Commercial Processes for the Extraction of Platinum Group Metals (PGMs)

Rekha Panda, Manis Kumar Jha and D. D. Pathak

Abstract Platinum Group Metals (PGMs) play a significant role in the manufacturing of catalysts, super alloys, electronics, space materials, biomedical equipments, jewellery, etc. due to their excellent electrical and thermal conductivity as well as chemical resistivity. The rising demand of PGMs in industrial applications and their limited natural resources have laid emphasis on the development of feasible and eco-friendly processes for the extraction of these metals from different sources to meet their future requirements. Present review reports commercial processes based on pyro-/hydro- and hybrid techniques to recover PGMs from various resources. The salient findings on different processes used for recovery of PGMs have been reviewed with respect to various methodologies and objectives.

Keywords Platinum group metals · Primary source · Secondary source
Spent catalysts · Waste recycling

Introduction

Platinum group metals (PGMs) comprises of six noble metals namely Ruthenium (Ru), Rhodium (Rh), Palladium (Pd), Osmium (Os), Iridium (Ir), Platinum (Pt) which are found together in the d-block of periodic table. These transition metals possess similar physical and chemical properties. The unique properties of PGMs such as catalytic activity, chemical inertness, resistance towards corrosion, thermal as well as electrical stability make them a vital component of many industrial applications, thus, they are also called 'Vitamin of modern industry' [1–4].

R. Panda (✉) · M. K. Jha
Metal Extraction and Recycling Division, CSIR-National Metallurgical Laboratory,
Jamshedpur 831007, India
e-mail: rekhapanda1608@gmail.com

R. Panda · D. D. Pathak
Department of Applied Chemistry, Indian Institute of Technology (ISM),
Dhanbad 826004, India

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Recent technological modernization involving advanced chemistry has commercially accelerated the use of PGMs in the field of vehicle and equipment construction, chemical industry, oil refining, medical practices, jewellery making, etc. [5]. Pt and Pd are of major commercial significance followed by Rh, Ir and Ru whereas Os has rare viable applications [6, 7]. The global demand of PGMs (Pt, Pd and Rh) is over 590 tons while their natural resources are only 66,000 tons all over the world. South Africa is the leading producer of PGMs in the world followed by Russia, Canada, Zimbabwe, USA and Colombia. Extensive deposits of PGMs are located in the norite belt of the Bushveld Igneous Complex covering the Transvaal Basin in South Africa, the Stillwater Complex in Montana, United States, the Thunder Bay District of Ontario, Canada, and the Norilsk Complex in Russia. PGMs are also found associated with base metal (Cu, Ni) sulfide minerals where their content is almost 2–10 g/t [8]. Nowadays, reefs like Merensky, Upper Group Two (UG-2) and Plat reefs are also mined due to presence of significant quantity of PGMs in them [3, 9]. They are also recovered as by-products depending on their concentration in the ore [2, 10].

It has been observed that high value of PGMs coupled with their increasing demand has fuelled its processing from low-grade resources using elaborated techniques [3]. Despite expensive multi-step processes, different innovative methods are continuously being explored to extract PGMs from primary resources. But the depletion of high grade PGMs resources due to continuous mining, has laid emphasis on their production of PGMs from secondary resources viz. automobile catalysts, e-waste, industrial waste (solid/liquid), etc. Hence, in order to explore improved possibilities for the recovery of PGMs, an attempt has been made to provide a general overview on prevailing commercial technologies. The present paper gives an overview of the commercial processes developed for the recovery of PGMs from various resources using pyro-/hydro- or hybrid techniques. The paper will be helpful for researchers in future to develop new process flow-sheet for extraction of PGMs keeping in view the drawbacks of the existing commercial process.

