# **Recovery of Palladium from the Spent Automobile Catalysts**

#### Subjects: Mineralogy

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The spent automobile catalysts (SAC) is the major secondary source of palladium and the production of SAC is increasing rapidly over years. The price of palladium keeps rising over the years, which demonstrates its preciousness and urgent industrial demand. Recovering palladium from the spent automobile catalysts benefits a lot from economic and environmental protection aspects. Hydrometallurgical methods such as chloride leaching with oxidants possess a high selectivity of palladium and low consumption of energy, and are cost-effective and flexible for different volume feeds compared with pyrometallurgical methods. The recovery ratios of palladium and other platinum-group metals should be the focus of competition since their prices have been rapidly increased over the years, and hence more efficient extractants with high selectivity of palladium even in the complexed leachate should be proposed in the future.

spent automobile catalysts palladium recovery

hydrometallurgy platinum group metals

palladium leaching

## 1. Introduction

Platinum group metals (PGMs) such as platinum (Pt), palladium (Pd), and rhodium (Rh) are widely used in automobile, chemical engineering, petroleum, electrical, and electronic industries due to their distinct physical and chemical properties: catalytic activity, electric conductivity, and corrosion resistance [1][2][3][4][5]. The increasing demand for PGMs causes a high consumption rate of high-grade PGMs ore. The increasing depletion of highgrade PGMs ore forces people to turn to the exploitation of low-grade ore. However, the cost of exploring PGMs from low-grade ore is much expensive and brings critical environmental issues <sup>[G][Z]</sup>. Although researchers have studied fungible materials to partially replace the use of PGMs in products such as automobile catalysts, the net consumption of PGMs is still high due to the increasing demand for engines in automobiles. About 65% of palladium, 45% of platinum, and 84% of rhodium are used every year for catalytic converters to decrease harmful emissions from engines [3][5][8][9]. With the enforcement of stricter emission regulations, the rapid development of the new-energy automobile industry will lead to a larger drain on PGMs supply. Meanwhile, PGMs in spent catalysts from numbers of outdated vehicles need to be properly recycled.

Compared with natural raw ore, the spent automobile catalysts indeed own several advantages. Palladium, like gold, is an international precious metal spot and trading species. Palladium surpassed the price of platinum for the first time in the year 2018, and then exceeded the price of gold in the year 2019 <sup>[10]</sup>. Spot palladium hit a record

high at 481.7 RMB/g or 2397.2 USD/oz in 2021, while platinum was only 219.6 RMB/g or 1092.7 USD/oz and gold hovered at 361.4 RMB/g or 1798.6 USD/oz. As for rhodium, its price reached as high as 3631.8 RMB/g or 18074.0 USD/oz, which was ten times of that of gold. <sup>[10]</sup>. The price of palladium keeps increasing at a fast speed at present as shown in **Figure 1**. Palladium could partially substitute platinum in catalytic converters for most gasoline-fueled vehicles, and industries favored using palladium over platinum in catalytic converters because the price of palladium was lower than platinum decades ago, which resulted in amounts of palladium remaining in the automobile exhaust catalysts <sup>[11][12][13][14]</sup>.



Figure 1. The price tendency of gold, platinum, and palladium from the year 2012 to 2021.

The great consumption of palladium products leads to a great amount of waste and scrap containing palladium. Recovery of palladium from the spent automobile catalysts has become an important source of palladium supply <sup>[15]</sup>. Compared with natural raw ore, the spent automobile catalysts indeed possess several advantages for palladium recovery. For one thing, the concentration of palladium in raw ore is pretty low, in the range of 2~10 ppm (g/t), and is generally associated with base metal sulfide minerals. While the spent catalysts are up to  $1-9 \times 10^3$  ppm, that is, thousands of times higher than that of raw ore. The recovery ratios of palladium from the spent automobile catalysts with hydrometallurgical technologies, e.g., traditional cyanide leaching or chloride leaching, could reach over 95%, and through pyrometallurgy, such as iron capture, the recovery efficiency of palladium is as high as 99% <sup>[2]</sup>. For another, the next is the carrier of spent catalysts commonly is Al<sub>2</sub>O<sub>3</sub>, activated carbon, and cordierite, which indicates no need to deal with ferromagnetic silicate gangue like raw material. Besides, the spent

catalysts are easy to collect due to their concentrated usage, and some industries have formed completed recovery processes <sup>[5][16]</sup>. The advantages listed above make the spent catalysts relatively easy to process, together with low capital investment, low environmental pollution, and high economic benefits. Recovery of palladium from the spent catalysts is beneficial from the perspectives of economic efficiency and environmental protection.

