM alloy, which facilitates dissolution in the acidic environment.

Several studies have addressed Mg and Ca vapor treatment [92–94] to extract Pt and Rh from spent autocatalysts.

Yu-ki Taninouchi et al. [95] studied the physical concentration method involving treatment with FeCl₂ vapor at about 1200 K (927 °C), followed by magnetic separation. It resulted in an efficient alloying of PGMs (Pt, Pd and Rh) with Fe, the major components of the catalyst (cordierite and alumina) remaining unreacted, while the CeO₂ and La₂O₃ species were transformed into oxychlorides. Thus, FeCl₂ vapor treatment can potentially improve the efficiency and throughput of existing PGMs recycling processes when used during the pretreatment step.

Sasaki and Maeda [96] examined the effect of Zn vapor treatment prior to acid leaching for PGM recovery from catalytic converters. They demonstrated that the studied treatment improved the dissolution of PGMs during leaching in aqua regia, also improving the

extractions of PGMs in hydrochloric acid at a high temperature. In the case of Pt and Pd, treatment with Zn vapors was effective, while for Rh a considerable improvement was observed.

2.2. Hydrometallurgical Processes

Hydrometallurgical processes involve the recovery of PGMs by dissolving waste containing PGMs in a suitable solvent/leaching agent, followed by separation and purification [97]. These processes present a number of advantages over pyrometallurgical recycling: use of lower process temperatures, higher purification yields, reduced energy consumption, co-metal extraction potential and better process control. However, the duration of the process, the nature of the reagents, the costs and the management of liquid waste and gaseous emissions must be taken into account [9].

A hydrometallurgical process involves several stages: the leaching stage in which PGM complexes are formed, followed by the separation of dissolved precursors and the purification of PGMs from the leach solution.

Leaching efficiency is influenced by several factors: the concentration of leaching reagents, pH value of the leachate, leaching time, leaching temperature and stirring conditions [98].

Pretreatment processes are used with the aim of increasing the leaching efficiency of PGMs by improving the dissolution rate, kinetics and reducing the cost of the process. Pretreatment also helps to avoid the use of solvents with high acidity. The basic methods in pretreatment are: oxidative roasting, reduction roasting, alloying and mechanochemical activation [59].

Recently, highly efficient recovery of PGMs (100%, 92% and 61% for Pt, Pd and Rh, respectively) from spent autocatalysts has been demonstrated also without pretreatment. The proposed leaching system was a HCl–H₂O₂–NaCl medium under mild conditions (70 °C, 2 h), while the high solid per liquid ratio (S/L 70%), provides very promising ground for upscaling in industrial conditions [10].

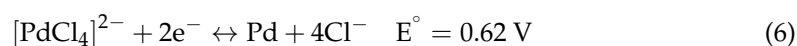
There are several hydrometallurgical techniques for the recovery of PGMs: hydrochloric acid leaching, cyanide leaching, halogen leaching, microwave assisted leaching and thiosystem leaching.

2.2.1. Chloride Leaching

Chloride leaching is a process in which PGMs are leached in a chloride-based environment under acidic conditions and in the presence of an oxidant (Cl₂, HNO₃, NaClO, NaClO₂, NaClO₃, H₂O₂) [9,54,68,99–101].

The oxidation potential of oxidizing agents influences the degree of leaching of PGMs. A higher potential is needed for Pt leaching, while Pd and Rh need a lower potential.

The equations below show standard electrode potentials of the PGM-chloro complexes [54]:



If the oxidizing agent has an electron potential higher than that of the PGM, then the complete dissolution of the PGM is kinetically favorable.

Actually, the chloride-based system is one of the most consolidated leaching systems, where PGMs chloro-complexes are quite stable into chloride acid solutions. The most stable chloro-complexes are [PtCl₆]^{2−}, [PdCl₄]^{2−} and [RhCl₆]^{3−}, and their formation is strongly dependent on chlorine media concentration, where chlorine acid and additional Cl[−] sources could be used in balance [9]. PGMs dissolution is enhanced with higher chloride concentration, because an increase in the Cl[−] concentration decreases the equilibrium potential [102].

In the formation of Pt and Pd complexes, the oxidation valence of palladium and platinum are mainly divalent and tetravalent and the coordination number of their corresponding chlorine complexes are 4 and 6, respectively. The most stable oxidation valence of rhodium is trivalent, and the complex formed when the coordination number is 6 is more stable. The exploitation of the coordination chemistry of precious metal ions is critical in deriving successful separations and the reactivity of the PGMs depends on the oxidation state of the metal ion as well as the nature of the extracting ligands [103].

Table 4 reports the primary PGM-chlorine complexes that form in leaching system with hydrochloric acidic solutions at various concentration values. Specifically, PGMs chloro-complexes form starting from molar concentration values of ≥ 0.1 for Pd, ≥ 3 for Pt, and ≥ 6 for Rh. In particular, for dilute systems, various chloro-complexes species are presents involving solvation water and part of them interchanges their oxidation state.

Table 4. PGM species found as chloro-complexes in aqueous chloride media at different concentration values.

