Research Progress on Metallurgical Recovery of Platinum Group Metals from Spent Automotive Catalysts

Donghan Huang*

Powder Metallurgy Research Institute, Central South University, Changsha, China.

8204230402@csu.edu.cn

Abstract. This paper reviews recent advances in metallurgical technologies for recovering platinum group metals (PGMs) from spent automotive catalysts. The composition, catalytic principles, and failure mechanisms of automotive catalysts are introduced, followed by a systematic analysis of the principles, current applications, and advantages and disadvantages of three recovery processes. pyrometallurgy, hydrometallurgy, and biohydrometallurgy. Pyrometallurgy offers large processing capacity but is energyintensive and causes significant pollution. Hydrometallurgy achieves high recovery rates but involves complex wastewater treatment. Biohydrometallurgy is environmentally friendly but still at a developmental stage. In the future, PGM recovery technologies should evolve toward greener, less toxic, and more efficient approaches, promoting the sustainable recycling of PGM resources.

Keywords: Waste cars, catalysts, platinum group metals.

1. Introduction

Platinum group metals (PGMs), including ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt), have become critical strategic resources in defense and modern hightech industries due to their economic value, rarity, environmental significance, and scientific importance[1]. However, PGM mineral resources are highly concentrated and their ore grades are extremely low, typically only 2-10 g/t, leading to high supply risks and costly mining. In contrast, the PGM content in spent automotive catalysts can reach 0.2-0.5%, far higher than that in primary ores, making recycling a key pathway to ensuring resource security and reducing environmental burdens. Most of the demand for PGMs comes from spent automotive catalysts. Compared with natural ores, recycling PGMs from waste catalysts has several advantages. First, the concentration of Pd in primary ores, about 2-10 ppm (g/t), is extremely low, while it reaches $1\text{-}9\times10^3$ ppm in spent catalysts. Second, the supports of waste catalysts are typically Al_2O_3, activated carbon, and cordierite ($2MgO\cdot2Al_2O_3\cdot5SiO_2$), which do not require removal of ferromagnesian silicate gangue during processing[2]. However, if spent catalysts are discarded without proper recycling, not only would this cause a significant loss of valuable PGM resources, but the contained heavy metals and chemicals could leach into soil and water through rainfall, posing threats to ecosystems and human health. Therefore, efficiently recovering PGMs from spent automotive catalysts is both a vital approach to alleviating global PGM supply-demand conflicts and a key measure to achieve the dual goals of “resource recycling” and “environmental protection”.

Currently, PGM recovery processes from spent automotive catalysts mainly fall into three categories, pyrometallurgy, hydrometallurgy, and biohydrometallurgy. Pyrometallurgy uses hightemperature smelting to concentrate PGMs into collector metals, such as lead or copper. It offers large processing capacity and strong adaptability, but also faces challenges, including massive dust emissions during collection[3], complicated concentration processes, and limitations in collector metal recovery. Hydrometallurgy dissolves supports and metals using acidic or alkaline solutions, followed by precipitation, extraction, and other separation steps to refine PGMs. It is characterized by high recovery efficiency and good selectivity, but faces difficulties in dissolving certain catalyst supports, e.g., cordierite, and may generate large amounts of acidic wastewater. Due to low recovery efficiency and slow reaction kinetics, its industrial application is limited[4]. Biohydrometallurgy, an emerging technology, uses microbial metabolism, e.g., sulfuroxidizing bacteria and ironoxidizing bacteria, to leach PGMs[5]. It is environmentally friendly and energy-efficient but suffers from slow leaching rates and long processing cycles, remaining largely at the laboratory stage. At present, stateoftheart recovery methods focus not only on achieving higher PGM recovery rates but also on economic and environmental considerations, following green principles.

This paper focuses on the recovery of PGMs from spent automotive catalysts, analyzing the composition and failure mechanisms of automotive exhaust catalysts, the principles and current applications of existing metallurgical processes, and exploring pathways for circular utilization and sustainable development of PGM resources.

