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# PERSPECTIVES ON PLATINUM GROUP ELEMENTS

***Platinum Group Elements (PGE), a group of metals with unique physico-chemical and catalytic properties, are used in different strategic technologies and their importance in modern chemical industry is outstanding. The present article aims at a concise update concerning main current and future uses, production, resources, and recycling prospects.***

The importance of platinum group elements (PGE) in modern industrial chemistry is outstanding: they constitute, individually and in alloys, the major catalytic systems for oxidation, hydrogenation, petrochemical, and emission control reactions. The global market for PGE catalysts was estimated at US dollars 14 bn in the year 2020 with projection to a size of US dollars 22 bn by 2027 [1].
The PGE include six d-block metals and comprise platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir), and osmium (Os): a further classification into the two sub-groups palladium-group elements (PPGE: Rh, Pt, Pd) and iridium-group elements (IPGE: Os, Ir, Ru) is due to similar geological behavior. They are among the rarest elements in the continental crust, ranging from 0.018 ppb for Rh to 0.599 ppb for Pt. Concentrations are sometimes expressed as '4E' referring to Pt+Pd+Rh+Au, the dominant metals by use and value. Although association with gold is rare in primary deposits, the world's largest ores are linked to copper-nickel sulphides and chromitites in which the noble metals cannot be separated by physical methods [2, 3].
The unique properties of PGE include catalytic activity, chemical inertness, corrosion and high-temperature oxidation resistance, high melting points, low coefficients of thermal expansion, high electrical and thermal conductivity, malleability and ductility [4, 5]: these characteristics are widely described in scientific literature since the early advent of catalysis, when experiments on a platinum wire in 1815 led to the first industrial application of an heterogeneous catalyst inaugurating a long standing use in air purification [6].
The singularity of the PGE market is stressed by the application of a specific weight unit, the troy ounce, in use for bullions already during the Middle Ages and corresponding to around 31.103 grams: fixings are traditionally quoted twice daily at the London Platinum and Palladium Market (LPPM) - but also Zürich and New York are active trading centers - and boast wide fluctuations, as a result both of technological developments and economic press news.
Periodic publication of specialized reports from various private and governmental organizations ensures a steady and definite outlook on the sector [7-9]: the present note aims at a concise update concerning uses, market and resources.

## Uses

For a long time, platinum and palladium were used almost exclusively for process catalysts in the chemical industry: the introduction in 1975 of catalytic converters on passenger cars and light-duty trucks in California generated a demand increase with strong market impact.
Today the PGE play a crucial role in many advanced sectors including automotive (catalytic converters, spark plugs, oxygen sensors), chemical and petroleum (catalysts and laboratory equipment), electrochemical (anode coatings), electronics (hard disk drives and multilayer ceramic capacitors), medical and dental (dental alloys, biomedical devices, and anti-cancer drugs), glass manufacturing (flat screens), as well as jewelry and investment areas [10].
In 2021 the most extensive application was in emissions control catalysis: platinum in automobile cat-

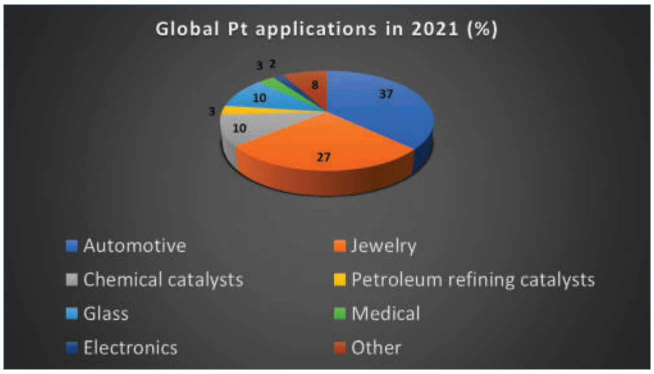


Fig. 1 - Global platinum applications, in % (from Platinum Quarterly Q4 2021, WPIC, March 2022 [8])

