Recovery of platinum group metals from spent automotive catalysts: A review

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ABSTRACT

In the last decades, a worldwide investment in the recovery or substitution of platinum group metals (PGMs) has been financed. PGMs have been classified as critical raw materials (CRMs), thus a circular economy model should be implemented for their effective recovery. PGM recovery from primary ores is expensive, due to low concentrations of their ores (lower than 10 g/tn) and sophisticated processes implicated, while secondary resources have been proven technoeconomically feasible sources for PGM recycling. Secondary resources of PGMs, such as spent automotive catalytic converters, contain considerably higher PGM concentrations than their corresponding ores. It is estimated that spent automotive catalytic converters deliver more than 57% of PGMs' European supply, being considered a crucial resource for PGM recovery. Novel recovery techniques focus not only on high recovery rates, but also on cost efficiency and environmental protection. From an industrial viewpoint, pyrometallurgy is the dominant recovery technique, hydrometallurgy is secondly chosen and biometallurgy (bioleaching, bioabsorption) is applied for lab-scale recovery -at this moment. In the present review, all major PGM recovery techniques are presented and discussed. Hydrometallurgical processes could gain a foothold in industrial scale recycling, by adopting a direct, sustainable leaching design. Milder leaching conditions, greener solvents and high solid mass leached, are the keys for the hydrometallurgical upscaling.

1. Introduction

Platinum Group Metals (PGMs), that include Platinum (Pt), Palladium (Pd), Rhodium (Rh), Osmium (Os), Iridium (Ir) and Ruthenium (Ru), are widely used in high-tech applications ameliorating the quality of life, due to the unique properties of high corrosion and oxidation resistance, high electrical conductivity and catalytic activity. PGM uses refer to automotive catalytic converters (i.e. Three-Way-Catalyst (TWC), Diesel-Oxidation Catalyst (DOC), Selective Catalytic Reduction (SCR)), chemical catalysts (i.e. ammonia oxidation catalyst), petroleum catalysts (i.e. gasoline reforming catalyst), ceramics (i.e. glass resistant to corrosion, thermocouples), electrical/electronical equipment (i.e. mobile phones, printed circuit boards (PBCs), flat screens, hard discs), jewelry, fuel cells, dental implants (i.e. corona prostheses), medical applications (i.e. orthopedic implants, chemotherapies), pharmaceuticals (i.e. drug precursors), investments and criminology (i.e. stain for fingerprints and DNA). Consequently, various industries depend on PGM's sustainability and availability (Fig. 1).

In fact, PGM content on earth's upper continental crust is approximately 0.01 ppm and PGM ore mining takes place in limited geographical areas (Fig. 2), resulting in Europe's dependence on these suppliers. In order to address this supply challenge, the EU Commission created a CRMs list, which is updated every three years. PGMs are included in the CRM list of 2017, being associated with high supply risk and significant economic importance. Referring to primary PGM production, the process is extremely expensive, complex, unhealthy and challenging for the production countries. Concerning the current situation, both PGM sources and products are traded globally without serious trade restrictions, expecting that PGM demand will further increase. Under these circumstances, PGMs should be sustainably supplied, in order to ameliorate the global economy, political prosperity, environmental protection and quality of life.

