Recovery and Enrichment of Platinum Group Metals from Spent Automotive Catalysts by Pyrometallurgy: A Review

Jibiao Han, Xianglin Bai, Quan Yang, Biao Wang, Wangrui Ma, Yong Li, Bin Yang, Xilong Wu, and Yu Zhao

Abstract The world platinum group metals (PGMs) reserves and the recovery of PGMs secondary resources are discussed in this review. For many countries, the low reserves, large consumption, and high external dependence of PGMs are common problems nowadays. Therefore, the recycling of catalysts which contain PGMs has become an important method to alleviate the shortage of resources. This paper mainly introduces the pyrometallurgical recovery and enrichment process of spent automotive catalysts, including plasma melting and metal capture method, which has the advantages of high enrichment rate, large-scale, and short process, and iron, copper, and lead are often used as metal collectors to capture and recover PGMs. The advantages and disadvantages of different technologies are summarized, and the improvement and progress of PGMs recovery process are prospected, which provide a new idea for green and efficient recovery of spent automotive catalysts.

Keywords Platinum group metals (PGMs) · Spent automobile catalyst · Pyrometallurgy recovery · Metal capture method · Enrichment

Introduction

Platinum group metals (PGMs) include platinum, palladium, rhodium, iridium, ruthenium, and osmium. They are widely used in automotive catalysts, petrochemical industry, national defense construction, electronic industry, jewelry, pharmaceutical,

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and other fields because of unique catalytic properties, high melting point, and corrosion resistance. PGMs also have increasingly important applications in new energy, materials, and other frontier industries, such as hydrogen energy industry, new energy vehicles, and environmental protection materials, and have become an important metal material to promote the development of science and technology [1–5].

PGMs play an important role in national development and life, but extremely scarce mineral reserves and unevenly distributed mineral resources have become the reasons that restrict their rapid development. According to the data of the United States Geological Survey (USGS), the global PGMs reserves are about 70,000 tons in 2021. The platinum group metal resources in South Africa, Russia, and Zimbabwe account for more than 98% of the total global resources that the distribution is very concentrate [6]. The reserves of PGMs in other countries are very scarce, the USA accounts for about 1.28% of the world, while China only accounts for about 0.58%. Most countries in the world rely on imports of PGMs. The demand for Pt, Pd, and Rh has decreased due to the COVID-19 epidemic, but with the continuous development and progress of social economy, PGMs has shown an overall upward trend [7].

The total consumption of PGMs in China has become the first in the world and has increased year by year since 2009. The consumption of platinum and palladium reached 165 t in 2019, accounting for more than 27% of the world's, which is mainly used in the field of automotive catalysts. Car ownership of China has also ranked first in the world for many years. According to the data of China's National Bureau of Statistics, car ownership of China has reached 310 million by June 2022 [8]. A large number of cars were scrapped when they reached their service life. The recycling volume of scrapped cars was 15 million in China in 2020, including about 10 million spent automobile catalysts. Based on the average 2 g of PGMs per car, China will have 20 tons of PGMs rich automotive catalysts scrapped for recycling every year. Although the automobile catalyst is classified as hazardous waste, the content of platinum group metals in spent automobile catalyst is more than 2000 g/t, which is hundreds of times than platinum group ore. It will not only cause environmental pollution, but also cause a waste of resources if discarded or stacked [9, 10]. The efficient recovery and utilization of waste automobile catalyst will have long-term economic benefits and social value and reduce the contradiction caused by the uneven supply and demand relationship and distribution of Pt.

Nowadays, automotive catalysts are mainly composed of carrier, coating, active components, etc.; the carrier is mainly cordierite, and the coating is γ-Al_2O_3 which also adds lanthanum, cerium, praseodymium, neodymium, and other rare earth elements to reduce the addition of PGMs. Under the synergistic effect of these PGMs and rare earth, they catalyze and purify automobile exhaust [11]. The methods of recovering platinum, palladium, and rhodium from spent automobile catalysts mainly include pyrometallurgical process, hydrometallurgical process and biohydrometallurgy process, and even microwave enhanced method is used [12–17]. Pyrometallurgical process has become the main process flow for the treatment of spent automobile catalysts with its unique advantages, includes metal collection method and chlorination evaporation method. Its principle is to separate the active components from other components and enrich them to obtain precious metals. According to the calculation of China's car ownership, the content of PGMs far exceeds China's reserves, and under the background of rapid development of electric vehicles, more and more spent catalyst will be produced. It is great significance to carry out the comprehensive utilization of spent automotive catalyst secondary resources to promote the sustainable development of industries.