Processing of Primary Resources to Recover PGMs

Although extensive deposits of PGMs are available but deposits for their economical extraction are inadequate [11]. Primary ores of PGMs are broadly divided into four types: (i) Stratiform deposits ($\sim$10–1000 MT) containing 3–10 g/t PGMs; (ii) Norite intrusions ($\sim$10–1000 MT) having 1–3 g/t PGMs (iii) Ni-Cu bearing sills ($\sim$10–1000 MT) with 2–15 g/t PGMs and (iv) Placer deposits containing coarse PGMs (mainly Pt). PGMs ores are mined through conventional underground or open cut techniques followed by grinding. Further, gravity-based separation and flotation is generally used to produce a PGM-rich concentrates [12].

PGMs from high grade chromite ores (containing 200–2000 g/t PGM along with 0.4–2.8% Cr_2O_3) are conventionally recuperated by matte-smelting-refining process as shown in Fig. 1 [3, 11]. The chromite rich ores are generally processed by conventional flotation in a mill-float-mill-float (MF2) open circuit prior to recovery of PGMs, in order to prevent the accumulation of chromite fines generated during over grinding of ores. Initially, the ore is ground by crushing and ball milling in several stages or by SAG (semi-autogenous grinding) and then followed by smelting. The matte obtained undergoes hydrometallurgical treatment for removal of impurities such as Fe, Co, Ni and Cu leaving 10–50% of PGMs in the slime [13]. Emission of SO_2, accumulation of highly refractory chromite spinel layers in the furnace and environmental pollution as a result of high temperature smelting are some of the major limitation of the conventional smelting and converting processes [14–16].

Several researchers have also reported hydrometallurgical or the combination pyro-hydrometallurgical processes as a pre-treatment step for the recovery of PGM from ores/concentrates [17–22]. Hydrometallurgical processes consisting of leaching operation for enrichment PGMs from base metal (Cu, Ni, Co, Fe) sulfide minerals have also been employed. During this process, the base metals are dissolved leaving behind the PGM concentrate for further refining. The same process has also been used in Ni and Cu-Ni refineries for the enrichment of PGMs [23]. Apart from high grade ores, hydrometallurgical processes have also been developed for the commercial extraction of PGMs from low grade refractory sulfide ores and concentrate as presented in Table 1.

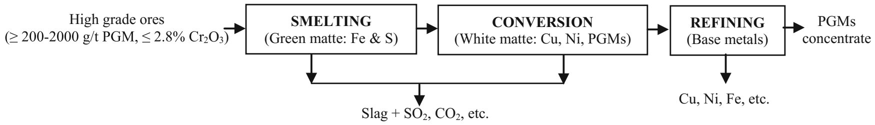

Fig. 1 Conventional matte-smelting-refining technology to get PGM concentrates [3]

Table 1 Technologies for commercial extraction of PGMs from low grade ores

Processes	Medium	Scale	References
Anglo American Corporation/University of British Columbia Process	Sulfate	Pilot	[24, 25]
Albion process	Sulfate	Commercial	[26–32]
Galvanox™ process	Sulfate	Pilot	[32–34]
Total pressure oxidation process	Sulfate	Commercial	[24, 25, 35]
Hydro copper process	Chloride	Commercial	[36–39]
Kell process	Sulfate + Chloride	Pilot	[40]
Nitrogen species catalyzed process	Sulfate + Nitrogen	Commercial	[25, 35]