As for the primary production of PGMs, mining ores are divided to Platinum Group Element (PGE) dominant ores (Merensky Type, Chromite Type, Placer Type, Dunite Pipe), Ni–Cu dominant ores (Class I-IV Ni–Cu Ores) and Miscellaneous ores (Copper Molybdenum Ores, Ni Laterites, Black Shales, Carbonate Ores, Porphyry Copper Ores) (Cole, 2002). Both PGM and Cu–Ni dominant ores are feasible ones for
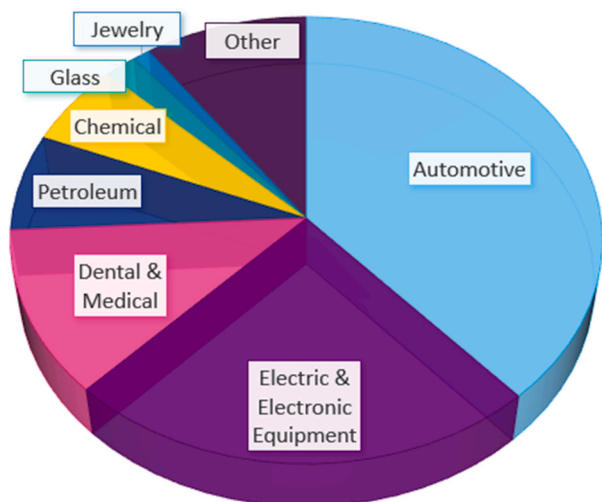
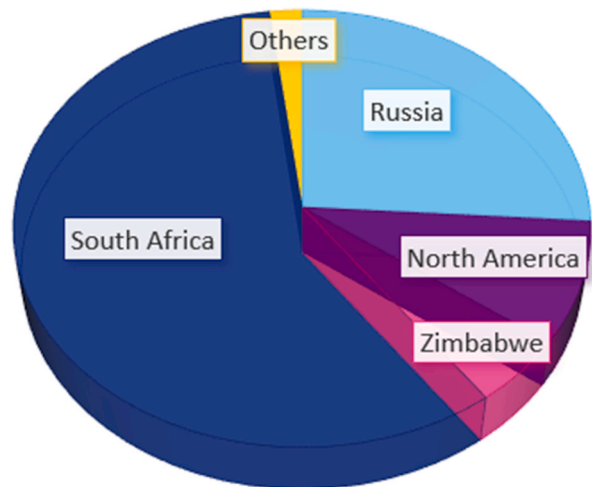**Fig. 1.** Industrial applications of PGMs (for the year 2010).

Fig. 2. Geographical areas of PGMs mining ores (Glaister and Mudd, 2010).

exploitation. On the other hand, the PGM content in miscellaneous sources is very low; therefore, the recovery is not possible or has little economic advantage for the primary producers. The common extraction process refers to pyrometallurgy combined with hydrometallurgy, where platinum group metal ores (e.g. Merensky Reef ore grades contain 3–8 g/t PGM, associated with nickel, copper, as sulfides) are mined, grinded, subjected to gravity separation and flotation; then, the PGM concentrate (typically 200 to over 2000 g/t PGM with 0.4%–2.8% Cr_2O_3) is melted at high temperatures (>1500 °C) and PGMs are refined via hydrometallurgy (Mpinga et al., 2015). According to hydrometallurgy process, PGM concentrate is leached into an autoclave under high pressure conditions to oxidize sulfates; then, PGM separation and refining lead to the lowest impurities content. Process difficulties, such as PGM ore oxidation, remobilizations and additional metal content during floatation, should be considered. It should be highlighted that during PGM ore treatments, considerable amounts of PGMs get lost, affecting the global economy. In general, 27% of total PGM loss occurs during the mining process, compared to 15% of overall processing. Besides, 13% PGMs' loss refers to the concentration stage (Sinisalo and Lundström, 2018).

Concerning primary production feasibility, PGM content is quite low (~10 g/ton), PGM ratio varies and high energy is consumed. Moreover, even the smelters/refineries recover almost 96% of PGMs, concentration

recovery is only 85% of PGMs. Compared to primary production, secondary sources exploitation is preferable, since higher PGMs concentrations are involved, 70–100 times less energy is consumed, higher recovery yields are achieved and the environmental footprint, which highly relates to mining, is improved.

Spent automotive catalysts are the richest PGM secondary resource, being widely exploited for the PGMs recovery. It is estimated that processing 2 mg of spent automotive catalysts can prevent the mining of 150 kg PGM ores (Fornalczyk and Saternus, 2009). Spent Light-Duty Vehicles (LDV) catalysts contain about 1–3 g PGMs (i.e. Pt, Pd, Rh), while Heavy-Duty Vehicles (HDV) catalysts contain 12–15 g PGMs. As for a catalyst monolith/honeycomb, PGMs are combined with base metals (e.g. Cu, Ni, V, W), washcoat materials (e.g. γ-Al_2O_3, $CeZrO_2$, activated carbon) and cordierite materials (2MgO• $2Al_2O_3$• $5SiO_2$ of various stoichiometries); thus, the purification of precious metallic form is quite challenging. Moreover, PGMs have similar chemistry, while PGMs' inert chemistry results in refining challenges.

End of Life (EoL) vehicles recycling is a well-established process, including EoL catalyst collection, sorting, dismantling (i.e. metallic cannister removal) and crushing of the catalyst monolith. Thereafter, the crushed monolith is grinded and milled, in order for a fine powder to be formed (Yakoumis et al., 2018). The PGM concentrated powder is subjected to recovery techniques, such as pyrometallurgy, hydrometallurgy and biometallurgy processes. Nowadays, state-of-the-art recovery approaches focus not only on higher PGMs' recoveries, but also on economic and environmental perspectives, by following green principle rules (Table 1).