alysts accounted for 37% of total demand, enabling car manufacturers to comply with mandatory and tightening emissions standards. Demand for jewelry accounted for an additional 27% and the remaining 36% was comprised of 10% for chemical catalysts (e.g., platinum-rhodium gauzes for ammonia oxidation), 3% for petroleum refining catalysts (e.g., platinum-rhenium catalysts for naphtha reforming), 10% for glass, 3% for medical, 2% for electronics, and 8% for other applications (Fig. 1). The sum of all catalyst demand (automotive, chemical and petroleum refining) amounted to approximately 50% of all platinum usage (3,487 thousand troy ounces out of a total global demand of 7,010 thousand troy ounces in 2021) [8]. In the same year, over 80% of palladium and 90% rhodium were used in emissions control catalysts, with the balance going to industrial catalytic applications, electronics and jewelry.

Concerning the other metals, an iridium-ruthenium catalyst is utilized in a relatively recent technology for acetic acid manufacturing [11] and a graphite supported ruthenium catalyst is used in a niche process for ammonia production [12]; iridium was also shortly adopted for lean $NO_x$ reduction prior to the introduction of $NO_x$ absorbers in automotive catalysts [13]. In 2021, the electrochemical demand for iridium and ruthenium accounted for approximately 38% and 13%, respectively, of global demand (~231 thousand troy ounces for Ir and ~1,016 thousand troy ounces for Ru) with a large portion destined to the chloro-alkali process for chlorine and caustic soda production. Modern processes rely on high performance electrode structures and catalytic coatings ensuring lower energy inputs and higher durability. Production of polyvinyl chloride (PVC) is the biggest global consumer of chlorine and its demand is driven by the construction sector [14].

Considering the global megatrends for population, energy consumption, raw materials extraction, pollution and climate change, it is expected that the demand for PGE in the mentioned sectors will continue to grow [15] and the catalytic systems for automotive emission control and ammonia oxidation will be briefly described.

The catalyst technology of the automotive sector is mature and a converter basically consists of a washcoat comprising PGE around 1-2% wt, alumina, rare-earths and other elements deposited inside the thin channels of a monolith (ceramic or metallic) and canned into a steel housing located underfloor along the exhaust manifold [16-18].

Three-way-catalysts (TWC) for gasoline engines convert over 90% of hydrocarbons (HC), carbon monoxide (CO) and oxides of nitrogen ($NO_x$) from gasoline engines into carbon dioxide, nitrogen and water vapor. They usually operate in the temperature range 350-650 °C, but can be exposed to 1100 °C due either to closeness to the exhaust ports of the engine or to misfire, i.e. the oxidation of an excessive amount of unburned fuel.

Diesel engines have high fuel efficiency and low CO emissions: in their case oxidation catalysts (DOC) are used to convert HC to water and carbon dioxide in the temperature range 100-650 °C, and catalysed soot filters (DPF) trap and oxidize particulate matter (PM), a carbonaceous compound comprising hydrocarbons, sulfuric and nitric acid.

PGE unique characteristics for the specific applications are catalytic activity at high space velocity (up to 150,000 $h^{-1}$), low deactivation by sintering and support interaction, meaningful activity at the starting temperatures of regulatory driving cycles, and resistance to poisoning.

Pt and Pd are used in gasoline engines to reduce carbon monoxide (CO) and unburnt hydrocarbons (HC) emissions by oxidation to $CO_2$ and water, whereas Rh is particularly effective towards nitrogen oxides ($NO_x$) reduction. Lean burn engines increase the amount of $NO_x$, hence higher catalyst loadings are required. Also, in relation to engine volume, a gasoline vehicle requires 3 to 7 grams of PGE, whereas a diesel vehicle typically employs 5 to 10 grams: in 2021 over 79 million motor vehicles