This paper summarized the current situation and consumption of PGMs mineral resources in the world and the recovery of spent automotive catalysts, focused on the capture mechanism, recovery and enrichment technology of PGMs, discussed the direction and development of platinum group metal recovery process, so as to provide reference for the comprehensive utilization of secondary PGM resources.

Current Situation and Consumption of PGM Resources

PGM Resources

The world's PGMs resources and reserves are mainly concentrated in South Africa, Russia, Zimbabwe, the USA, and other countries. South Africa has the most abundant mineral reserves, which accounting for more than 90% of the world.

The output of Pt was about 180 tons in 2021 (Fig. 1), an increase of 8.4% compared with 166 tons in 2020. The output of palladium was 200 tons in 2021 (Fig. 2), a decrease of 7.8% compared with 217 tons in 2020, and the output of platinum and palladium WAS 178 tons and the 213 tons, respectively, in 2019, which maintained at a certain level.

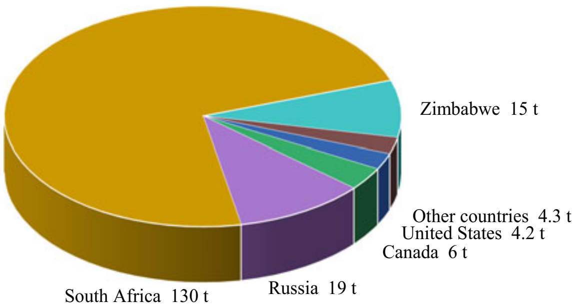

Fig. 1 World mineral production of platinum in 2021

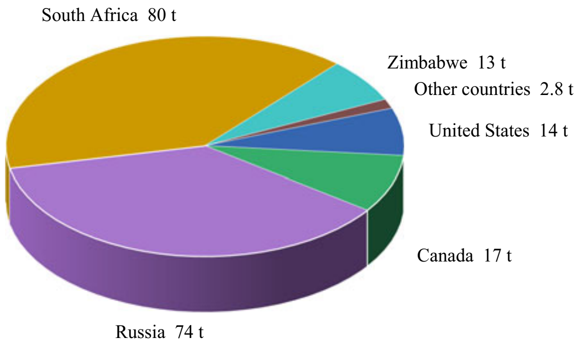

Fig. 2 World mineral production of palladium in 2021

Global PGM Supply and Consumption

The global supply of PGMs mainly comes from mineral resources. However, due to the scarcity and high price of PGM resources, the renewable output of secondary resources has also increased year by year. According to the International Platinum Investment Association, Johnson Matthey and other public information show that the secondary resource recovery of Pt accounts for more than 25% of the total output and shows an increasing trend year by year (Fig. 4). The secondary resource recovery of Pt reached 69t in 2019 (Fig. 3). The recovery of Pd accounts for more than 30% of the total output, and the recovery of palladium has been close to 100 t since 2018 (Fig. 3). It can be seen that the output from secondary resource recovery accounts for a large proportion of the global supply of platinum and palladium. PGMs are mainly used in petrochemical, automobile manufacturing, jewelry, and other industries, among which the automotive and chemical industry catalysts are the most widely used which accounting for more than 60%, and the consumption field is relatively concentrated (Fig. 4) [18]. The recycling of PGMs from secondary resources is of strategic significance for the application and development, and the