## 2. The Development of Recovering Palladium from the Spent Automobile Catalysts

With the rapid development of the automobile industry, palladium has been widely used in automobile catalysts due to its unique and excellent catalytic performance <sup>[17]</sup>. Around half of the global palladium is used to produce automobile catalysts. However, the recycled palladium from spent catalysts is less than 25% of its application <sup>[18]</sup>. The general overflow of recovery of PGMs from the spent catalysts can be broken into several steps: homogenization, preconcentration/pretreatment, leaching/dissolution, extraction/metal isolation, and purification. Methods of recovering palladium from spent catalysts can be divided into hydrometallurgical and pyrometallurgical methods. Hydrometallurgy includes traditional cyanide leaching, thiosulfate leaching, HCl(aq) + oxidants leaching, bio-recovery, and supercritical fluid extraction; pyrometallurgy includes incineration, chloride volatilization, and metal collection. In particular, the hydrometallurgical methods are reported more frequently because of their flexibility for raw material, lower energy consumption, and mild operation environment. In this section, the researchers introduce and evaluate related studies and technologies of recovering palladium from the spent automobile catalysts.

### 2.1. Pretreatment

The spent catalysts undergo mechanical processing such as segregation, crush, or milling and then are moved to a pyro/hydrometallurgical process, so as to make the leaching or separation of metals more effective. Thermal pretreatment is employed for spent catalysts to improve the recovery efficiency of metals by eliminating the hydrocarbons and charcoal presented on the surface of spent catalysts. Through thermal pretreatment in a suitable atmosphere (hydrogen, oxygen, nitrogen, or air), the undesired organic constituent of spent catalysts is removed, while desired metals are retained and moved to the next process <sup>[5][19]</sup>.

Differing from the thermal treatment above, the electromagnetic microwave can assist dipolar molecules and metal ions to chemically bind together. Microwave irradiation is widely applied in laboratories to improve extraction ratio and save time, and is especially fit for those alkali-insoluble or acidic-insoluble materials. Researchers have obtained the increased leaching efficiency of palladium from the spent catalysts with microwave assistance <sup>[20][21]</sup> <sup>[22][23][24]</sup>. The microwave technology has been applied to enhanced leaching, microwave drying, microwave carbothermal reduction, and microwave sintering, and it has broad prospects in metallurgical industry due to its unique conductive heating. In hydrometallurgical pretreatment, the spent catalysts are leached by using a suitable acidic or alkaline solution in the presence of iodine, bromine, chlorine, or hydrogen peroxide to deal with their carriers <sup>[25][26][27]</sup>. In this way, the encapsulation of PGMs by the carrier could be unpacked, and the contact area between leachate and precious metals is expanded. As a result, the recovery yield of palladium improved.

## 2.2. Hydrometallurgy

#### 2.2.1. Leaching or Extraction

The key to leaching is to effectively separate palladium from its carrier and gain leachate with a relatively high concentration of desired metals and minimize the presence of any contaminants. Technological factors such as temperature, reagents, reaction time, etc., could have a significant impact on the efficiency of metal leaching <sup>[28][29]</sup>. Hydrometallurgical methods are widely accepted for recovering PGMs from the spent catalysts due to their low reagent cost, high efficiency of metal recovery with a mild operational condition, no exhaust emission, and less investment of equipment. However, potential environmental risks still exist with the generation of waste liquid, requiring a wastewater treatment system in the following process. Furthermore, the content of PGMs in leachate is relatively low; thus, a suitable process for palladium recovery from leachate is needed.

#### 2.2.2. Separation or Recovery of Palladium from Leachate

Palladium needs to be further separated from other PGMs or base metals after hydrometallurgical leaching. The enrichment and purification methods of palladium from leachate studied at present include precipitation, solvent extraction (liquid–liquid extraction), and ion exchange. The final product after enrichment and purification could be palladium sponge or palladium chloride.

#### Precipitation

The precipitation method is a traditional one of separating palladium from leachate, which can be divided into diamminedichloro palladium precipitation and ammonium hexachloropalladate precipitation <sup>[30][31]</sup>. The former possesses a relatively high selectivity for palladium from other PGMs than the latter. The reactions happening during diamminedichloro palladium precipitation (Reactions (1) and (2)) illustrate that chlorine complex of palladium from chloride medium leaching reacts with ammonium hydroxide and forms soluble complex ([Pd(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>) while other metals turn into hydroxide precipitation; thus, palladium is separated from other metals. Hydrochloric acid is added for maintaining the pH of the leachate between 0.5~1.5 to form the yellow sediment of diamminedichloro palladium is purified after filtration. After the two steps of ammonification and acidification repeat several times, the recovery ratio of palladium is over 90% and the product purity exceeds 99.6% <sup>[32]</sup>.