2. Automotive Catalysts

2.1 Composition and Catalytic Principles of Automotive Catalysts

Automotive catalysts are the core component of the exhaust aftertreatment system in gasoline vehicles, designed to convert harmful gases (CO, CH_x, NO_x) into harmless CO_2, H_2O, and N_2. Since automotive exhaust catalysts must simultaneously treat CO, CH_x, and NO_x, they are also known as threeway catalysts (TWCs). The primary exhaust purification catalysts currently in use contain PGMs, and the purification reactions occur on the surface of these metals[6]. The performance of automotive catalysts directly influences exhaust emissions and thus impacts the environment. Over longterm use, catalysts gradually fail due to thermal, chemical, and mechanical factors.

The composition of automotive catalysts includes the substrate, coating, active components, and other functional layers. The structure of the catalyst and its conversion reactions are shown in Figure 1. The substrate, typically cordierite with a honeycomb structure, has a low thermal expansion coefficient and high porosity, providing a large specific surface area, freeflowing pathways for exhaust gases, and a hightemperature environment for catalytic reactions., about 2-10 ppm (g/t), The coating on the substrate generally consists of γAl_2O_3 and CeO_2-ZrO_2 solid solution (CZO). The γAl_2O_3 coating provides a support matrix for the active materials, ensuring uniform dispersion and reducing their aggregation[1]. CZO is capable of storing and releasing oxygen during exhaust gas catalysis, thereby enhancing conversion efficiency and improving catalytic stability.

PGMs are dispersed uniformly on the coating surface as active materials, catalyzing the conversion of exhaust gases into harmless CO_2, H_2O, and N_2. Specifically, Pt and Pd catalyze the oxidation of CO and CH_x into CO_2 and H_2O, while Rh catalyzes the reduction of NO_x into N_2[7,8]. The reactions are as follows.

$2CO + O_2 \rightarrow 2CO_2$

$2C_6H_6 + 15O_2 \rightarrow 6H_2O + 12CO_2$

$2NO \rightarrow N_2 + O_2$

$2NO_2 \rightarrow N_2 + 2O_2$

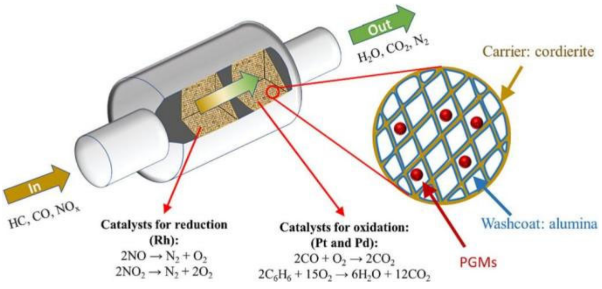

Figure 1. Schematic diagram of an automotive catalytic converter and its working principle9

2.2 Analysis of Failure Mechanisms

The deactivation of automotive catalysts arises from several mechanisms, including sulfur/phosphorus poisoning, oxidation of PGMs (PtO_2, PdO_2), carbon deposition, sintering and agglomeration of PGMs, encapsulation by the support, and reduction in specific surface area and pore volume. (1) Sulfur/Phosphorus poisoning: Sulfur oxides (SO_x) and phosphorus oxides (PO_x) in exhaust gases strongly interact with active metals, especially Rh, or the support surface, forming hardly reducible sulfide/phosphate layers that block active sites. (2) Oxidation of PGMs: Under high temperatures, Pt and Pd are readily oxidized into insoluble PtO_2 and PdO_2. This not only leads to the loss of catalytic activity but also significantly increases the difficulty of leaching noble metals during subsequent recovery. (3) Carbon deposition: Incompletely combusted hydrocarbons form porous carbon layers on the catalyst surface, hindering reactant diffusion and covering active sites. (4) Sintering and agglomeration: Hightemperature conditions promote migration and aggregation of PGM nanoparticles, resulting in larger particle sizes with catalytic activity dropping sharply when particle size exceeds 5 nm, and a decrease in specific surface area. (5) Encapsulation by the support: Excessive growth or sintering of coating materials causes collapse of the support's pore structure, further reducing the effective specific surface area and pore volume for reactions. These deactivation mechanisms are interrelated and collectively lead to the overall deterioration of catalyst performance.