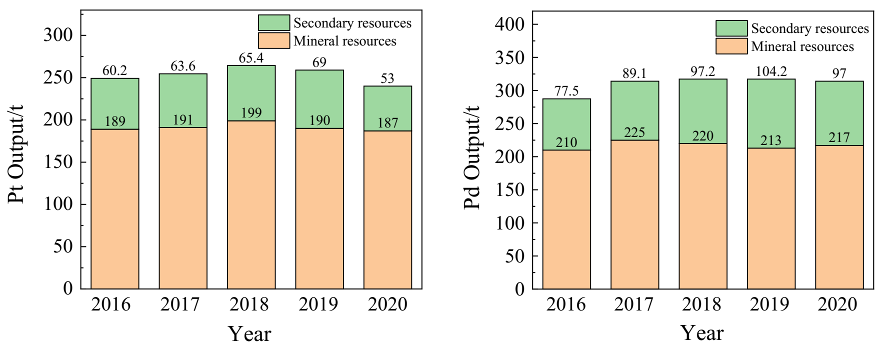

Fig. 3 Supply of Pt and Pd resources in from 2016 to 2020

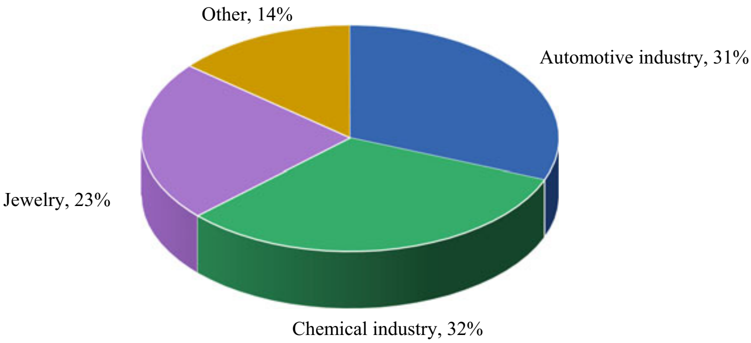

Fig. 4 Application fields of platinum group metals

field of recycling precious metals today is mainly based on the recycling of spent catalysts.

Metal Capture Method

Metal capture method is one of the most commonly used methods to recover precious metals from spent automobile catalysts by pyrometallurgy. It has the advantages of large treatment capacity, simple process, strong adaptability of materials, and no wastewater. Many companies in the world use this method to recover PGMs from spent catalysts, such as Johnson Matthey (UK), Umicore (Belgium), Sabinmetal (USA), Tanaka precious metals (Japan), Badische anilin und soda Fabrik (Germany), and Sino-platinum Metals (China), which have been used in the production process [14, 19]. Pyrometallurgical recovery process includes plasma smelting method, metal capture method, and chlorination volatilization method. Plasma smelting method also belongs to metal capture method because it uses metal iron to capture PGMs. The overall process of pyrometallurgy generally includes shearing, crushing, grinding, batching, ball pressing, smelting, and enrichment, refining and other processes (Fig. 5), in which Fe, Cu, Pb, and other kinds of collectors are generally used.

Iron Capture Method

Plasma smelting method uses plasma arc to melt and enrich precious metals. Although smelting has its particularity, it also belongs to the category of metal capture method (Fig. 6). In the process, iron is generally used to capture PGMs. Spent automobile catalyst, reductant, capturing agent, and slag forming agent are added to the furnace at a temperature above 1500 °C, PGMs and Fe have the same crystal structure and similar atomic radius, and Fe has strong affinity for PGMs, Fe