2. Methodology

2.1. Recovery techniques

Automotive catalytic converters are the biggest consumer of PGMs, estimated that above 360t of PGMs are needed for the production of autocatalysts for the year 2018 (Wei et al., 2019). Regarding the recycling of spent automotive catalytic converters, spent catalyst feed is to be received, focusing on homogeneous sampling and precise assaying, aiming at the upscaling of the recovery of noble metals. Pyrometallurgy, hydrometallurgy and biometallurgy methods and their parameters are reported, focusing on hydrometallurgical leaching trends.

2.1.1. Pyrometallurgy

Pyrometallurgy has been widely applied by automotive catalyst recycling industries. In general, pyrometallurgical procedure is automatized, used for upscaling recovery of PGMs and offers promising recovery yields. Nevertheless, special equipment is required, high temperatures and energy demand are incorporated rising the capital and the operational cost, while significant waste is produced (e.g. volatile

Table 1
The Green Principles of chemistry and engineering.

	Green chemistry principles	Green engineering principles
1	Safer solvents and auxiliaries used	Output-led design
2	Renewable feedstock used	Durability than immortality
3	Prevention focused	Commercial 'afterlife' oriented
4	Atom economy	Renewable resources preferred
5	Low waste produced	Complexity conserved
6	Accident potential minimized	Efficiency maximized
7	Real time analysis to prevent pollution	Material diversity minimized
8	Catalytic reagents used	Non-hazardous inputs and outputs used
9	Less hazardous chemical synthesis designed	Energy and materials in separation and purification minimized
10	Chemical derivatives reduced	Prevention instead of treatment
11	Safer chemicals designed	Meet the need
12	Energy efficiency designed	Efficient use of energy, mass, space, time

waste, slag). A significant drawback of pyrometallurgical processes is the cost of oven' continuous operation. Due to this reason, different types of secondary resources are fed (automotive catalysts, electronic scrap, industrial scrap), in order for the operation not to be discontinued. Such variety of secondary feedstock results in high level of impurities.

Novel pyrometallurgical techniques focus on appropriate metal collector/flux use, milder smelting conditions, and pretreatment of the material (Peng et al., 2017). New trends for smelting refer to plasma melting technology (Dong et al., 2015) and fluxes incorporation (CaO, CaF$_2$, cryolite) (A Devyatykh et al., 2018). Plasma smelting offers high recovery yields, higher heat output requiring small dimensions, while less wastewater and gas emissions are generated. Smelting is the most crucial step in pyro-recovery and several challenges must be overcome, such as sulfur dioxide emissions generated from sulfur-matte exploitation and chromite contaminations, which restrict PGM recovery and create hazardous working conditions.

Melting to slags/alloying with metal collector and chlorination/fluorination are common methods used (A Devyatykh et al., 2018). Moreover, electrorefining, matte leaching (pyro-, hydrometallurgy) and cementation result in promising PGM recovery yields. In the case of spent catalytic converters recycling, spent monolith is crushed, milled and smelted (>2000 °C), while mixed with fluxes, collector metals and additives; then, PGM concentrate is separated and further refined (Fig. 3). It should be noted that materials used in autocatalytic converters, such as CeO$_2$, ZrO$_2$ and Al$_2$O$_3$, have high economic value as well, but slag melting process challenges their co-extraction.

2.1.1.1. Metal smelting collection. Metal smelting collection is the most mature technique used in plants, where the crushed catalyst mixed with fluxes is melted into a crucible, which contains a collector metal (>1600 °C), such as Cu, Fe, Pb, Ni, or matters (Ni$_2$Se$_3$–CuS). After melting, the base metal is removed and PGMs are refined. Generally, matte separation is well known for metal-bearing sulfide ores in primary PGM production, where PGMs are collected by metal base-rich matte placed into an electric furnace, the base metal incorporated into catalyst is extracted and PGMs' content is received as a residue (Bezuidenhout et al., 2013). Melting point, rheological behavior, solubility, droplet size andenvironmental factor are parameters to be controlled. Moreover, impurities can form complexes with PGMs, during the calcination stage.