were globally produced and 360 tons of PGE were "stocked" in the specific segment.
Due to Pd prices being cheaper than Pt and its role towards $NO_x$ reduction in gasoline engines, improved fuel quality with S-lean fuels led to the substitution of Pt by Pd in the mid-Nineties, introducing an interplay between these elements, although the "sister" metals are not interchangeable in the catalytic functions. The situation changed with extreme increases in Pd prices due to strong demand in combination with export restrictions from Russia. The price of palladium was over twice the price of Pt in May 2022. Today, binary Pt/Rh or Pd/Rh catalysts in varying loadings and proportions are used worldwide for gasoline engines, while Pt with a small proportion of Pd is used in diesel vehicles. In the different sub-sectors pertaining the auto industry, catalytic converters have the highest average operating margins: new catalysts are normally introduced with changes in legislation and producers are able to charge a premium.
Efforts for viable alternatives of PGE were impressive but experimental outcomes were so far limited to PGE thrifting, improved dispersion/re-dispersion capability, and selected deposition in the washcoat layers: partially successful attempts concerned the addition of base metal oxides (e.g., perovskitic compounds).
The case of platinum-rhodium bulk metal gauzes for ammonia oxidation to nitrogen monoxide represents an historic application in the chemical process sector: use of a Pt sponge was first patented in 1838 and the current catalysts of choice comprise binary alloys approximately composed of 90% wt Pt and 3-10% wt Rh and ternary alloys Pt/Rh/Pd. Knitted gauzes are made with wire diameters ranging from 60 μm to 120 μm and the reaction is highly exothermic: plants may operate at low, medium, or high pressure (1, 3 to 5, or 10 to 13 atmospheres respectively) and the operating temperatures (between 850 °C and 930 °C) vary accordingly. At industrial conditions, the selectivity to nitric oxide NO ranges between 90-97%, primarily due to reduction in efficiency at higher pressures. The catalysts lifetime ranges from several months to 1 year depending on process pressure [19, 20].
Bulk metal Pt possesses high selectivity for NO and the non-porous wire gauze catalyst avoids undesired secondary reactions. Rh is added to enhance the mechanical strength of Pt during the manufacturing process and also decreases the volatility of Pt during high-temperature reaction, especially in the high-pressure process. In fact, nitric acid manufacture consumes platinum metal because of the volatilization of $PtO_2$ causing metal loss between 0.05~0.3 g per ton of produced nitric acid. To cope with this problem, a recovery technique was introduced in the late 1960s employing a palladium gauze. A further change in design occurred in the mid-2000s with ternary rhodium-platinum-palladium alloy gauzes stacked in the lower portion of the "pack" of gauzes. Global output of nitric acid exceeded 65 million metric tons (100% $HNO_3$ basis) per annum in 2020 of which 80% goes into nitrate production for fertilizers, with demand growing steadily [21]. It is approximately estimated that this output represents a PGE gauze inventory of around 20 tons: a single year of PGE automotive application far outweighs the global PGE amount necessary for the major chemical process.
PGE role in the specific reaction is unrivalled and technological improvements during the last century concerned elements ratios, manufacturing technique and "pack" distribution: thin-wall monoliths based on bulk iron oxide found geographically limited diffusion to replace part of the platinoid gauzes.
Quoted automotive and nitric acid examples are typical: although cheaper and less efficient alternative materials might be potentially available, industrial catalysis teaches that processes employing PGE, once adopted, generally remain in use with a continuous technological development.
Concerning future applications, auto-catalysts will remain the major field in the medium term: global demand for catalytic converters continues to rise and national emissions legislations lead to higher PGE loadings with demand growth higher than volume changes in vehicles sales. For example, between 1990 and 2019 - the last pre-pandemic year - annual cars sales rose from around 54 millions to 92 millions, whilst PGE use in auto-catalysts rose from 2.2 millions troy ounces per annum to 13.8 millions troy ounces per annum. However, long-term demand of PGE will be strongly influenced by the different ongoing developments of electromobility. Battery electric vehicles (BEV), which are currently gaining

market share, do not require meaningful amounts of PGE; on the contrary, a hydrogen engine in fuel cell electric vehicles (FCEV) uses a platinum catalyst as a key component and requires several times more platinum than an internal combustion engine.

## Production and Market

More than 100 different platinum-group minerals are known with many rare and poorly characterized forms. Associated minerals include different Pt-Fe alloys such as isoferroplatinum $Pt_3Fe$, sulphides such as braggite (Pt,Pd,Ni)S, cooperite PtS, and others (Fig. 2) [22].