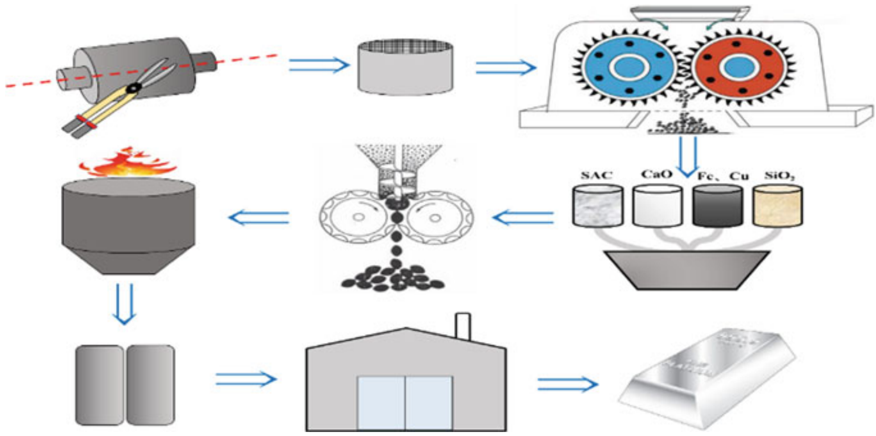

Fig. 5 Overall process steps of metals collection method

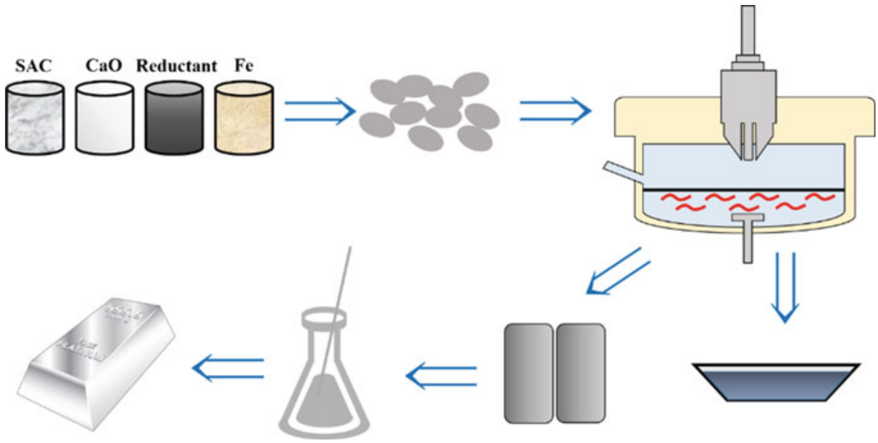

Fig. 6 Process of iron capture and recovery of PGMs by plasma smelting

can form a continuous solid solution with PGMs under high temperature conditions, so that the PGMs in the spent automobile catalyst can quickly enter the metal phase to achieve the effect of separation, and Fe is also a very low-cost collector, which is beneficial to industrial production. By plasma smelting and enrichment, the recoveries of Pt, Pd, and Rh can reach more than 98%, 98%, and 97%, respectively. The total content of PGMs in the slag is about 10 g/t, which has high commercial value.

The capturing mechanism is that PGMs are deposited into the alloy phase due to the influence of the gravity of particles in the recovery process. Metal droplets pass through the slag and precipitate in the metal phase under the action of gravity to form PGMs rich alloys. Benson analyzed the mechanism of extracting PGMs from raw material slag based on the hydrodynamic model and proposed a method that can estimate the drop rate. It is not a simple gravity effect, but related to the affinity of Fe and PGMs, only when the particles in the catalyst are greater than 200 microns, can be enriched by gravity sedimentation. The capture of PGMs can only be achieved through the adsorption agglomeration sedimentation of Fe. After calculation, it is concluded that the optimal capture diameter of Fe droplets is 0.1–0.3 mm, and the recovery rate of Pt can reach more than 90%. In the experiment, the overall recovery rate of PGMs are more than 95% [20, 21].

Sino-platinum Metals Co., Ltd has introduced a plasma furnace and smelted spent automobile catalyst in China. Li studied Fe_3O_4 as a collector to recover PGMs and carried out industrial exploration. The experimental results showed that the comprehensive recovery of PGMs was more than 97%, and the total amount in the slag was 10.9–12.9 g/t [20, 21]. Plasma smelting Fe capture method has the advantages of high metal recovery rate, wide applicability, and high production efficiency, but there are also expensive equipment and large demand for consumables. During the smelting process, silicon dioxide caused by local high temperature is reduced to silicon, making the alloy generate high silicon iron that is difficult to dissolve in acid and alkali, affecting the subsequent separation process.