Noble Metals.	Species	Concentration	Ref.
Pt (II)	$[\text{PtCl}_4]^{2-}$	$C_{\text{HCl}} \geq 1 \text{ M}$	[104,105]
Pt (IV)	$[\text{PtCl}_6]^{2-}$	$C_{\text{HCl}} \geq 3 \text{ M}$	[104,105]
Pd (II)	$[\text{PdCl}_4]^{2-}$	$C_{\text{HCl}} \geq 0.1 \text{ M}$	[104]
Pd (IV)	$[\text{PdCl}_6]^{2-}$	-	-
Rh (III)	$[\text{RhCl}_6]^{3-}$	$C_{\text{HCl}} \geq 6 \text{ M}$	[104,106,107]
	$\text{RhCl}_5(\text{H}_2\text{O})^{2-}$	*	[104,106]
	$[\text{RhCl}_4(\text{H}_2\text{O})]^{2-}$	*	-
Rh (IV)	$[\text{RhCl}_6]^{2-}$	-	-
	$[\text{RhCl}_5]^{2-}$	$C_{\text{HCl}} \geq 0.4 \text{ M}$	[104,107]

* Species present in diluted acid systems.

Ana Paula Paiva's and colleagues' study aimed at maximizing the recovery of PGMs with a high concentration of them in the leachates and minimizing the co-dissolution of aluminum by approaching the leaching process with concentrated HCl solutions (with H_2O_2 as oxidant) and low liquid/solid ratios. The optimized conditions found were 11.6 mol L^{-1} HCl, 1%vol H_2O_2 , 60°C , $\text{L/S} = 2 \text{ L kg}^{-1}$ and 3 h, leading to PGM yields of 90–98% Pt, 99% Pd and 70–96% Rh, and leachate compositions of $0.41\text{--}0.78 \text{ g L}^{-1}$ Pt, 1.6 g L^{-1} Pd, $0.062\text{--}0.066 \text{ g L}^{-1}$ Rh, depending on the catalyst sample [97].

Viet Nhan Hoa Nguyen et al. [108] investigated the separation of Pd and Pt from a mixture of these metals by the simultaneous use of leaching and solvent extraction system with concentrated HCl, commercial extractants and oxidizing agents. The selective dissolution of Pd over Pt metal was possible by the leaching process followed by extraction, which used a mixture of concentrated HCl, TBP (tributyl phosphat) in kerosene and H_2O_2 . Complete extraction of Pt was possible by replacement of H_2O_2 and kerosene with NaClO_3 as an oxidizing agent and MIBK (methyl isobutyl ketone) as a polar diluent in the solvent mixture.

The simultaneous leaching and extraction systems were found to be more efficient than the aqueous HCl and H_2O_2 system in terms of selectivity and leaching capacity for Pd. The Pd (II) and Pt (IV) ions from the charged TBP phases were thus completely stripped by a mixture of HCl and thiourea. The purity of these metal ions in the respective stripping solutions was greater than 99.9%.

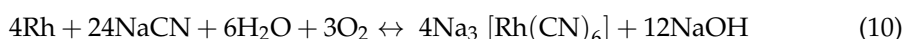
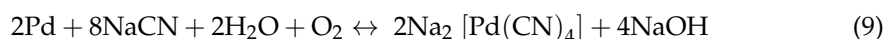
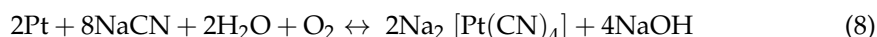
Inela Birloaga and colleagues [66] presented an innovative hydrometallurgical methodology for the recovery of precious metals from various waste streams, consisting of a single leaching system (HCl , H_2O_2 and $\text{C}_2\text{H}_4\text{O}_2$) of all elements and then selective recovery of elements from solution by chemical reduction/processes. For the leaching of Pd and Pt from spent autocatalysts, the influence of hydrochloric acid concentration and process time was evaluated. A recovery of 100% for Pd and over 89% for Pt was obtained using:

5 M HCl; 1.96 M H₂O₂; 1.67 M of C₂H₄O₂; 250 rpm of stirring for 3 h; room temperature; 10% of solid concentration.

Paolo Trucillo and collaborators [109] proposed a hydrometallurgical process for the recovery of platinum from diesel catalysts, which has as a first step leaching with aqueous solutions of H₂O₂ (up to 0.2 M) and light concentrations of HCl (0.4 M), followed by a refinery where the platinum is deposited over a granular activated carbon. The results revealed that a low concentration of HCl results in longer leaching times but the process conditions can be adjusted to achieve complete recovery of platinum with negligible extraction of other metals from the catalyst, minimizing the subsequent adsorption process. Optimum conditions were observed in leaching at 20 °C with a 0.13 M H₂O₂ 0.4 M HCl solution followed by the adsorption step at 20 °C using an activated carbon with a high BET surface area and a high content of reducing surface groups.

2.2.2. Leaching in Cyanide Solution

At an industrial level, cyanide leaching is used to leach precious metals from ores [110]. Regarding the leaching of PGM from SACs, sodium cyanide is an important leaching agent, due to its capacity to form stable metal complexes at high pressure and temperature. The following equations show the chemical reactions in cyanide leaching of PGMs



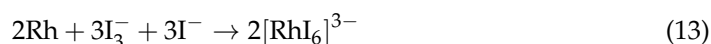
The dissolution of PGMs in cyanide follows the order Pd > Pt > Rh, given by their melting points (Pd (1552 °C) < Pt (1772 °C) < Rh (1966 °C)) and is independent of other parameters such as the initial concentration of NaCN, the oxygen pressure and the reaction temperature [111].