Regarding copper-collector for the PGMs recovery, the feed material is smelted into an electric arc furnace (1450–1600 °C) with fluxes (e.g. SiO$_2$, CaO), copper collector (e.g. CuO, CuCO$_3$) and reductants (Peng et al., 2017). Another efficient copper-collection technology refers to crushing, milling, homogenization, pelletizing, drying, melting, and electrolytic refining, where the final anode contains 20–25% PGMs

(Dong et al., 2015). As for iron-collection method, smelting with plasma smelting technology at 1500–2000 °C results in promising recovery rates, where 7% PGM pass through the iron phase. During lead collection, the spent catalyst is grounded, mixed with additives (e.g. Na$_2$CO$_3$, KC$_4$H$_5$O$_6$) and smelted (1100 °C). Thereafter, volatilization and final purification are followed. Although the Rh recovery is around 70–80% (Juvonen et al., 2002), PbO emissions should be taken into consideration.

2.1.1.2. Chlorination volatilization. During chlorination process, noble metals are leached (hydrometallurgical procedure), PGM chlorocomplexes (e.g. $PtCl_6^{2-}$, $PdCl_4^{2-}$, and $RhCl_6^{3-}$) are formed; then, separation is carried out via volatilization, repump washings or absorption on activated carbon bed (carbochlorination) (Kim et al., 2000). Although volatilization requires low temperatures between 250 and 700 °C, corrosion effect and gas emissions should be considered. It should be noted that volatilization is promoted by utilizing carbon monoxide as a reductive agent, especially combined with chlorine (Dong et al., 2015). Dong et al., arrived in recovery rates of 95%Pt and 92%Rh, by incorporating carbochlorination using CO/Cl$_2$ (4:6) system at 550 °C for 1 h. Another significant observation was that during carbochlorination, hazardous CO and Cl$_2$ were emitted, which have a negative environmental footprint.

2.1.2. Hydrometallurgy

Hydrometallurgy, under specific conditions, could contribute to PGMs sustainability in an eco-friendlier manner than pyrometallurgy. Compared to pyrometallurgy, hydrometallurgy offers several advantages, such as higher purification yields, scalability, milder process temperatures, minimized energy consumption, process control and promising recovery yields. However, waste management (liquid wastes, gas emissions), process duration, as well as reagents' cost and nature should be considered (Saguru et al., 2018). Concerning hydrometallurgy's stages, during the leaching stage PGM-complexes are formed (with or without pretreatment); then, the dissolved PGM precursors are separated from the leaching media and refined via purification. Regarding thermodynamics, high stability of the metal complexes enhances the dissolution efficiency. Leaching efficiency is affected by leaching reagents' concentration, specified solid-to-liquid ratio (S/L), grain size, entrapment of soluble species into less soluble/insoluble ones, pH value of leachate, leaching temperature, stirring conditions and leaching duration (R. Rao, 2006).

Regarding spent catalyst recycling, feed material is grinded and homogenized, in order to be further dissolved (Fig. 4). Various leaching systems have been examined, such as aqua regia (HCl/HNO$_3$), cyanides (CN), mineral acids (H$_2$SO$_4$, HCl, HNO$_3$), chlorides (NH$_4$Cl, CuCl$_2$,
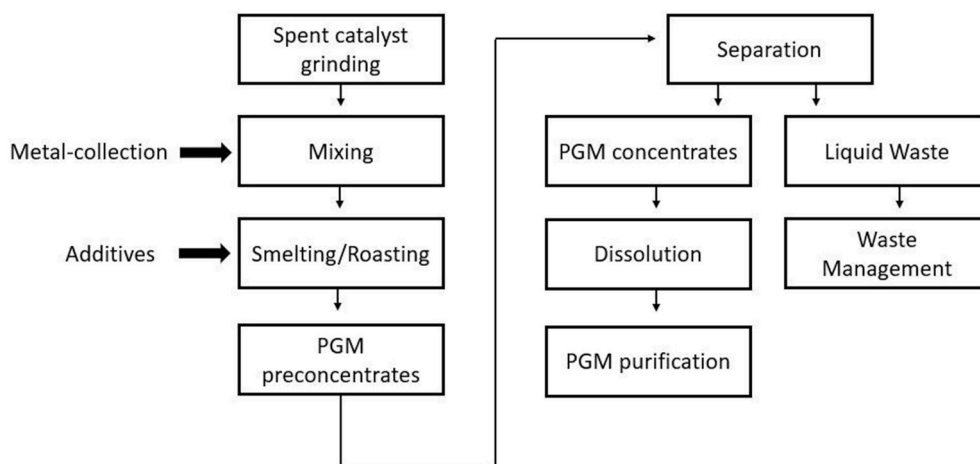

Fig. 3. Pyrometallurgy combined with hydrometallurgy for PGMs recovery.