In order to reduce the temperature and avoid the formation of high silicon iron, Dong studied to recover the secondary resources of PGMs and developed the low-temperature solid-state iron capturing technology. Under the condition of reduction temperature of 1220 °C and reduction time of 6 h, the recovery rates of Pt, Pd, and Rh were 98.6%, 91.7%, and 97.6%, respectively, and the analysis results showed that PGMs were preferentially converted into atomic states or atomic clusters in the process of solid-state reduction. It is bonded with free electrons in the new metal Fe to form a PGMs containing ferroalloy to realize separation [22]. Ding used low melting point flux to realize liquid iron capture at 1300–1400 °C, and the process was carried out at low temperature, avoiding the formation of high silicon iron, and then obtained ferroalloy containing PGMs through the smelting [23].

Copper Capture Method

The method of capturing PGMs with copper was developed earlier, and the process of recovering with copper capture was first adopted by Umicore Company in Belgium, the recovery rate of PGMs could reached more than 95% [24, 25]. Spent automobile catalyst, copper or copper oxide, reductant, and flux are added to the smelting furnace, usually electric arc furnace to smelting (Fig. 7).

Yamada used copper capture method to recover Pt containing materials, and the total content of PGMs in its smelting slag was reduced to 1 g/t, with obvious enrichment effect [26]. Nippon Company of Japan used copper capture PGMs for industrial production, then obtained copper alloy, the copper alloy could be blown into a concentrate with a content of 30% PGMs through oxygen blowing, and the copper oxide obtained by blowing could be returned to the smelting process for further use. The Serbian Research Institute proposed a process to cast the smelted copper alloy into

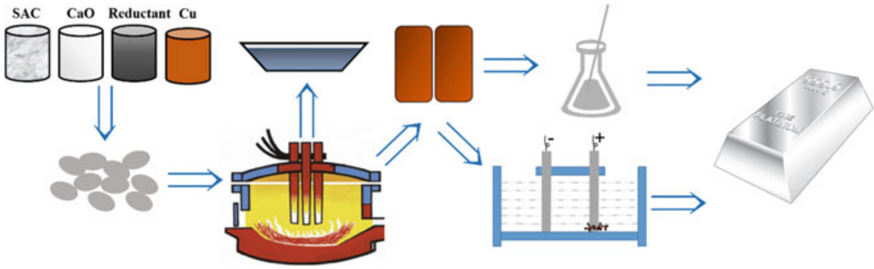

Fig. 7 Recovery of PGMs by copper capture in electric arc furnace smelting

an anode plate with a content of 1% PGMs. After electrolytic refining, PGMs were deposited in the anode mud for recycling. The cathode copper plate could be reused, and the overall recovery rate of PGMs were as high as 99% [27, 28]. Kolliopoulos studied the recovery behavior of copper in the capture and recovery of spent automobile catalyst. They believed that there were two recovery mechanisms in the capture process: one was the infiltration adsorption process, that is, PGMs particles were adsorbed on the copper droplets, which entered the metal phase through the slag, and the other was to form a solid solution with copper at the bottom in the form of sedimentation through the slag, because the relative atomic mass of platinum is heavy, it has a high sedimentation rate, so it has a high recovery rate [29]. Zhang studied the capturing of Pd by copper alone, and using energy spectrum, X-ray photoelectron spectroscopy, and first principle calculation, it was clear that Pd not only migrated into the metal phase, but also replaced copper atoms into the copper lattice to form a Cu-Pd alloy [30]. The smelting temperature of copper capture is low and the recovery rate of PGMs is high. It can not only be industrialized, but also can be recycled. Using copper as a collector also has great advantages, but the subsequent separation process has limited its development, because the subsequent purification and impurity removal process produces a large amount of wastewater, causing pollution, and the process flow is long, which directly affects economic benefits.