2.2.3. Leaching with Halogens

As an alternative to cyanides for PGMs leaching, halogens (F₂, Cl₂, Br₂ and I₂) are used. Of these, iodine forms the most stable complexes with PGMs.

For example, standard redox potentials of [PtI₆]^{2−} (0.40 V) is lower if compared to [PtCl₆]^{2−} (0.74 V) and [PtBr₆]^{2−} (0.65 V), therefore the dissolution of Pt using iodine/iodide solutions is more promising than the other halogen systems [56].

The following equations show the dissolution reactions of PGMs in iodine solution.

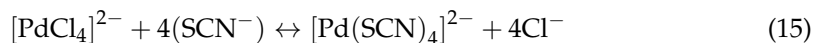
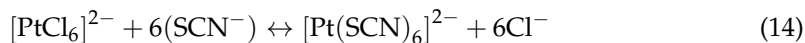


2.2.4. Leaching with Thiosystems (Thiosulfate, Thiocyanate, Thiourea)

Thiosystem leaching (thiosulphate, thiocyanate and thiourea) is still under-investigation for the leaching of PGMs and precious metals from spent catalysts [111]. However, PGMs form stable complexes with thiosystem ions, being more stable than their chloro/bromo/iodo counterparts [112].

Thiosulfate leaching was reported as early as 1880 for gold extraction [113]. It was shown that by increasing the concentration of (S₂O₃)₄^{6−} the dissolved concentration of Pt also increases [114].

Several studies have shown that Pt and Pd form stable complexes with thiocyanate that can be leached under acidic conditions [115,116]. The stability of Pt and Pd complexes with the hydrophobic thiocyanate ligand (SCN^-) has also been reported [116,117].



Thiourea ($(\text{NH}_2)_2\text{CS}$) also forms extra-stable complexes with Pt and Pd [118,119]. The use of thiourea over cyanide has a number of advantages such as higher metal recovery and lower sensitivity for base metals [120,121].

2.2.5. Leaching Media: Efficiency, Environmental Impact, Recent Trends

Figure 10 presents detailed evaluations of different leaching methods from the point of view of environmental impact, economic feasibility and reliability. It is found that leaching with aqua regia and cyanide are the most reliable methods, but they have a high impact on the environment, being toxic and corrosive. Halogen leaching presents high recovery rates and a moderate toxicity, but has problems in terms of corrosion and technological reliability. Leaching with thiourea and thiosulfate has the advantage of having a moderate impact on the environment, but it is not feasible from an economic point of view and moreover the technologies are less reliable compared to the other methods of leaching.

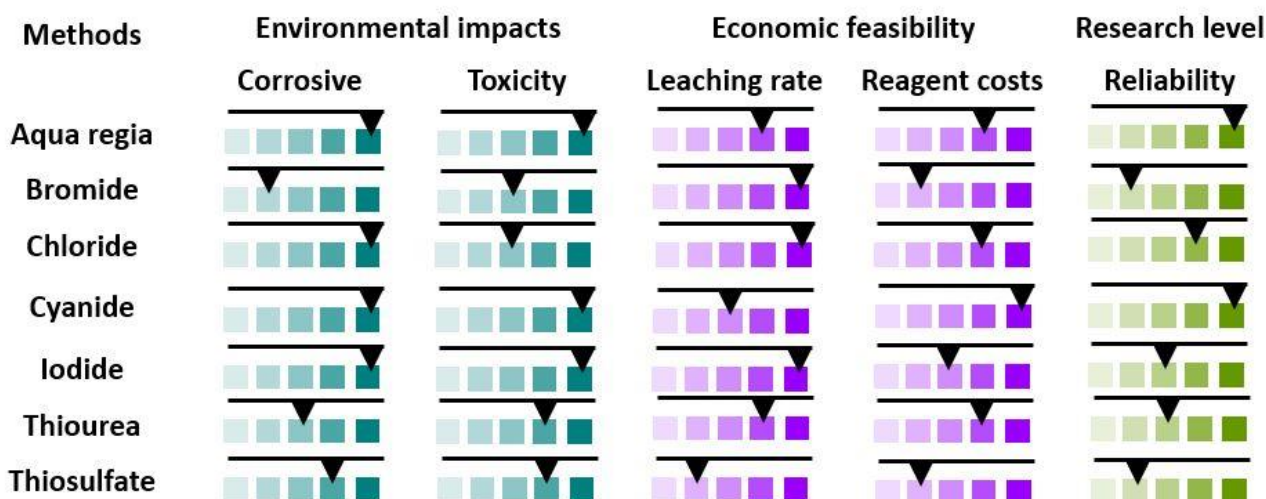


Figure 10. Basic assessment indices of different leaching methods (according to the data from [88]).

Recent efforts in PGMs recovery aim to the search of techniques which minimize the energy consumption and use milder reagents in order to minimize the residual waste.

Parameters for eco- and cost- effective leaching are summarized in the review from Yakoumis et al. [9], where the different leaching solutions are widely discussed.

In further work carried out by Yakoumis et al. [10], a $\text{HCl-H}_2\text{O}_2\text{-NaCl}$ medium under mild conditions (70°C , 2 h) leaching system was proposed, without SAC pretreatment, leading to high solid per liquid ratio (S/L 70%), thus demonstrating very promising ground for upscaling in industrial conditions.