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│    Homogenization   │
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│   from leachate     │
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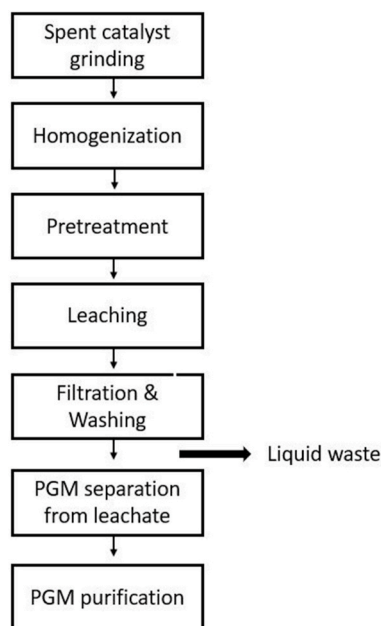
Fig. 4. Hydrometallurgical process for PGMs recovery.

Table 3
The PGMs (Pt, Pd, Rh) chloro-complexes.

Pt	Pd	Rh
Pt (II): $PtCl_4^{2-}$	Pd (II): $PdCl_4^{2-}$	Rh (III): $RhCl_6^{3-}$
Pt (IV): $PtCl_6^{2-}$	Pd (IV): $PdCl_6^{2-}$	Rh (III): $[RhCl_4(H_2O)_2]$
		Rh (IV): $RhCl_5(H_2O)^{2-}$

Fig. 5. The most common extraction methods over years from 1975 to 2020.

FeCl$_3$), hydroxides (NaOH, NH$_4$OH) and carbonates (Na$_2$CO$_3$, (NH$_4$)$_2$CO$_3$) (Rzelewska-Piekut and Regel-Rosocka, 2018). State-of-the-art leaching systems focus on minimizing the reagents' toxicity, reducing or eliminating waste generation, improving recovery yields, minimizing process duration, as well as energy consumption (Table 2).

Among leaching systems, the chloride-based system is preferential and thoroughly investigated, where PGMs chloro-complexes are quite stable into chloride acid solutions (Table 3); consequently, the noble complexes can be easily dissolved (Bernardis et al., 2005). The most stable chloro-complexes refer to $PtCl_6^{2-}$, $PdCl_4^{2-}$ and $RhCl_6^{3-}$ for Pt, Pd, Rh, respectively (Birgersson et al., 2004). It should be mentioned that the chloro-complexes' formation highly depends on chlorine media concentration, where chlorine acid and additional Cl$^-$ sources could be used in balance.

Concerning the recovery of PGMs from the pregnant leach solution, precipitation (Matsumoto et al., 2019), solvent extraction (Swain et al., 2010), ion exchange resins (Nikoloski and Ang, 2014), cementation (Thi Hong et al., 2016), ionic liquids (Lee, 2012), deep eutectic solvents (DES) (ionic liquid group) (Smith et al., 2014), switched solvent systems (Schuur et al., 2019), electrowinning (Pitroda et al., 2017), molecular recognition technology (Izatt et al., 2015), and cloud point extraction (Suoranta et al., 2015) have been proposed. It is vital that recovery methods require the minimum possible steps, utilize non-hazardous reagents, and increase the cost savings. The most popular recovery methods refer to precipitation, solvent extraction and ion exchange, while molecular recognition technology, optimized ionic exchange resins and greener solvents (e.g. switched solvent systems, Deep Eutectic Solvents (DES), ionic liquids) are the newest and most promising methods used (Fig. 5). Another promising upscaling technology refers to electrowinning, where high purity separations are achieved, and

inexpensive equipment is used. In general, each separation method should be tested on scale-up to ensure their industrial competitivity.