3. Metallurgical Recovery Process

The recovery of PGMs from automotive catalysts mainly involves the following steps, separation and pretreatment, enrichment, extraction, separation, and refining/purification. The major steps are shown in Figure 2. Pretreatment aims to remove impurities, crush the support, and conduct fine grinding to facilitate subsequent separation of PGMs. The enrichment, extraction, and separation stages are the most critical in PGM recovery, primarily comprising pyrometallurgy, hydrometallurgy, and biohydrometallurgy. After enrichment, extraction, and separation, the leachate (from hydrometallurgy) or alloy (from pyrometallurgy) still contains a large number of impurities. Refining and purification are then required to improve the purity of PGMs. This section focuses on introducing the three main metallurgical methods.

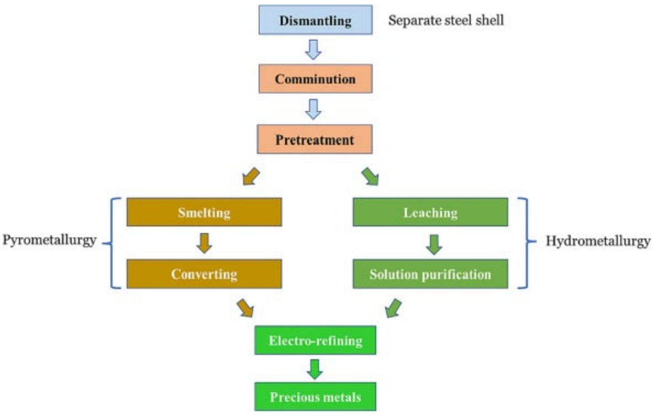

Figure 2. Main steps in SAC recovery9

3.1 Pyrometallurgy

Pyrometallurgy is an industrial method for recovering platinum group metals (PGMs: Pt, Pd, Rh) from spent automotive catalysts. Its core principle is to exploit differences in density and melting point between PGMs, the support, and other impurities. Through hightemperature smelting, noble metals are enriched and subsequently refined to high purity[10].The metal collector method is the central technology in pyrometallurgical recovery of PGMs from spent automotive catalysts. By smelting at high temperatures, noble metals are selectively concentrated into a specific metallic phase, enabling efficient separation.

Commonly used collector metals include iron and copper. When iron is used as a collector, plasma furnaces operating at around 2000 °C are required. Under these conditions, PGMs dissolve in the iron melt to form continuous solid solutions. Copper collection is typically carried out in electric arc furnaces, using copper powder, copper oxide, copper carbonate, or copperbearing materials as collectors.

At high temperatures, collector metals melt into droplets that are uniformly dispersed in the slag. Reduced PGM particles are attracted to and absorbed by these metal droplets, which then aggregate and settle at the bottom of the vessel under gravity, thereby achieving enrichment and separation[10]. The metal collector method is suitable for treating insoluble supports and lowgrade PGM catalysts. It offers strong raw material adaptability, low operating costs, mild reducing atmospheres, high collection efficiency, and large production capacity. It is particularly effective for insoluble supports and catalysts with very low PGM content. In selecting collector metals, factors such as melting point, solubility with PGMs, slag-alloy separation, and metal losses must be considered. Zheng et al.[11] employed an iron collector pyrometallurgical method and conducted indepth studies on the effects of chemical bonding and surface tension in the formation of immiscible phases (metal and slag). For recovering lowgrade PGMs from residues of hydrometallurgical leaching, they optimized slag design to reduce flux consumption. To achieve maximum separation, a slag system with low viscosity, low melting point, and low density (CaO-Al_2O_3-SiO_2-Na_2O-B_2O_3-CaF_2) was developed. The simulated equilibrium of slag reactions under optimal conditions is shown in Figures 3a and 3b.