Lanaridi et al. [122] proposed benign deep eutectic solvents (DESs) in addition with a small amount of oxidizing agent (HNO_3) as leaching media for the extraction of PGMs. DESs are characterized by low toxicity and low vapor pressure, which render them suitable to replace commonly used organic solvents and, in addition, they are cheap and biodegradable. In another study, Lanaridi et al. have proposed a novel separation approach for PGMs leached in hydrochloric acid by employing supported (polymerized)-ionic liquid phases (polySILPs) [123].

Ionic liquid was used also by Van den Bossche et al. for selective palladium leaching from SACs [124] and phosphonium ionic liquids have been used for the separation of palladium (II), platinum (IV), rhodium (III) and ruthenium (III) from their multi-component model mixtures of composition based on real solutions after leaching of PGM-containing wastes [125]. A review of IIs used in solvent extraction of PGMs is reported by Fyrmansyah et al. [126], while Lee et al. reviewed the ion exchange separation techniques for PGMs in different leaching systems [127].

The review from Zheng et al. analyzed the new technologies for the separation and purification of PGMs, including solvent extraction, membranes separation, supercritical fluids, solid-phase extraction, photoreduction, and electrochemical methods, with focus on challenges and perspectives for their commercial exploitation [94].

2.2.6. Assisted Leaching Methodologies

Hydrometallurgical processes can be improved by heating with microwaves and ultrasounds [128,129].

Microwaves provide an environmental friendly way of heat transfer, which is fast, direct, selective, and volumetric [85,130].

Suoranta et al. have demonstrated that microwave-assisted leaching in hydrochloric acid (37–38%) can be as effective as concentrated aqua regia to extract $\geq 90\%$ PGMs at a temperature of 150 °C and a liquid-to-solid ratio ≥ 10 [131]. A local superheating mechanism was proposed to explain the better performance of microwave-assisted leaching. In addition, PGM particles could be selectively heated [130].

Another recent study [132] compares the performances of microwave-assisted leaching of PGMs in 6 M HCl at 150 °C with those in 6 M HCl + 10 vol% H₂O₂, with the aim of investigating how the leachability is influenced by the addition of the oxidation agent.

Wang et al. have used the microwave-assisted roasting of SACs using sodium chlorate and sodium bisulfate at 300–330 W and 500 °C followed by water leaching, obtaining in 60 min a recovery of 99.74% for Pd and of 94.79% for Rh, which was higher and faster than in absence of MW (120 min, <90% recovery) [133].

Microwave assisted leaching was also recently tested at pre-industrial pilot scale and it was demonstrated that the optimization of the leaching process resulted in the reduction of HCl acid concentration from 12 to 6 M [134], thanks to fast and homogeneous volumetric MW heating able to enhance the leaching efficiency.

Ultrasound-assisted nitric acid pretreatment was used by Karim and Ting [73] in a bioleaching process which uses the cyanogenic bacteria *Pseudomonas fluorescens* and *Bacillus megaterium* for improving recovery rate of PGMs from SACs.

2.3. Biometallurgical Process

Biotechnological processes integrated with hydrometallurgy and electrometallurgy are considered emerging sustainable and clean technologies for metal recovery [135–137]. These processes use microorganisms (bacteria, fungi, archaea, or a combination of them) and enzymes to transform metals into soluble form, by proton generation (formation of organic or inorganic acids), by oxidation and reduction reactions and by complexing agents [138–142].

Recovery methods from biometallurgy have a number of advantages such as the fact that they use more environmentally friendly solvents, selective recovery of metals, lower energy consumption, lower carbon footprint and no hazardous gases. However, the variation of several parameters such as oxygen, pH, leaching temperatures, concentration of sorbent and sorbate, constitutes a challenge, playing a crucial role in leaching but also in the extraction of PGMs [9].

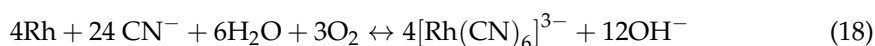
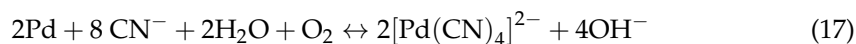
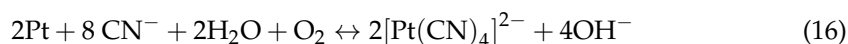
In the mobilization of metals, microbes play the role of a catalyst [143]. Microorganisms mobilize the metal from the solid matrix in an environment with a pH between 1.5 and 3.0, step followed by the production of organic and/or inorganic acids [142,144,145].

The main known bioleaching mechanisms are acidolysis, redoxolysis and complexolysis.

Acidosis and redoxolysis are produced by autotrophic prokaryotes, which include acidophilic chemolithoautotrophic microbes, and complexolysis is predominantly produced by heterotrophic cyanogenic bacteria [137].

Currently, literature data regarding bioleaching of PGMs is limited. PGM recovery by biohydrometallurgical processes is difficult due to the complex nature of SACs. Biological cyanidation involves the production of cyanide by bacteria as a secondary metabolite from glycine by oxidative decarboxylation [73,74].

PGMs form stable chemical complexes with the cyanide ion.



One of the first studies regarding the biometallurgical recovery of Pt from SACs, using *P. Plecoglossida*, resulted in a value of 0.2% Pt. This is due to the resistant nature of Pt and the fact that biogenic cyanide has a low yield in the presence of solid waste [146].