PGE occur mostly in either a siderophilic (iron-loving) state or a chalcophilic (sulfide-loving) state in ores preferentially bound with iron, nickel, copper, and sulfur rather than with oxygen and the deposits may be subdivided into two groups [23]:

a) deposits with the PGE as main products and Ni and Cu by-products (e.g., most reefs of the South African Bushveld Igneous Complex, Fig. 3), containing less than 1-2% sulfide minerals;

b) ores with Ni and Cu as the principal products and the PGE as co-products, containing more than 10% sulfide minerals (e.g., Noril'sk in Russia).

Today, virtually all the PGE production comes from sulphide ores: alluvial deposits no longer play the past role.

Ores are very low-grade, with mined concentrations typically ranging from 2 to 6 g/t (i.e., 2-6 ppmw) and ratios depending on the deposit. For example, inside the Bushveld area (with an extension over 84,000 km$^2$, and about 9 km thick) the Merensky reef contains typically 5 to 7 g/t Pt+Pd and a Pt to Pd wt ratio of 3:1, whereas the UG2 reef has grades of 4 to 8 g/t Pt+Pd, slightly higher Pd content (Pt:Pd = 2.5:1), and significantly higher Rh, Ir and Ru contents. The most important sulfidic nickel-copper deposit is Noril'sk on the Russian Taimyr peninsula, the world's largest nickel producer, with typical grades 10 g/t Pt+Pd and a Pt to Pd wt ratio nearly 4:1, making Russia the world's largest producer of palladium [24].

The level of extraction is related to element concentrations and to actual demand and price of the individual PGE. In 2021, the global production of the six PGE amounted to over 460 tons, several orders of magnitude lower than many common metals [14].

The method used to mine PGE deposits is site specific, and different procedures are used for processing sulfide-poor ores (e.g., Merensky and UG2 reefs) and sulfide-dominant ores (e.g. Noril'sk) due to the relative chemical, mineralogical and physical properties. In any case, the mining process is complex, resource intensive, and lengthy: extraction, concentration, and refining may take several months. In South African mines, the first steps involve crushing and grinding of the ore, followed by physical separation, usually via froth flotation, to produce a mineral concentrate, with typical recoveries of 60% to 90% of the sulphide depending on the degree of oxidation and PGE content ranging from 0.01% to 0.02% wt. After drying, pyrometallurgical separation

Fig. 2 - Braggite mineral inclusion (silvery mass at center). Photograph by James St. John, distributed under a CC-BY 2.0 license

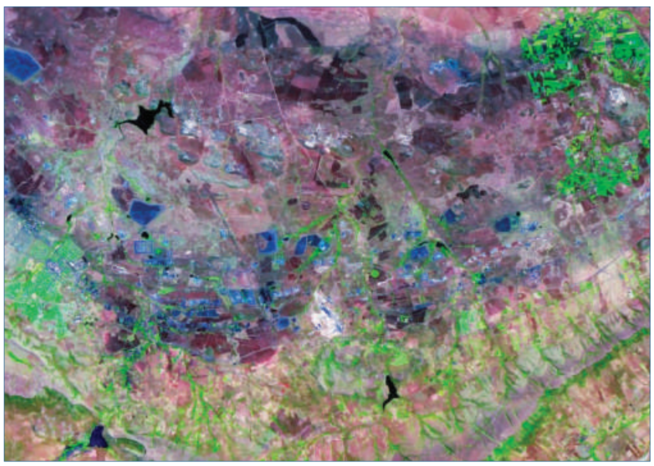

Fig. 3 - 2006 NASA satellite image of the Bushveld Igneous Complex (BIC) in South Africa (PGE mines, tailings piles, and leach ponds in blue in a 2,000 km$^2$ area). Courtesy of NASA/METI/AIST/Japan Space Systems and U.S./Japan ASTER Science Team

Fig. 4 - PGE mine at Rustenburg (SA). Courtesy of Impala Platinum Holdings Limited

follows at around 1500 °C, resulting in a Cu-Ni-Fe-S matte containing about 0.2-0.4% wt PGE. In the next stage, hydrometallurgical techniques such as leaching processes in sulfuric acid with oxygen are used to sequentially leach Ni, Cu, Fe, and then Se, As, and Te to achieve an undissolved solid residue called bullion concentrate, containing about 50-70% wt total PGE for the refinery. The final stage is based on selective extraction using either ion exchange processes, electrolytic processes, or solvents, and the purities of the metals are typically between 99.9% and 99.99% [25].