 $H_2PdCl_4 + 4NH_3 H_2O = [Pd(NH_3)_4] Cl_2 + 4H_2O + 2HCI (1)$ 

$$[Pd(NH_3)_4]Cl_2 + 2HCl = [Pd(NH_3)_2Cl_2 + 2NH_4Cl (2)]$$

Researchers made use of diamminedichloro palladium precipitation to recover palladium from the leachate of spent catalysts <sup>[33]</sup>. The precipitation reactions of this method were indicated as Reactions (3) and (4): Chlorine was added to oxidize metal Pd(0) into Pd(II) completely; Pd(II) in leachate can form crimson sediment ( $[Pd(NH_4)_2]CI_6$ ) after over-dose ammonium chloride is added into the leachate because of the low solubility of the sediment.

$$Pd + 2Cl_2 = PdCl_4$$
 (3)

$$PdCl_4 + 2NH_4Cl = [Pd(NH_4)_2]Cl_6\downarrow (4)$$

Spent catalysts were processed with aqua regia under the conditions of a temperature 90 °C and reaction time 2.5 h, and then the filter liquor was obtained after filtration. The ammonia and hydrochloric acid were added into filter liquor to obtain the precipitate of palladium. After repeating the process of ammonification and acidification three times, the recovery ratio of palladium was over 98%. The precipitation method is only suitable for relatively simple leachate due to its poor selectivity. Besides, unit operations such as filtration and purification of palladium sediment are intermitted, which causes inconvenience for continuous production.

#### **Solvent Extraction**

The solvent extraction, also called liquid–liquid extraction, can be described as palladium ion reacting with an extraction agent and then forming and enriching palladium complex in the organic phase. After the separation of organic and inorganic phases, palladium can be stripped from the organic phase with a suitable stripping agent. The geometric structure of [PdCl<sub>4</sub>]<sup>2-</sup> is planar square, which makes it the most stable complex among other chlorides PGMs. The extraction agents include sulfide, phosphate, and amine derivatives. Sulfide derivatives such as di-n-octylsulfide, thioether, and sulfoxides have been widely used for extracting palladium from leachate of waste materials <sup>[27][34][35][36][37]</sup>. Phosphate derivatives such as tri-n-butyl phosphate (TBP), tri-n-butylphosphate, thio-phosphoric acid, phosphonic acid and trihexyl(tetradecyl) phosphonium chloride (Cyphos IL 101) have also been reported <sup>[37][38][39]</sup>. Amine derivatives, including amine and oxime, such as tri-n-octylamine and, thiodiglycolamides have recently been employed as the extraction agents for Pd(II) and Pt(IV) from leachate <sup>[40][41]</sup> <sup>[42]</sup>.

Researchers studied 2-hydroxy-5-nonylacetophenone oxime (LIX 841) with kerosene diluter to extract palladium from leachate of spent catalysts, which contained platinum, palladium, iron, manganese, nickel, etc. The palladium could be effectively extracted when the content of LIX 841 in kerosene was >0.2%. Then thiourea and hydrochloric were used as stripping agents, and the total recovery ratio of palladium was >99% <sup>[43]</sup>. Ramachandra used LIX 841 and Alamine 336 to extract platinum and palladium (A/O = 3), and then platinum and palladium were stripped with 0.5 mol/L thioureas and 0.1 mol/L hydrochloric acids, respectively. The recovery ratios of the two precious metals both were > 99% <sup>[44]</sup>. Using the regenerated organic phase could still achieve high recovery efficiency for palladium and platinum even after several extracting and stripping cycles. Thioether, a kind of organic sulfide, is easy to bond with palladium and form PdCl<sub>2</sub>·(R' -S-R)<sub>2</sub> neutral extraction complex, which possesses a high selectivity for palladium. Thioether can extract palladium from a complicated solution containing a large number of base metals and other PGMs. The extraction reaction of palladium is shown as Reaction (5).

$$PdCl_4^{2-} + 2(R' - S - R)_{(0)} = PdCl_2 \cdot (R' - S - R)_2 + 2Cl^- (5)$$

Though organic sulfide above owns a high selectivity for palladium, its extraction speed of it is slow. In addition, the synthetic process of thioether accompanies with a smelly raw material of mercaptan, which limits it to be mass-produced. So, researchers studied the performance of synthesized benzylisooctyl sulfoxide (BSO) for palladium extraction. The result showed that between the concentration of  $C_{(HCI)} = 0.1 \sim 4.0$  mol/L, the extraction ratio of Pd<sup>2+</sup>

using BSO gradually increased with the increase in acidity. At the concentration of  $C_{(HCI)}$  = 4.0 mol/L, the extraction ratio of Pd was beyond 99%. However, the high acidity of the solution is harmful to equipment.