Undoubtedly, refining is the most expensive and challenging stage of PGM recovery, because of the noble metal's similar chemistry, reagents' cost, and process duration. The main PGM refiners include Johnson Matthey, BASF, Umicore, Anglo American, Krastsvelmet refinery and Vale Refinery. During the complex refining cycle, PGMs are precipitated as complex salts, PGM salts are recrystallized and calcined into electric furnaces under controlling conditions, producing PGMs foams or pure powders (Gouldsmith, 1963). Another refining process relates solvent extraction with ion exchange (Bernardis et al., 2005). Ion exchange resins are commonly used in the final refining stage, as well as for the extraction of low concentration target metals, due to their expensive supply. In case of electrorefining, the anode refers to the impure metal and the cathode to the pure metal. A promising refining technique refers to the combination of solvent extraction with electrowinning (SE/EW), resulting in faster and higher copper refining levels than the one achieved via solvent extraction (Jamsa-Jounela et al., 2003). Therefore, an investment in SE/EW technique for PGM refining could be supported.

2.1.2.1. Pretreatment stages. Pre-treatment is introduced before the leaching process to improve dissolution rate, avoiding the use of high acidity solvents. Reduction roasting, oxidative roasting, alloying and mechanochemical activation are basic pretreatment methods used. Through reduction roasting, PGMs passivation layer is removed, especially in case of Rh, stabilizing noble metallic form. As for oxidative roasting pretreatment, PGMs metallic phases (or alloys) are formed, while base metal sulfides are converted to metal oxides. Oxidation heating is also performed to remove impurities of the metallic surface, which inhibit the PGMs recovery (de Sá Pinheiro et al., 2004). In case of spent automotive catalytic converters, oxidative heating tends to remove unburned hydrocarbons that deteriorate the catalyst surface to be chemically attacked. Calcination treatments involving salts (Na, Li, K) at temperatures above 800 °C accelerate the leaching kinetics. Concerning PGM alloying treatment, alloying with more reactive metals (Cu, Pb, Ni, Al) promotes the base metals leaching; consequently, PGMs' surface is more easily exposed to chemical interactions. As for mechanochemical activation, simultaneously milling and leaching take place, minimizing the process cost by shortening the process steps (Ficeriová and Baláž, 2010).

In case of Rh, reductive heating under H$_2$ conditions results in almost 80%Rh recovery yield. Otherwise, Rh kinetics are very low, requiring

Table 2
State-of-the-art leaching requirements.

Parameters for Eco- and Cost- effective leaching	
Non-toxic and corrosive reagents	Milder leaching conditions
Minimized waste produced	Liquid waste reused
Minimized process cost	Minimized process steps
Minimized process duration	Improved leaching efficiency
Scale up availability	Commercial competitivity

stronger leaching conditions. Common reductive agents include formic acid, Al powder, AlCl$_3$, NaOH, thiourea and sodium borohydride. As for formic acid reduction pretreatment, leaching efficiency is ameliorated at lower lixiviant concentrations, minimizing the environmental impact and the cost of reagents' used (Trinh et al., 2017). Another pretreatment refers to calcination at 800 °C with 10 wt% Li$_2$CO$_3$, where leaching in HCl media results in Pt and Rh 95% and <50% for Pd recovery yields, respectively (Kasuya et al., 2014). It is also proposed that recovery of PGM-Zn alloy from spent automotive catalytic converters is achieved by reduction pretreatment with Zn-vapor, where leaching in aqua regia of hydrochloric acid is further improved (Sasaki and Maeda, 2014). Concerning mechanochemical pretreatment, the PGM-rich waste is mechanically activated in proportion to oxidizing agent and complexing agents; then, the as-activated waste is leached in chlorine media, resulting in recovery yields of 77%, 62% and 97% for Pt, Rh, Pd, respectively (Wei et al., 2019).

Referring to cyanide leaching, stable PGMs' complexes are formed (i. e. $Pd(CN)_4^{2-}$, $Pt(CN)_4^{2-}$, $Rh(CN)_6^{3-}$), but slow kinetics are obtained at ambient conditions, so that high temperature and pressure are required. It is evident that pretreatments and leaching stimulation techniques tend to improve the leaching conditions, where aqua regia and cyanide-based systems are used. Several works have investigated the amelioration of aqua regia leaching (HCl/HNO$_3$) after pretreatments (Barakat and Mahmoud, 2004), (Tyson and Bautista, 1987), (Jafarifar et al., 2005), as well.