Due to low concentration, PGE mining produces huge amounts of waste (in South African activities the gangue makes up over 90% by mass of the ore), consume large quantities of energy and water, and flue gas contains high concentrations of sulfur dioxide ($SO_2$) [26].

In South Africa, the majority of ore bodies is mined from underground operations (even at 2,200 m depth) (Fig. 4) [27] with high fixed costs: activities are frequently linked to operational and social issues. The influence of the South African supplies on PGE pricing is also reflected by the exchange rates between the local currency and the US$ dollar. In PGE mining, 80-90% of operating costs are in local currency: labour typically accounts for 60% of operating costs and electricity around 15% and both are strongly linked to the local economy. Hence, the currency strength is another factor exerting a strong effect on PGE price and mining profitability, i.e. local currency weakening might lead to falling PGE price and vice versa [28].

On the other side of the globe, the location of the Siberian town of Noril'sk within the Arctic Circle makes operations difficult in view of remoteness and climate conditions. It is completely isolated from Russia's road and rail systems and the 1,500 km connection to the refinery is only possible in summer during the navigation period of the Yenisey river. Relative supply volumes have been declining in the last years due to falling ore grades and depletion of state stocks of unknown volume, which occasionally relevantly contributed to export shares [29].

South Africa hosts the "Big Three" companies and 90% of the global reserves (Fig. 5), estimated around 70,000 tons; Russia is the second player with around 6%, and Zimbabwe, Canada and the USA follow distantly [9]: at the current consumption rates, known reserves are not going to be exhausted even in case of significantly higher annual demand and suggest lifetimes around 150 years. In 2021 83% Pt and 77% Pd came from the first two countries only: supply dominance along with vulnerability as a function of technical (e.g. depth of mining, working safety), infrastructural (e.g., power outages), social (e.g., water availability, local unrest) and geo-political issues represent concerns. Therefore, in 2011 the European Union (EU) commission put PGE on the list of critical raw materials, due both to their economic importance and increased supply risk: the same classification had already been introduced in Japan (Ministry of International Trade and Industry, 1984) and in the USA (National Research Council, 2008). As a result, projects such as PLATIRUS (PLATInum group metals Recovery Using Secondary raw materials) were launched within the framework of EU Horizon 2020 fund to address supply security by developing novel recycling processes for auto-catalysts and electronic wastes [30].

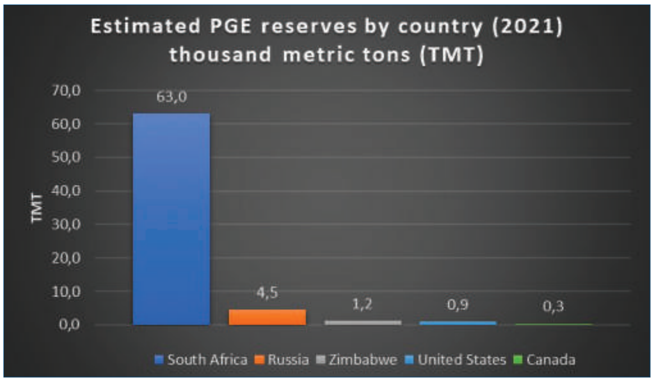


Fig. 5 - PGE reserves in thousand metric tons (from U.S. Geological Survey, Platinum-group Metals, Mineral Commodity Summaries, January 2022 [9])

In the meantime prices trigger: in 2021 it was estimated that the average prices of palladium, platinum, and ruthenium increased by 18%, 35%, and 88% on a yearly basis; the prices for rhodium doubled and for iridium more than tripled; iridium, rhodium, and ruthenium all reached record values.