Lead Capture Method

Lead is an excellent collector of PGMs. Developed countries began to use lead to capture and recover PGMs as early as 1980. This is the oldest pyrometallurgical method for treating spent automobile catalysts and detecting PGMs. Lead capture is generally used in electric furnace. PGMs are separated from the carrier to obtain crude lead containing PGMs at high temperature, and then lead is oxidized in ash blowing furnace or converter to obtain PGMs enrichment (Fig. 8). Compernolle used the spent automobile catalyst after crushing, added lead oxide and other fluxes, smelted at 1100 °C for 2 h, and the lead button obtained after smelting was soot blown at 1000 °C, resulting in the volatilization of some lead [31]. In order to reduce

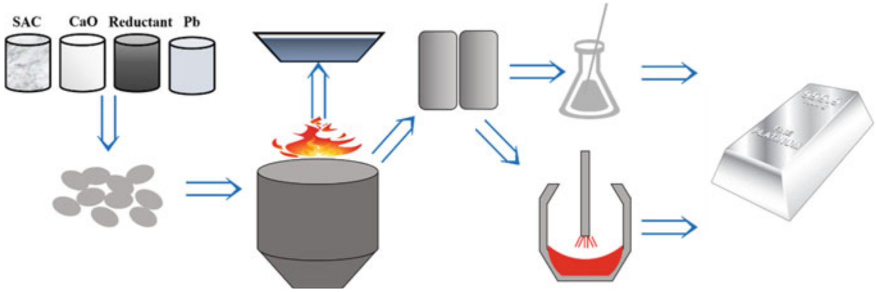

Fig. 8 Recovery of PGMs by lead capture in electric furnace smelting

the loss of lead buckle in the process of soot blowing, gold and silver can be used as a protective agent to reduce the loss and increase the recovery rate. For example, Zhu used silver as a protective agent to recover Pt and Pd, and the recovery rate could reach more than 92.5% [32, 33]. Ni used lead assays to capture PGMs in ores at 1080–1100 °C, which could enrich Pt, Pd, Rh, Ir in lead particles [34].

Other Capture Method

Experts and scholars have also carried out a variety of research methods, such as using metal Bi for capture, or using waste printed circuit boards for capture, and even using cyanide tailings and other wastes for capture. Zhang used metal Bi as the collector. Under the condition of smelting at 1100 °C for 10 min, the recoveries of Pt, Pd, and Rh were 95.02, 98.90, and 97.00%, respectively. PGMs preferentially entered the Bi phase, reducing the free energy of the system and formed metal droplets to converge and settled into the metal phase [35]. The waste circuit board was used as the capture agent, the carrier material was used as the slag-forming agent, and the melting could be carried out by adding the flux and reducing agent. After melting, the automobile catalyst and the gold, Pt, Pd, Rh in the waste circuit board could be comprehensively recovered, which were enriched in the Cu-Sn alloy. The PGMs had a high distribution ratio at the slag gold interface. This process was simple, and the spent automobile catalyst and waste circuit board could also be comprehensively recovered to achieve the purpose of treating waste with waste, However, the volatilization of toxic and harmful gases in the process limits its development [36, 37]. Liu provided an economic and environmental protection technology for treating spent automobile catalyst with cyanide tailings, in which Fe collector is produced by carbothermal reduction process, the melted PGMs enter the alloy phase, while Pb, Cr and other elements were fixed in the slag, and the process cost was low, and had high trapping efficiency [38].

Conclusion and Prospect

The spent automobile catalyst will be accompanied by the arrival of the service life which increases year by year. As an important secondary resource, the efficient and comprehensive utilization of waste automobile catalysts is an important way to solve the contradiction between supply and demand of PGMs and can bring huge economic value and environmental benefits. In view of the current research progress of pyrometallurgy recovery technology, it has the effects of large processing capacity, high efficiency, high capture rate, and easy production, but there are still some problems, such as high temperature, high energy consumption and low recovery rate for specific metals. On the whole, Fe capture has better economic benefits. Although the technology of pyrometallurgy recovery of PGMs has made great progress in general, there are still many problems, and if the recovery rate, efficiency, or energy consumption can be changed by changing the process route, or reducing the temperature with appropriate flux, changing the type of collector or slag composition, it will provide a new technical idea for the recovery of PGMs from spent automobile catalysts and realize the sustainable development of platinum group metal resources.

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