Cordierite supports have high melting points (>1900 °C), which are difficult to reach in conventional electric furnaces, making slag formation challenging. Plasma arc smelting offers advantages such as concentrated energy, high smelting temperature, rapid heating, and controllable atmosphere. Its principle is to use a plasma arc to provide sufficient temperature to melt metals, allowing PGMs in waste catalysts to combine with collector metals, forming alloys that settle to the bottom. Meanwhile, support materials react with added fluxes and enter the slag phase, thus separating PGMs from the catalyst support[10]. Plasma smelting shows strong potential for PGM recovery. In practice, plasma smelting of cordieritetype catalysts often adopts the copper collector method. Under relatively low temperatures (1450-1600 °C) and weakly reducing or neutral atmospheres, fluxes (e.g., SiO_2, CaO), copper collectors ($CuCO_3$, CuO, Cu), and reducing agents (usually powdered coke) are used. Zhang et al.[12] captured Pd from spent automotive catalysts using CuO under optimal conditions, and the capture mechanism is illustrated in Figure 3c. The process occurs in two steps: (1) migration of Pd onto the copper surface, and (2) alloying between copper and palladium. Thermodynamic parameters for the optimized process were obtained: melting temperature 1350 °C, CuO accounting for 15% of catalyst mass, carbon addition as reducing agent at 5%, CaO/SiO_2 mass ratio of 0.5, SiO_2/Al_2O_3 mass ratio of 2.2, and capture time of 2 hours. Under these conditions, the Pd recovery rate reached 97%.

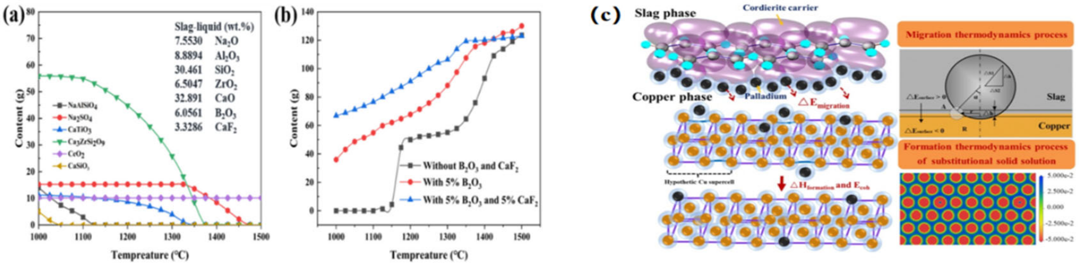

Figure 3. Simulated slag reaction equilibrium under optimal conditions: solid phase (a), liquid slag (b)[11]; (c) thermodynamic mechanism of Pd capture by copper in spent catalyst materials[12]

3.2 Hydrometallurgy

The principle of hydrometallurgy is to dissolve metal components using acids or alkalis, followed by concentration and purification of the target metals. The general process, shown in Figure 4a, includes grinding of spent catalysts, homogenization, pretreatment, leaching, filtration and washing, separation, and purification. Compared with pyrometallurgy, hydrometallurgy offers numerous advantages, such as lower operating temperature, higher purification rate, reduced energy consumption, potential for coextraction of metals, and better process control[13]. The hydrometallurgical process involves several stages: leaching to form PGM complexes, separation of dissolved precursors, and purification of PGMs from the leach solution. Leaching efficiency is influenced by the concentration of leaching agents, pH of the leachate, leaching time, temperature, and stirring conditions.

The most common method in hydrometallurgy is the dissolution of active components, primarily using hydrochloric acid combined with oxidizing agents to dissolve PGMs into solution. Due to their unique atomic structures, PGMs readily form soluble coordination compounds with halogen elements. Among these, PGM-chloride complexes are highly stable in acidic solutions[14], while the catalyst support remains essentially insoluble, enabling selective leaching. The leaching behavior of PGMs can be described by their ability to form stable complexes with chloride ions through the following reactions[15]:

$$PtCl_6^{2} + 4e \rightarrow Pt + 6Cl\text{ , } E^0=0.74V \tag{1}$$

$$PdCl_4^{2} + 2e \rightarrow Pd + 4Cl\text{ , } E^0=0.62V \tag{2}$$

$$RhCl_6^{3} + 3e \rightarrow Rh + 6Cl\text{ , } E^0=0.44V \tag{3}$$

From the above reactions and redox potentials, it can be seen that oxidizing agents with reduction potentials greater than 0.74 V can effectively promote the leaching of PGMs in chloride solutions. Nitric acid, hydrogen peroxide, and perchloric acid exhibit the following reactions and redox potentials[15]:

$$NO_3 + 4H^+ + 3e \rightarrow NO + 2H_2O\text{ , } E^0=0.96V \tag{4}$$

$$ClO_4 + 8H^+ + 7e \rightarrow 1/2\ Cl_2 + 4H_2O\text{ , } E^0=1.39V \tag{5}$$

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O\text{ , } E^0=1.77V \tag{6}$$

It can thus be concluded that nitric acid, hydrogen peroxide, and perchloric acid are effective oxidizing agents for the leaching of PGMs in chloride solutions.