Another study examined the role of biogenic cyanide for PGMs extraction from SACs, reporting a higher yield [74].

Recently, it has been shown that ultrasound-assisted nitric acid pretreatment with the role of removing interfering metals present in SACs, leads to a higher rate of bioleaching of PGMs by producing more cyanide [73].

Biosorption involves a number of retention mechanisms such as ion exchange, adsorption, complexation, chelation, reduction and precipitation [147].

Microbial cells are considered biological adsorbents (biosorbents) for the retention of metal cations, except alkali metals [148,149].

Biosorption presents advantages such as increased selectivity at very low metal concentrations in solution, good energy efficiency and the possibility of regenerating some biosorbents [150].

The adsorption capacity is given by the existing chemical groups on the extracellular surfaces of the microbial cells (phosphoryl, hydroxyl, carboxyl, sulfhydryl, phosphate, carbonyl, sulfate, amino, thioether, amide, phenol).

The performance of the mechanism is determined by a series of factors such as: metal characteristics (chemical, molecular weight, ionic radius, oxidation state), process parameters (temperature, pH, concentration of sorbent and sorbate), biosorbent properties (structure, nature) and binding sites (type, availability) [147].

2.4. Mechanochemical Processing

Nowadays, the evolution of the circular economy concept is focused not only on higher PGM recovery rates, but also on higher economic and environmental standards by following green principle rules [130,151–154]. Currently, the research and innovation efforts are focused on greening and optimization of conventional PGM recovery methods toward decrease of their acid dependence, energy consumption and the increase of the efficiency of simultaneous recovery of target metals [9,130,153–155]. One of the emerging recycling technologies is based on mechanochemical treatment [156–160] as numerous advantages of the method are beneficial for recycling secondary PGMs resources with high recovery yields in a sustainable, environmentally friendly and technoeconomically feasible processing.

2.4.1. Mechanochemical Method—Advantages for PGM Recycling

Mechanochemistry is a branch of chemistry, where chemical reactions are initiated or triggered by mechanical means such as compression, shear, or friction [161–165]. The mechanical forces provide the energy required for the activation of chemical reactions as the heat, light, or electrical potential providing the energy in the thermo-, photo-, or electrochemistry, respectively [156–159,162,166–168]. Mechanochemical reactions can lead

to preparation of compounds, phases, and microstructures that are completely different from the products of the regular chemical reactions [161,162,165,166]. It was registered that large batches of energy, well above kT , can be locally released during mechanochemical treatment. This is considered as a key reason to obtain the proceeding of reactions that cannot occur thermally as it was found for photochemical reactions induced by the energy of photons [161,165,166]. Macroscopic deformation affects simultaneously many defect sites of the solid, which makes the mechanism of mechanochemical reaction additionally complicated. In this regard, the selection of treatment parameters is of critical importance to improve a chemical reaction of interest as effectiveness, selectivity, co-products formation, etc.

Selection of an appropriate milling device is the first issue for practical implementation of mechanochemistry both in laboratory and on industrial scale. The type of ball mill and the working regimes influence the thermodynamics, kinetics and the final result of the mechanochemical processing. Milling devices have been used to induce comminution with application of the lowest amount of energy, or to induce mechanochemical interactions introducing a maximum amount of energy into the reagents. Current developments of mechanochemical devices and characterization techniques made it feasible to better control mechanochemical processing toward extraction of metals of interest [156,160,165].

Several milling parameters determine the energy transfer to the reactants: milling speed, ball-to-powder weight ratio, milling media and filling extent of the milling reactor. These parameters are highly interlinked to each other and are especially important for mechanochemical output [161,162,165]. Significant modification to the reaction products can be reached by the addition of small amount (1–5 wt%) of liquid or solid in the milling vessel, so called liquid- or solid-assisted milling [156,157,165,168]. Selected milling parameters determine the secondary effects that occur during the treatment and the specific phenomena related to the mechanochemical reaction. One of them is the temperature increase and the huge difference between the reached local and bulk temperatures during treatment [168]. In case of high energy milling, as a result of collision of the milling material, the local temperature peaks can be higher than 10^3 °C for a very short time period ($\approx 10^{-9}$ s). In parallel, the impacts of the milling balls and milling vessel in a planetary ball mill, lead to increase of the bulk temperature, but it's value is about ten times lower than the local temperature, typically ≈ 200 °C [168]. Thus, the mechanochemical processes are complex and involve multiple length and time scales. They are system specific and take place under a broad variety of conditions. The main variables that determine the output of a mechanochemical reaction are the milling device, the dynamic milling conditions, as well as the characteristics of the processed material.

2.4.2. Mechanical Pre-Treatment

The effect of fine grinding on metal extraction is one of the early subjects of mechanochemistry and it is still widely used at the industrial level. Nowadays, the potential of application of mechanochemistry as a pre-treatment step or as a main stage in extraction of metals of interest significantly increases (Figure 11) [156–162].