## Recovery and Sustainability

Within the current scenario, the recycling option (also termed "secondary production") is mandatory. Both economic and occupational benefits are to be expected from recovery of rare metals whose content in many spent products is relatively high; the environmental and energetic balance due to low metals concentrations and complex processing of natural ores can no longer be overlooked irrespective of the mine location; concrete means for market price stabilization against speculative fluctuations would be applied; and, last but not least, applications in high-tech products with strategic economic importance will be secured [31].

PGE recycling is a capital-intensive business: fixed costs represent over 75% of total cash costs and, as a result, a recycler needs to operate without solution of continuity even if the input feedstock is not optimal. Technically speaking, current industrial technologies are able to recover close to 100% of the PGE content in End-of-Life (EoL) products and methods are similar to the state-of-the-art technology for recovery from primary ores by combination of pyrometallurgical and hydrometallurgical processes [32]. Pyrometallurgy uses thermal energy to melt down secondary materials in order to concentrate target metals for further processing and separate unwanted substances into a slag and/or volatile phase. Hydrometallurgy uses acidic or alkaline solutions to separate target and unwanted substances via a leachate (solution) and a leaching residue [33, 34]. Both methods have good performance and recovery ratios, require large scale industrial facility to be economically feasible and produce toxic wastes. Pyrometallurgy is prevalent industrially by reaching high recovery yields and is characterized by high energy consumption with average leveled purification. Hydrometallurgy obtains high selectivity and purification at lower temperature conditions, with better process control and good recovery yields. Recently, sustainable and mild recycling methods such as selective electrochemical dissolution, bio-leaching, and others are being investigated at an R&D level [35].

In 2021, recycled platinum, palladium, and rhodium provided a significant proportion of global supply, accounting for about 24% of platinum demand, 33% of palladium and 36% percent of rhodium [14]. However, data represent average values: as a matter of fact, it is important to distinguish between 'closed-loop' and 'open-loop' applications since the classification strongly impacts on recycling rates. In "closed-loops" the user (e.g., the chemical plant or oil refinery) owns the PGE throughout its life cycle and the metal is continually recycled and reused for the same purpose; in "open-loops" the full life cycle of products is uncertain and no assurance can be given that the PGE content will be recycled in the end.

The chemical industry is an exemplary forerunner. Within catalytic applications, a typical example of "closed-loop" cycle is relative to Pt-Rh gauzes for ammonia oxidation: notwithstanding mentioned Pt losses occurring during reaction operations, hydrometallurgical treatment of spent catalyst with a recycling share over 95% widely ensures process profitability. On the other hand, the automotive catalysts represent an example of "open-loop". The global recycling amount of Pt from automotive was just slightly over 50% of specific demand in 2021: in Europe, this level is lowered by large export volumes of EoL vehicles, although catalyst collection would be required by the EU End-of-life Vehicles Directive (ELV) introduced in 2000. For catalytic converters recovery, multiple steps are involved in cascade and comprise collection, disassembling, decanning, electric furnace melting, oxidation at 1,300 °C and hydrometallurgical refining. Finally, the electronic sector is another case of "open-loop", where recycling accounted only for about 16% of the specific Pt demand in 2021: the EU Waste Electrical and Electronic Equipment (WEEE) Directive (2003) with the aim to promote the recovery of electrical scrap has only partially achieved its potential impact [36]. Such as for other critical materials, legislation and public awareness supported by a suitable infrastructure play a key role in the recycling process and are necessary requisites to overcome the alluring illusion of raw materials bonanza.

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**Elementi del gruppo del platino: prospettive**

Gli elementi del gruppo del platino (PGE), un gruppo di metalli con particolari proprietà chimico-fisiche e catalitiche, sono utilizzati in diverse tecnologie strategiche e hanno un'importanza eccezionale nella moderna chimica industriale. Il presente articolo mira ad un sintetico aggiornamento su principali usi attuali e futuri, produzione, risorse e prospettive di riciclo.