J. de Aberasturi et al.[16] employed an HCl-H_2O_2 system. After hydrogen treatment and thermal pretreatment (250 °C, 22 h), leaching was performed at 90 °C for 6 hours in a mixed solution of HCl (12 M), H_2SO_4 (18 M), and H_2O_2 (110 vol), achieving a 95% recovery rate of PGMs. Moreover, H_2O_2 as an oxidant helped reduce the emission of harmful gases. The simplified experimental process is shown in Figure 4b, with major steps including crushing and grinding, oxidative leaching, filtration, further dissolution, and ICPMS analysis.

Another commonly used hydrometallurgical technique is alkaline solution leaching, in which cyanide is used under high temperature and high pressure to directly dissolve PGMs, thereby enabling efficient extraction. Sodium cyanide can form stable complexes with PGMs under such conditions and is thus applied to recover PGMs from spent catalysts in alkaline media. The main leaching reactions[17] are as follows.

$$2Pt + 8NaCN + O_2 + 2H_2O \rightarrow 2Na_2[Pt(CN)_4] + 4NaOH \tag{7}$$

$$2Pd + 8NaCN + O_2 + 2H_2O \rightarrow 2Na_2[Pd(CN)_4] + 4NaOH \tag{8}$$

$$4Rh + 24NaCN + 3O_2 + 6H_2O \rightarrow 4Na_3[Rh(CN)_6] + 12NaOH \tag{9}$$

Cyanide decomposition reaction:

$$CN + H_2O \rightarrow HCN + OH \tag{10}$$

$$2HCN + O_2 + 2H_2O \rightarrow 2NH_3 + 2CO_2 \tag{11}$$

Chen et al.[18] reported that alkaline leaching pretreatment of spent automotive catalysts under the following conditions—catalyst particle size 0.074 mm, solid-liquid ratio 4, leaching temperature 160 °C, leaching time 2 h, system constant pressure 2.0 MPa, and initial oxygen partial pressure 1.0 MPa—effectively removed the catalyst support and harmful substances, such as carbon and gasoline residues. Subsequently, a twostep pressurized cyanidation leaching was carried out under conditions of NaCN concentration 10 g/L, liquid-solid ratio 4, leaching temperature 160 °C, leaching time 1 h, system pressure 2.0 MPa, and stirring speed 800 r/min. The recovery rates of Pt, Pd, and Rh reached 95-96%, 97-98%, and 90-92%, respectively.

The influence of NaCN concentration on PGM leaching is shown in Figure 4c. It was observed that with increasing NaCN concentration, the leaching amount decreased. This is because during the surface chemical reaction process, both CN^- and O_2 must be adsorbed on the metal surface. If the CN^- concentration is too high, many active sites on the metal surface become occupied by CN^-, which hinders the adsorption of O_2.

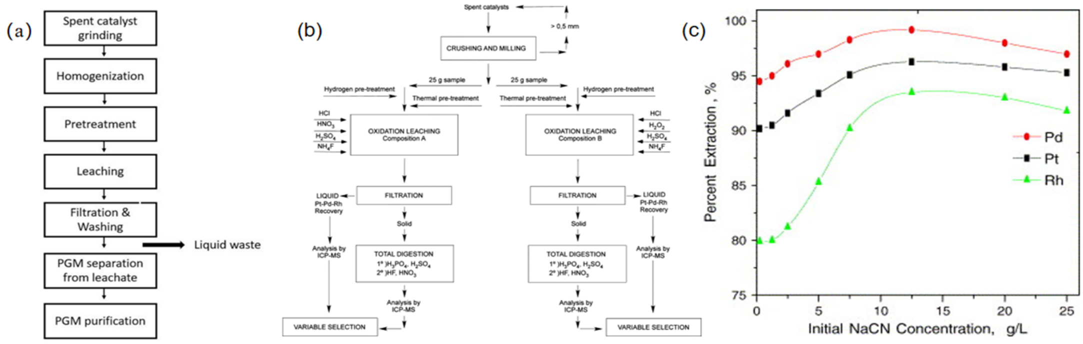

Figure 4. (a) Hydrometallurgical process for PGM recovery[14]; (b) simplified experimental flowchart[16]; (c) effect of NaCN concentration on PGM leaching[18] (160 °C, 1 h, O_2 pressure 1.5 MPa).