The solvent extraction method has been widely used in the metallurgy industry due to its excellent selectivity and relatively high efficiency compared with the precipitation method. Besides, regeneration of the organic phase is relatively easy. However, it is hard to recover the desired metal by one-stage extraction and stripping. In addition, segmented operations require a large investment for the factory area and also decrease the recovery efficiency.

#### Ion Exchange

The ion exchange method is based on the exchange reaction occurring between ion exchange resin and ions in solution. After the exchange reaction is finished, the resins are eluted with an eluting agent. This method is more economical compared with the two methods above, as the ion-exchange resin is cheap and can be recycled after regeneration. According to the properties of functional groups, ion-exchange resins can be divided into seven categories: strong acidic, weakly acidic, strong alkaline, weak alkaline, oligomeric, acid-base amphoteric, and oxidative reductive resins. The anion exchange resins are widely used for the extraction of PGMs because PGMs tend to form anion complexes.

Synthetic polyvinyl alcohol amidoxime(PVAAO) chelated fiber was used to adsorb palladium in the leachate of spent catalysts, and the adsorption ratio of palladium was >99%. The fiber was eluted with the solution containing 5% thiourea and 0.5 M nitric acid, and the elution ratio of palladium was >99% <sup>[45]</sup>. The adsorption performance of dt-1016 anion exchange resin for ultra-trace platinum and palladium was studied. The results showed that adsorption ratios of platinum and palladium in 0.025M HCl medium arrived at 99.60% and 97.95%, respectively. However, the resin regeneration was not introduced <sup>[45]</sup>.

Nikoloski performed comparative research among ammonia functional resin (Lewatit Mono Plus (M +) MP 600), polyamine functional resin (Purolite S985), and thiourea functional resin (XUS 43600.00). Thiourea functional resin (XUS 43600.00) showed the best adsorption performance in the experiments. Singh and Ruhela proposed polymeric beads encapsulated by dithiodiglycolamide to separate and recover palladium from the leachate of spent automobile catalysts. The sorption kinetics of palladium were fast, and the kinetics data fit well with the pseudo second-order equation model for the sorption of palladium ions onto the beads. More than 99% of palladium was eluted by using 0.01 M thiourea in 0.1 M HCl medium <sup>[46]</sup>. The ion exchange methods have become popular in the recovery of precious metals from the leachate in recent years due to their low cost and simple operation. However, the functional resins might easily be poisoned after repeating several times, and hence the adsorption ability of the resins could be degraded. The selectivity and regeneration of resins are of great importance for their further applications.

## 2.3. Pyrometallurgy

Pyrometallurgical technology has attracted attention for recovering PGMs from spent automobile catalysts for its simple and short-flow process, no pollution of wastewater, and large-scale application potential <sup>[11][47][48]</sup>.

Pyrometallurgy can be divided into incineration, chlorination volatilization, and metal capture methods. Incineration leads to the production of a large amount of gas waste. As a result, this method has hardly been reported on recovering palladium from spent automobile catalysts. The chlorination volatilization process has been used in industry for a long period of time owing to its high efficiency. Meanwhile, the vapor of volatile metals (e.g., calcium, magnesium, cadmium, and zinc) causes a great potential threat to human health. Metal capture is an effective method for PGMs recovery from spent catalysts even with a pretty low content of these metals. However, melting under high-temperature (1200–2000 °C) has high energy consumption and the investment for equipment is high.

#### 2.3.1. Chlorination Volatilization Method

Chlorination volatilization is based on the volatility difference of metal chlorides. Chlorine mixes with carbon monoxide, oxygen, carbon dioxide, phosgene, etc., as a chlorinating agent. Auxiliary agents such as KCl, NaCl, CaCl<sub>2</sub>, etc., are added to make palladium chloride volatize completely, so as to effectively separate palladium from the spent catalysts. Chlorination volatilization could achieve an excellent palladium volatilization ratio of 99% after reacting for 1~3 h at the temperature of 850~900 °C <sup>[49]</sup>. However, this method causes a great threat to the environment due to the production of a great amount of smoke dust deriving from volatile metals, and it needs great investment for equipment with high temperature resistance and corrosion resistance.