Mechanical pre-treatment aims to increase the reactivity of target substances and to promote the subsequent leaching process with additional purification by precipitation or selective metal extraction [156]. Mechanical milling of SACs is largely utilized as pre-treatment step in PGMs recovery process (Figure 9), which induces comminution and significant morphological and/or phase changes [156–161]. As a result, better contact and penetration of the leaching agent to the treated material, as well as faster dissolution of the product layer can be reached. On the other hand, PGMs leaching is dramatically hindered even in concentrated acid solution, due to their high chemical stability. In addition, usually the PGMs in SACs are agglomerated and can be also encapsulated into the inner layer of the monolith after long-term operation at high temperature [169]. SEM images of SACs clearly demonstrate high non-uniformity of auto-catalysts waste. Some of PGMs are scattered around the monolith carrier in the form of agglomerated metals or metal oxides, and

some PGMs are attached or wrapped in the carrier. Such a serious sintering reactions and PGM wrapping further increase the hardness and insolubility of the SAC waste. The high inertness of PGMs and extremely strong stability of cordierite support, significantly hinder a complete recycling of PGMs from spent automotive catalyst [169]. So, the PGMs leaching efficiency in the traditional metallurgical recovery process is critically reduced. In this regard, the specific characteristics of mechanochemistry and especially the increase of the reactivity of treated materials opens new possibilities to maximize the recycling efficiency [156,158–160,170]. The initiation of mechanically induced solid-state reaction is essential for effective metal recovery.

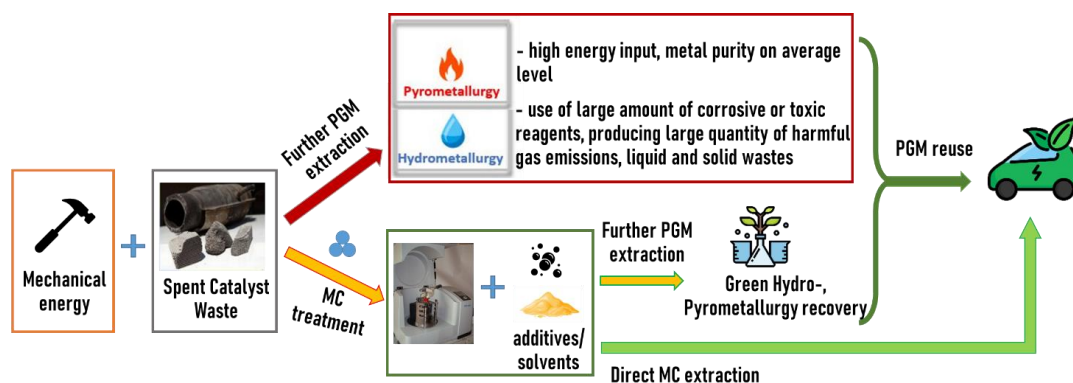


Figure 11. PGM recycling improvement by mechanochemical method.

2.4.3. Mechanochemical Leaching

The main processes occurring during the mechanochemical treatment have been identified as reduction of particle size, increase of specific surface area, dramatical evolution of crystalline structure and/or amorphization, fresh surface formation, bond breakage and generation of defects or other metastable forms. However, these effects are not stable and have different relaxation times (from 10^{-10} to more than 10^6 s). So, the separation of mechanical activation from the leaching process leads to a loss of some of these highly excited states due to their decay before leaching [156,159,162,165]. Thus, when the mechanical activation is a pre-treatment step, the subsequent chemical recovery reaction deals only with the long-lived slowly relaxing states. Integration of mechanical activation and chemical extraction into a common process (mechanochemical leaching) will utilize all the excitation states. Thus, the leaching agent serves both as a grinding additive which improves grinding performance, as well as contributes to higher extraction rates. During simultaneous milling and leaching, the activation energy required for PGM leaching decreases and reaction activity increases. Repeated fracturing and cold welding of reacting particles occurs during the collisions when the respective wastes are treated with appropriate chemicals in a milling device. Thus, solid-state reactions that cannot occur normally can be performed across the welded interfaces when several ingredients are milled together.

Recently published review studies on the applications of mechanochemistry for metal recycling from wastes discussed in depth the reaction mechanisms, equipment used, treatment procedures, and optimized processing parameters, as well as detailed approaches for improvement of the recycling process [156–160,165]. The method was successfully applied for recycling metals from wastes in a technically feasible and efficient way for some specific wastes, such as e-waste and low-grade tailings where significant recycling efficiency was registered. The main problems to be addressed and future perspectives on the development of mechanochemistry applied for metal recycling are also presented. Numerous key characteristics of mechanochemistry make the method greener and advantageous in comparison to traditional ones. Mechanochemistry promotes leaching reactions using solvent-free conditions (dry milling) or significantly smaller amounts of liquid (wet milling or liquid-assisted grinding), in comparison to the conventional chemical treatment, where the solvent is a medium for energy dispersion, dissolution/solvation and transportation of reagents. Dis-

advantage of mechanochemical leaching is that the milling pots and balls should be made of materials inert to produced aqueous slurry or solution of activated materials [156,159]. The continuous mixing process under ball milling offers an efficient way for mass and energy transport, enabling the reactions for effective dissolution of PGMs by using different additives (as halide or sulphur compounds, small amount of solvent and/or oxidizing agent, etc.) in recovery process. Additionally, the continuous mixing and formation of fresh surface during treatment is highly beneficial for liberation of PGMs from aluminosilicate carriers in SACs processing.