Processing of Secondary Resources to Recover PGMs

PGMs are vital component of several products like mobile phones, industrial catalysts, ceramic glazes, hard disks, aircraft turbines, etc. Catalysts and electronic wastes are two imperative secondary resources containing significant amount of PGMs due to their remarkable resistance to high temperature corrosion and oxidation. Among these, PGMs are widely used as a catalyst in various chemical reactions like reduction, reformation, hydrogenation, isomerisation, conversion, etc. [41–53]. Automobile industry is the largest consumer of PGMs. Almost 34% Pt, 55% Pd and 95% Rh out of their total demand is used for the manufacturing of catalytic filters-neutralizers of exhaust gases in automobile industries [54–57]. Varying amount of Pt, Pd and Rh are used in auto catalysts depending upon the type of vehicle, manufacturer, country, etc. which helps in regulating the harmful emission of CO, NO_x and hydrocarbons. During the catalytic conversion, Pt helps in converting hydrocarbons and CO to H_2O and CO_2, while Rh is highly efficient in reducing NO_x to N_2 whereas Pd alone can handle all three pollutants, but less efficiently compared to Pt and Rh [58, 59]. Thus, spent automobile catalysts are important supplementary source for the recycling and recovery of PGMs. Processing 2 mg of spent automobile catalysts to recover PGMs can prevent the mining of 150 kg of their ores [58]. The rise in demand of PGMs in automobile industries and strict environmental regulations make their recycling indispensable. The spent automobile catalyst contains an average of $\sim$4 g PGMs which is quite high in comparison to primary resources of PGMs [58, 60, 61]. Moreover, the high price of Pt, Pd and Rh, makes their recovery from used catalysts profitable. Based on their chemical composition and nature, the recycling of these PGM-bearing catalysts is carried out through hydrometallurgical as well as pyrometallurgical processes. Several corporations and industries like Umicore, Belgium; Hereaus, Germany; BASF/Engelhard, USA; Johnson Matthey, UK; Nippon/Mitsubishi, Japan, etc. have already developed successful commercial processes for the recycling of PGMs from secondary resources [2].

Pyrometallurgical process is usually employed to concentrate the PGMs followed by refining technology to recover them. Pyrometallurgical process including crushing, batching, granulation, smelting, separation, has become a traditional method to recover PGMs from spent catalyst [41, 58]. The spent catalyst is initially mixed with fluxes, collector and reductant during smelting and a PGM-collector alloy is obtained which further undergoes purification [41]. The choice of collector plays an important role during smelting. The selection between collector and PGMs is based on their mutual solubility, melting point and chemical properties. Metals like Cu, Ni, Pb and Fe are generally considered good collectors [1]. PGM-Pb collection is one of the oldest methods [62, 63] that has been used to process secondary resources in Inco, Johnson Matthey, Impala, etc. before 1980s. The process is simple to operate, require low smelting temperature, followed by simple refining process, and needs less investment but the major disadvantages are low recovery of Rh and generation of hazardous lead oxide. PGM-Cu collection is another method for treating the spent auto-exhaust catalyst in an electric arc furnace with addition of fluxes (SiO_2, CaO, etc.), collector ($CuCO_3$ or CuO) and reductant [64, 65]. PGMs are collected at low temperature and weak reduction atmosphere. A semi-industrial process combining pyrometallurgy and electrolytic refining for the recovery of PGMs from spent auto-exhaust catalyst using metal copper collection has been performed by the Institute for Mining and Metallurgy Bor, Serbia as shown in Fig. 2 [66]. The Nippon PGM Co. Japan works on the well-known Rose Process (Fig. 2) which is basically copper collection process. The final concentrates contain almost 30% of PGMs whereas the Cu_xO produced can be reused during the smelting process [1, 58].

The Umicore operated at Hoboken, Belgium is an integrated metal smelter and refinery, which also recovers PGMs along with other metals from auto-catalysts/printed circuit boards/electronic components [67]. PGM-Fe collection process mainly involves the method of plasma arc smelting and mineral phase reconstruction. The plasma arc smelting technology was very popular during 1980s to recover PGMs from spent auto-exhaust catalyst [68–70]. High energy density, high temperatures and flexibility in the plasma gases are the vital advantages of this technology [71]. The Plasma arc smelting process for recovery of PGMs from the spent auto-exhaust catalyst has also been commercialized in Texasgulf, USA and Safina, Czech Republic [41, 70]. On the other hand, the short lifetime of plasma gun accessory restricted its practical industrial application. Based on the findings,