Although hydrometallurgy is based on simple principles and can be executed with standard reagents and equipment, it has advantages such as low energy consumption, low production cost, and suitability for smallscale applications. However, this process relies heavily on large quantities of corrosive and toxic chemical reagents, requiring robust equipment, engineering solutions, and corrosion prevention measures to ensure safe operation, thereby posing significant operational safety risks. In addition, hydrometallurgical recovery generates complex and difficulttotreat waste liquids and residues, complicating waste storage and increasing the risk of environmental pollution. If harmful substances such as nitrogen oxides or cyanides leak during the leaching process, they may further contaminate the environment and threaten the health of operators.

3.3 Biohydrometallurgy

Biohydrometallurgy is considered the most sustainable metallurgical process, with a lower carbon footprint and reduced chemical consumption compared to pyrometallurgy and hydrometallurgy. It encompasses bioleaching, biooxidation, and bioadsorption, using bacteria or fungi for extraction, oxidation, or adsorption. These technologies have demonstrated strong performance and economic potential in the mining and recycling industries.

Biohydrometallurgical recovery of PGMs from spent catalytic converters involves bioleaching (leaching step) and bioadsorption (extraction step), as illustrated in Figure 5. This process relies on interactions between PGMs and biological materials (e.g., bacteria), followed by absorption of PGMs into different media such as NaCN, NaOH, or HCl.

Biocyanidation is the main application of biohydrometallurgy in PGM recovery. Shin et al.[19] developed a twostage system for the production and accumulation of biogenic cyanide. The batch and continuous systems achieved 954.8 mg/L and 6594.5 mg/L of biogenic cyanide, respectively. When 1000 mg/L of biogenic cyanide was applied for SAC leaching at 150 °C, the recovery efficiencies for Pt, Pd, and Rh were 92.1%, 99.5%, and 96.5%, respectively.

Biohydrometallurgical recovery methods offer many advantages, such as the use of environmentally friendly solvents, selective metal recovery, lower energy consumption, reduced carbon footprint, and absence of harmful gases. However, whether using conventional hydrometallurgy or biohydrometallurgy, achieving recovery rates above 90% from SAC requires extensive pretreatment steps. Moreover, the slow leaching rate and high cost of bacterial preparation significantly constrain the industrial feasibility of biohydrometallurgy.

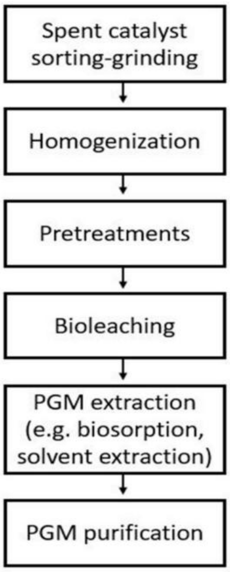

Figure 5. Biohydrometallurgical steps for PGM recovery[14].

4. Conclusions and Outlook

Due to the wide application of PGMs in industrial catalysts, functional materials, and electronic products, their limited natural reserves restrict the development of related fields. Furthermore, variations in PGM content from different sources, together with environmental pollution issues during processing, impose stricter requirements on secondary resource enrichment technologies. This review has outlined the processes currently used for recovering PGMs from spent automotive catalysts.

Pyrometallurgy, hydrometallurgy, and biohydrometallurgy have already become key approaches for future PGM recovery. Pyrometallurgy offers advantages such as short processing cycles, low wastewater discharge, and relatively low economic cost. However, it requires large amounts of energy and capital investment, while also causing environmental pollution. In contrast, hydrometallurgy enables small-scale processing under mild reaction conditions with low energy consumption, though the process itself is complex and generates large volumes of wastewater containing spent chemical reagents. Biohydrometallurgy, on the other hand, is flexible and cost-effective, while avoiding secondary waste generation.