One of the major drawbacks in the PGMs recovery from SAC waste comes from the nature of car catalysts [169]. Spent catalytic monoliths have different surface morphology, impurities and contamination. SACs contain PGMs with very low and various concentrations. The PGM-bearing phases have also diverse composition, particle size, morphology and distribution on the carrier surface and bulk, that significantly hinders leaching procedure. On the other hand, shoot and unburned hydrocarbons' deposition makes the catalyst surface to be inert to chemical treatment [169].

A significant advance in a high-rate PGM extraction efficiency was observed in recent investigations based on the mechanochemical leaching or mechanical activation of materials in combination with post-treatment processing (hydro- or pyrometallurgy) [156,158–160,170]. These reports revealed numerous potential benefits for PGMs recovery from waste, but there is a lot to be done to reveal the power of mechanochemistry in recycling of PGM from different primary ores, low-grade tailings and end-of-life materials, as well as from SACs.

Mechanochemical process was suggested to recover valuable metals from e-waste scraps by co-milling with different reagents [156,158–160,170,171]. After dry co-milling with a mixture of $K_2S_2O_8$ and NaCl, high metal recovery rates of 95.5% of Pd were obtained by processing with 0.5 mol/L diluted HCl in 15 min. The mechanism of mechanochemically induced solid-state reactions during ball milling was proposed offering the advantages of high recovery rate and quick leaching speed [171].

X. Wei et al. (2019) [172] suggest a pretreatment method of mechanochemical activation with the hydrochloric acid leaching system with a total PGMs leaching rate of 93.42%. The article analyzed the physio-chemical characteristics of the spent automotive catalyst composite, which contains mostly aluminosilicate carriers with less than 0.1% PGMs. The high leaching rates of 77.2%, 62.1% and 97.4% for Pt, Rh and Pd, respectively, were obtained in a greener and optimized way [172].

One-pot mechanochemical conversion of the metals, including spent catalysts, to simple water-soluble salts, or to metal-organic catalysts was demonstrated in [173]. Green and direct noble metal activation and recycling of elementary palladium and gold was obtained by mild, clean, solvent-free and room-temperature chemistry. The exact conditions were established for mechanochemical activation of metal Pd and Au in a form of powder, pellets, or wire with a mild oxidant Oxone[®] and readily available inexpensive halide salts (NH_4Cl , KCl). The study reports a new sustainable and eco-friendly approach for solvent-free recycling of noble metals avoiding harsh oxidative or complexation reagents, which proceeds at room temperature. Suggested material processing generates sulphate by-products of Oxone reduction, however it allows replacement of aggressive HNO_3 , aqua regia, molten salts or cyanides.

Therefore, mechanochemistry offers a high potential to replace classical extractive metallurgy decreasing the number of technological stages with possibility for one-pot and one-step SACs processing, together with high efficiency (higher leaching yields and selectivity) and significantly lower environmental footprint (solvent-free processing, dramatic reduction of chemical's consumption, very low toxic emissions and wastes) [156–160,170–173]. Crushing and grinding the PGMs scrap together with additives give rise to sufficient release of the precious metal from the aluminosilicate carrier, and this can greatly reduce the dissolution time and simultaneously improve the leaching efficiency toward PGMs recovery.

3. Secondary Sources of PGMs for the Synthesis of Catalysts

To close the PGMs loop it is important not only to recover PGMs efficiently and in a sustainable way from secondary sources but also to reuse them. The reuse of PGMs from spent autocatalysts was already achieved in the frame of the EU project PLATIRUS [174] through the development of an innovative and cost-efficient process to recover PGMs from secondary source materials to brand new automotive catalysts with the recycled materials [21]. Among the aims of the already mentioned CHemPGM project, is to close the PGMs loop not only by fabricating autocatalysts starting from recovered PGMs, but also by fabricating other types of catalysts for carbon neutrality, possibly starting directly from the pregnant leach solutions of SACs. Efforts will be devoted to investigate if the leaching systems of our hydrometallurgical and/or mechanochemical treatments of SACs may be valuable precursors for the synthesis of new catalysts, which will allow us to eliminate the PGMs separation and the costly purification steps of the recovering process. Challenge will be to separate already in the leach liquor the PGM precursor/s of interest for the fabrication of PGMs based nanoparticles or catalysts. A deep understanding of the multimetallic catalyst composites for catalytic activity improvement would be desirable in order to use as catalysts precursors the PGMs complexes contained in the leach liquor. In addition, besides of PGMs leaching also the leaching of cerium will be pursued. Cerium is a valuable and critical element contained in high quantities in the leaching systems and used in catalysts for CO oxidation, water–gas shift reaction and HC conversion. Increased activity, by cerium spillover onto Pt, may be facilitated by atomic-level mixing of Pt and Ce in the alloy precursor [175].

As already stated previously, the most consolidated recovery methods of PGMs from the leach solutions are precipitation, liquid-liquid extraction (or solvent extraction) and ion exchange, while the new emerging ones use deep eutectic solvents (DESs), ionic liquids (ILs) and electrowinning [127]. The recovery of individual PGMs by single-stage separation from leach liquors of spent autocatalysts has been rarely investigated. Moreover, as far as we know, only a few examples are found in the literature about the synthesis of PGM NPs or PGM-based catalysts directly obtained starting from the leach liquors of SACs. A recent work on the leaching of a Pt-Rh SAC [62] demonstrated for the first time that after pH correction strongly acidic solutions ($\text{pH} < 0.5$) obtained after hydro-metallurgical treatment of the SAC may be a valuable secondary source of PGMs nanoparticles to be employed in TiO_2 -based catalysts. According to this study, and as predictable, the difficulty in NPs formation from the leach solution lies in the high acidity of this solutions ($\text{pH} < 0.5$) and the presence of accompanying/contaminating ions of non-precious metals, as shown in Table 5 where the composition of the leach solution is shown. The PGMs precipitation strongly depended on the solution pH: the yield of the precipitated PGM NPs increased considerably from 40% to almost 100% when the pH was adjusted to 7–8.