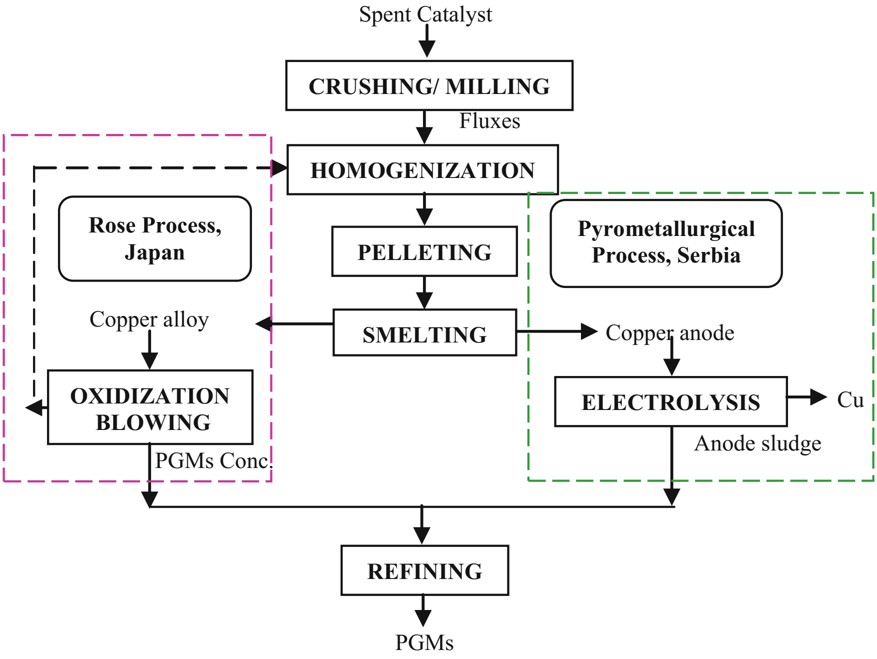

Fig. 2 Industrial process for the recovery of PGMs from spent automobile catalyst [1]

a mineral phase reconstruction process was proposed to recover PGMs from spent auto-exhaust catalyst [72]. The Johnson Matthey process involves smelting of crushed catalyst with flux materials in a crucible containing molten collector metal (Fe or Cu), using a plasma torch [62]. The operation is carried out at temperatures between 1500–1650 °C where the alloy of collector metal is tapped off and $\sim 95\%$ PGMs are recovered by conventional refining methods. From the above studies, it can be concluded that metal smelting collection process is appropriate for processing various secondary materials containing PGMs. The affinity of PGM particles towards the collector metal is an important factor behind the success of this process whereas other factors like fluxes, collector, smelting equipment, operating system, etc. should also be considered. From industrial point of view, PGM-Cu collection technology has wide applications due to high efficiency, low smelting temperature, less pollution and easy industrialization.

Hydrometallurgical processing for the recovery of PGMs mainly involves dissolution using suitable acidic and alkaline solutions in the presence of additives like O_2, I_2, Br_2, Cl_2, H_2O_2, etc. [7, 73–82]. The spent catalyst containing PGMs is pre-treated before hydrometallurgical processing. The PGMs present in the catalysts are encapsulated by specific substances which lead to decrease in their leaching efficiency. Thus, pre-treatment steps such as fine grinding, roasting, reduction, pressure leaching, etc. are necessary prior to leaching of PGMs. Several researchers have reported various pre-treatment methods (oxidization roasting, reduction roasting, pre-leaching, etc.) to destroy organic substances on the surface of spent catalysts or change the supporter forms which hinders the leaching of PGMs present in spent catalysts [41, 58]. After pre-treatment, leaching of the spent catalysts are carried out for maximum dissolution of PGMs. HCl is the most common complexing agent, while HNO_3, Cl_2, or H_2O_2 can be used as oxidant [41, 83]. Aqua regia, commonly used leachant for dissolution precious metals, but not all PGMs can be dissolved with it. Several researchers have studied the use of aqua regia [84–90] to recover Pt, Pd, Rh, etc. from different spent catalysts on the commercial scale. Although leaching rate of PGMs is high in aqua regia but keeping in view environmental aspects, the process has some major drawbacks due to the generation of NO_x, Cl_2 and acid fumes during leaching. From the leach solution obtained, purification and separation of PGMs could be achieved by the method of cementation, solvent extraction, ion exchange, etc. An alternative method is to leach the ceramic material of the catalyst with NaOH or hot H_2SO_4 under pressure where PGMs (Pt, Pd, Rh) are insoluble and remains in the residue. But owing to relatively low yield of PGMs and generation of huge quantities of wastewater, the process is infeasible. The general flow-sheet for extraction of PGMs from spent catalyst using hydrometallurgical technique is shown in Fig. 3 [1].