Future technological development will be deeply focused on “greening” the processes, as sustainability requires environmentally friendly solutions. Research priorities include improving conventional processes that are high in pollution and energy consumption—for example, developing new leaching systems that are cyanide-free, chlorine-free, or low-toxicity, as well as exploring the industrial application potential of biohydrometallurgical technologies. At the same time, closed-loop treatment and resource recovery of secondary pollutants—such as chlorine-containing exhaust gases, heavy metal residues, and high-salinity wastewater—will become key indicators for evaluating the advantages and disadvantages of PGM recovery processes.

References

[1] Xv, B. et al. Recovery of platinum group metals from spent automotive catalysts: Review of conventional techniques and vacuum metallurgy. Resour. Conserv. Recycl. 215, 108103 (2025).

[2] Xu, B. et al. A Review of Recovery of Palladium from the Spent Automobile Catalysts. Metals 12, 533 (2022).

[3] eng, Z. et al. Pyrometallurgical Recovery of Platinum Group Metals from Spent Catalysts. JOM 69, 1553-1562 (2017).

[4] Xv, B. et al. Recovery of platinum group metals from spent automotive catalysts: Review of conventional techniques and vacuum metallurgy. Resour. Conserv. Recycl. 215, 108103 (2025).

[5] Hedrich, S., Fritze, M. & Schippers, A. MetallRecycling mittels Biohydrometallurgie. Chem. Ing. Tech. 95, 1897-1908 (2023).

[6] Hirata, H. Recent Research Progress in Automotive Exhaust Gas Purification Catalyst. Catal. Surv. Asia 18, 128-133 (2014).

[7] Schäfer, J. & Puchelt, H. PlatinumGroupMetals (PGM) emitted from automobile catalytic converters and their distribution in roadside soils. J. Geochem. Explor. 64, 307-314 (1998).

[8] ritsanaviparkporn, E., BaenaMoreno, F. M. & Reina, T. R. Catalytic Converters for Vehicle Exhaust: Fundamental Aspects and Technology Overview for Newcomers to the Field. Chemistry 3, 630-646 (2021).

[9] Xia, J. & Ghahreman, A. Platinum group metals recycling from spent automotive catalysts: metallurgical extraction and recovery technologies. Sep. Purif. Technol. 311, 123357 (2023).

[10] Jia, M. et al. Recent Developments on Processes for Recovery of Rhodium Metal from Spent Catalysts. Catalysts 12, 1415 (2022).

[11] Zheng, H. et al. Slag design and iron capture mechanism for recovering lowgrade Pt, Pd, and Rh from leaching residue of spent autoexhaust catalysts. Sci. Total Environ. 802, 149830 (2022).

[12] Zhang, L., Song, Q., Liu, Y. & Xu, Z. Novel approach for recovery of palladium in spent catalyst from automobile by a capture technology of eutectic copper. J. Clean. Prod. 239, 118093 (2019).

[13] Grilli, M. L. et al. Platinum Group Metals: Green Recovery from Spent AutoCatalysts and Reuse in New Catalysts—A Review. Crystals 13, 550 (2023).

[14] Yakoumis, I., Panou, M., Moschovi, A. M. & Panias, D. Recovery of platinum group metals from spent automotive catalysts: A review. Clean. Eng. Technol. 3, 100112 (2021).

[15] Wei, X. et al. Understanding the features of PGMs in spent ternary automobile catalysts for development of cleaner recovery technology. J. Clean. Prod. 239, 118031 (2019).

[16] Jimenez de Aberasturi, D., Pinedo, R., Ruiz de Larramendi, I., Ruiz de Larramendi, J. I. & Rojo, T. Recovery by hydrometallurgical extraction of the platinumgroup metals from car catalytic converters. Miner. Eng. 24, 505-513 (2011).

[17] Dong, H., Zhao, J., Chen, J., Wu, Y. & Li, B. Recovery of platinum group metals from spent catalysts: A review. Int. J. Miner. Process. 145, 108-113 (2015).

[18] Chen, J. & Huang, K. A new technique for extraction of platinum group metals by pressure cyanidation. Hydrometallurgy 82, 164-171 (2006).

[19] Shin, D., Park, J., Jeong, J. & Kim, B. A biological cyanide production and accumulation system and the recovery of platinumgroup metals from spent automotive catalysts by biogenic cyanide. Hydrometallurgy 158, 10-18 (2015).