#### 2.3.2. Metal Capture Method

In the metal capture process, the solubility, melting points, and chemical properties of both capturing agents and palladium have to be considered. Spent catalyst powder containing PGMs is melted in a furnace together with a collector (Lead, Copper, Iron, Nickel, etc.) and fluxing agent (lime, cryolite, borax, soda ash, etc.) to generate a metallic alloy (M-PGMs) and a slag. Palladium is collected by metal and transferred into the metallic alloy, while the carrier of spent catalysts is moved into the slag. Alloy and slag are easy to separate due to the density difference. This method is widely applied, especially for spent catalysts with insoluble carriers and low content of PGMs.

Because copper could be recycled as a high-purity copper with electrolysis, copper capture is more suitable for recovering PGMs. The waste catalyst was melted together with copper metal or copper oxide, flux agent, and reducing agent under a high temperature, and then the copper alloy gathering PGMs and oxidized slag were formed. Under the optimum experiment conditions of CaO/SiO<sub>2</sub> 1.05, CuO 35~40%, reduction agent 6%, 1400 °C and 5 h melting time, the recovery ratios of Pt, Pd and Rh were 98.2%, 99.2%, and 97.6%, respectively <sup>[24]</sup>. The flowchart of copper capture for recovering PGMs from waste catalysts is shown in **Figure 2**.



Figure 2. The flowchart of copper capture for recovering PGMs from spent catalysts.

The advantage of the copper capture method is that it can make full use of existing non-ferrous metal melting equipment, and thus the investment and processing cost can be saved. Besides, it has a large production capacity which makes it possess great competitiveness in industry. However, a large quantity of the anode slime containing both PGMs and copper is produced during the copper alloy electrolysis, which needs a complicated process to recover PGMs, causing the mechanical loss and low recovery ratio of precious metals <sup>[50]</sup>.

Iron capture of precious metals from low-grade waste catalysts has been studied <sup>[51]</sup>. Because the melting point of iron (1538 °C) is high, iron capture of palladium from spent catalysts is in the plasma reactor. The heat generated by plasma made  $Al_2O_3$  directly melt and there was no need to add other reagents to reduce its melting point. After the alloy was dissolved by  $H_2SO_4$ , precious metals were enriched in residue. The recovery ratio of palladium by plasma smelting iron capture reached 98%. Plasma smelting possesses the advantages of a fast reaction speed and a controllable atmosphere. The plasma smelting furnace, however, as a kind of special equipment, is very expensive. Under the condition of extremely high temperature, the service life of the plasma gun is short (100~150 h) and the cost of maintenance and repair of the furnace body is high. Ding et al. <sup>[52]</sup>

feasibility of recovery of PGMs from leaching residue of spent auto-exhaust catalysts with iron capture by designing slag ahead to reduce slag volume and save cost. However, it is difficult to obtain stable technical indexes unless the operation is accurate enough and the spent catalysts are homogeneous.

The lead capture method of recovering PGMs uses an arc furnace or a blast furnace. C or CO is typically used to produce and maintain a reductive atmosphere in the furnace. Capturing happens during the reduction reaction by building the metallic bond between lead and PGMs. PGMs and lead transfer into lead alloy while the carrier of spent catalysts converts into slag phase, and then PGMs are concentrated. Compared with copper capture, the big problem of lead capture is the volatilization of Pb compounds, which are inevitable during high-temperature melting, resulting in great potential danger to labor health and environmental safety.

The matte serves as a collector due to the close affinity of matte for PGMs during the smelting of spent catalysts. By adding metal (e.g., nickel) and sulfur or metal sulfide (e.g., NiS) with flux (e.g., CaO, Na<sub>2</sub>CO<sub>3</sub>, or their mixture), PGMs could be enriched in the matte phase at a relatively low temperature (1000~1450 °C). The smelting atmosphere should be well controlled because the oxidation of nickel will cause difficulty in refining after the separation of PGM-containing matte from slag. Besides, the silicon acidity of slag, defined as the mass ratio of oxygen in SiO<sub>2</sub> to that in Al<sub>2</sub>O<sub>3</sub> and MgO, should be accurately controlled to avoid metal loss and optimize the smelting process. The equipment of matte capture can be directly combined with copper smelting equipment. However, the generated sulfur and its related oxides, which pose a threat to the environment, should be properly disposed of [11].

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