The chemical and metallurgical industries have used the method of cyanide leaching to recover PGMs [13, 91] due their ability to form stable complexes in alkaline medium. PGMs extraction by cyanidation show poor kinetics at room temperature and atmospheric pressure, thus, effective leaching of the PGMs is

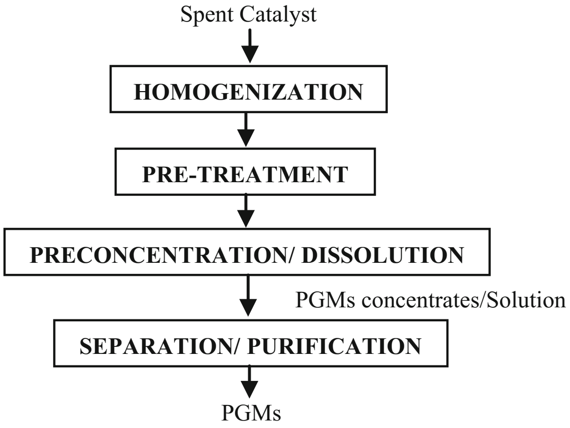

Fig. 3 Hydrometallurgical processing of PGMs [1]

carried out at high temperature and pressure. In cyanide leaching process, the rate of reaction rate is proposed to be controlled by a surface chemical reaction, which is similar to gold cyanidation mechanism [92]. Cyanide leaching of PGMs requires special equipment as well as proper management of the toxic waste generated which may lead to severe environmental problem. Thus, the industrial application of this process is difficult and it is still in exploratory stage. Several processes for the commercially extracting PGMs from secondaries have been successfully developed. Platinum Lake Technology Inc., Canada [93] has successfully developed a hydrometallurgical process for the recovery PGMs (95% Pt and 98% Pd) from spent automotive catalysts. Nippon PGM Co. has reported the production of PGMs from different resources on commercial-scale [94]. Heraeus, Germany has reported the recovery of PGMs from spent materials using hydrometallurgical processes consisting of leaching in HCl in presence of oxidant followed by selective precipitation and ion exchange [2]. BASF Catalysts LLC, USA also developed a novel process for the recovery of PGMs from membrane electrode assemblies (MEAs) eradicating the release of HF (highly toxic gas) generated during the current combustion recycling process [2]. Studies have also been carried out at the Mining and Materials Processing Institute of Japan to recycle PGMs from the residue of automobile catalyst with high leaching efficiency [7]. Hydrometallurgical route offers a faster rate of metal recovery at low capital costs. In addition, the energy consumption is low compared to pyrometallurgical process, which requires high temperatures to melt the raw material. Moreover, the wastewater generated at the industrial scale could be treated in effluent treatment plant and possibilities could be explored for further recovery of value added products.

Conclusion

Based on the review it can be concluded that the recovery and recycling of PGMs from both primary and secondary resources are essential due to their rising demand in various industrial applications. Due to significant conflict between availability of natural resources of PGMs and their increasing demands, it is necessary to exploit indigenous resources of PGMs. Several pyrometallurgical and hydrometallurgical processes for recovery of PGMs are already available but development of modern and productive technologies to utilize indigenous resources as well as improvement in prevailing technologies, will be helpful to meet the future demand of PGMs in various applications. More emphasis should be laid on the recycling of PGMs from secondary sources (spent automobile catalysts, e-waste, industrial wastes, etc.) in order to economise the natural resources and to minimise the environmental pollution in connection to production of PGMs. Thus, R & D efforts should be made to develop hybrid processes consisting of physical beneficiation/pyro-/hydro-/electro metallurgy for efficient recovery of PGMs from various resources.

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