Table 5. Metal ion concentrations after leaching with $\text{HCl}/\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ ($\text{S}/\text{L} = 1/100 \text{ g}/\text{cm}^3$, 3 h, 70°C , 300 rpm) [62].

Chemical Element	Concentration of Metal Ions in Leach Solution (mg/dm^3)
Pt(IV)	22.79
Rh(III)	2.03
Fe ions	2.27
Mg(II)	24.87
Cu(II)	0.14
Zn(II)	0.67

In another recent study [176], a cheap process based on hydrometallurgy is described to directly recycle PGMs from Pd-Rh SACs to synthesize carbon supported PGMs based catalysts. SACs were firstly leached by a $\text{HCl}+\text{H}_2\text{O}_2$ system, resulting in Pd and Rh chloro-complexes. The optimized leaching rates of Pd and Rh were $97.99 \pm 2.64\%$ and

$87.70 \pm 1.23\%$, respectively. Then Pd precursor was separated from the leach solution by precipitation, to remove most impurities. The Pd precursor or Pd chloro-complexes solution was used to synthesize carbon supported catalysts directly via an ethylene glycol (EG) reduction method. To synthesize carbon-based catalysts, in fact, EG reduction method is a common way starting from the PGM chloro-complex solution [176,177].

In another work by Racles et al. [178] a SAC was treated with $\text{HCl} + \text{H}_2\text{O}_2$ in very mild conditions to extract approximately half of its PGMs content, mainly as chlorides. The noble metals were subsequently charged into functionalized mesoporous silica by complexation with mercapto groups to synthesize a heterogeneous catalyst for hydrosilylation and oxidation reactions. In addition, also the cordierite scrap after PGMs leaching was tested for potential use in the primary purification of wastewaters.

Therefore, it can be emphasized that it may be possible to directly synthesize PGM-based catalysts from the PGMs leach solution through the hydrochloric acid and oxidant systems. For PGM catalysts, the main raw materials are thus PGMs chlorides and PGMs chlorates [176].

Chloro-complexes contain a wide variety of PGMs anionic species (Table 4) with low molecular weight and two oxidation state for species, exhibiting stable anions as ion pairs counterpart. These ions may be coupled with counter ions from different organic ligands [179–181] that generate stable ion pairs with low charge density and different selectivity. As first-ligand generation we cite ammonium chloride, butanedione oxime, zinc and magnesium powders which are only a few examples of counter ions which may be coupled with generic noble metal charges. However, these ligands present some stability problems thus requiring the search for new innovative ligands.

Quaternary ammonium and sulfoxide derivatives salts are an example of tunable and stable complexes of new compounds. Stable and complex chlorine solution systems which contain ion pairs mixture of PGMs are highly desirable. These stable systems can be perturbed by using the common ion effect technique (salting out) in order to obtain selective catalytic precursors by focused separations. The salting out effect not only influences the selective separation of catalysts by providing catalytic precursors, but it also affects the recovered quantities.

In another approach, the chlorine complex solution may be coupled with organic ligands [182,183] as a counter ion pair and, by imposing supersaturated condition, catalyst nanoparticles with a high specific surface area may be obtained for application as catalysts.

In CHemPGM project, hydrometallurgical leaching of SACs will be carried out involving already consolidated low acid solutions (namely $\text{HCl} - \text{H}_2\text{O}_2 - \text{NaCl}$ as oxidant) with low liquid/solid ratios and novel ones aiming at maximizing PGMs recovery thus guaranteeing high PGMs concentration in leachates. PGMs chloro-complexes in acid solution are therefore our starting precursors for catalysts in case of the hydrometallurgical process. The composition of leach solution in case of mechanochemical process is still under investigation by X-ray fluorescence (XRF) analysis, and will be published in a future work.

Conventional and novel techniques [184] will be considered in the synthesis of supported PGM-based catalysts, always being inspired to green and sustainable principles.

4. Conclusions

The rapid growth demand of critical raw materials for the EU industry and the need to close CRMs loop has pushed the development of environmentally-friendly recycling processes of end-of-life devices. This paper presents an overview about the current trends in PGMs recycling from spent automotive catalysts, and focuses on the study of a new emerging green technologies. In addition, analysis of the pregnant leach solution from consolidated hydrometallurgical routes in chloride media is carried out, aiming at finding the way to obtain direct precursors for the synthesis of novel catalytic materials, thus reducing the separation and purification recovery steps. These research activities ladder up to the goals of the “Chemistry of Platinum Group Metals-CHemPGM” project whose main objective is to provide a deep insight into the chemistry and mechanisms associated

with the recovery of PGMs from secondary sources and reuse of the recovered PGMs for the synthesis of new catalysts in order to secure the PGMs value chain and achieve carbon neutrality.

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