2.1.2.2. Conventional acid leaching systems. Long-established leaching systems utilize aggressive leachates, such as high acidity aqua regia (HCl/HNO$_3$) and cyanide solutions media (CN, sodium cyanide). Referring to cyanide media leaching, PGMs deriving from spent catalysts have been recovered via autoclave leaching using solution of NaCN–NaOH system at 160 °C (Sibrell et al., 1994). Cyanide solution is hydrolyzed at temperatures above 100 °C, where the higher the temperature the faster the hydrolysis. Referring to the dissolution of Pt-complex into aqua regia, the activation energy for leaching Pt is suggested to be 72.1 kJ/mol, as the reaction is controlled by surface chemical reactions (Baghalha et al., 2009). Aqua regia and cyanide media systems tend to be replaced, because of hazard waste produced, like decomposition of gaseous products (NO$_x$, Cl$_2$, acid fumes), leading to unhealthier working conditions. The exposure to hazardous by-products could be limited, in case of feed material pretreatments.

The mainstream for PGMs leaching refers to HCl–H$_2$O$_2$ system (Table 4). The addition of oxidizing agents is preferential, since it leads in greener leaching. Leaching system HCl (12 M)-H$_2$SO$_4$ (18 M)-H$_2$O$_2$ (110 vol) leads in 95% PGMs recovery at 90 °C for 6 h, after hydrogen and thermal treatments (250 °C, 22 h), while the oxidizing agent H$_2$O$_2$ implies the reduction of the pollutant gases (J. de Aberasturi et al., 2011). In the work of Sarıoğlan et al., the utilization of HCl (10%)-H$_2$O$_2$ (5%) media at 90 °C for 3 h resulted in 98% recovery yield for Pd; thereafter, precipitation by using 7% NaBH$_4$ at reduction temperature of 100°C is followed (Sarıoğlan, 2013). In the work of Sun et al., roasting treatments (700–900 °C, 10 °C/min) tend to improve leaching rate of HCl (10%)/H$_2$O$_2$ (1%) system (Sun and Lee, 2013). The well-tested HCl

(2 M)-H$_2$O$_2$ (1 M) system has been used at 25 °C for 1 h, where 84% of Pd was recovered after 10 min s of dissolution (Paiva et al., 2017).

2.1.2.3. State-of-the art leaching systems. Hydrometallurgy trends refer to sustainable leaching systems, by using non-hazardous reagents (H$_2$O$_2$, NaCl, NaClO, NaClO$_3$, O$_3$, HNO$_3$) (Table 4), as well as by following milder leaching conditions (lower acidity, milder temperature, shorter leaching duration). The HCl–H$_2$O$_2$ leaching system has been further improved following greener principles, when balancing HCl/H$_2$O ratio with the addition of oxidizing agents and chlorine sources (NaClO, NaCl, AlCl$_3$, CuCl$_2$) (Table 5).

In the work of Harjanto et al. (2006), HCl(5 M)-NaClO (3%)-H$_2$O$_2$(1%) upon leaching at 65 °C for 3 h, Pt 88%, Pd 99%, Rh 77% recovery yield was obtained, with the aid of reduction pretreatment. By the partial substitution of HCl with NaClO, lower acidity is adjusted without changing the dissolution efficiency of PGMs (Harjanto et al., 2006). Referring to NaCl additional source, leaching system HCl–H$_2$O$_2$–NaCl has been used after calcination (600-1000°C) at 90 °C for 2 h, suggesting that HCl concentration is the most crucial factor, compared to S/L ratio and H$_2$O$_2$ concentration (Ding et al., 2019b). An alternative oxidizing agents was used, namely O$_3$ under chloride acid environment (Fornalczyk et al., 2018), proving that under high temperature conditions 21.1% of Pt is recovered, by using O$_3$ flow 1 g/h, while 47.8% Pt, by using 3 g/h O$_3$ flow.

Concerning additional chloride sources, in case of AlCl$_3$, three chloride ions per molecule are incorporated, and it is believed that aluminum addition reduces the substrate dissolution (Dawson and Kelsall, 2007). In the study of Angelidis et al., PGMs were leached into HCl (5%)-AlCl$_3$ (0.33 M)-NaOCl (4%) at 70 °C for 1 h, after reduction pretreatment with acid H$_2$SO$_4$ (10%) and reductive agent N$_2$H$_6$SO$_4$ (0.1 M), leading in recovery yields of 90–99% for both Rh and Pt, as well as AlCl$_3$, Al$_2$(SO$_4$)$_3$ and CeO$_2$ can be recovered (Angelidis, 2001). As for CuCl$_2$ additional source, Rh-complex dissolution seems to be affected both by leaching temperature and leaching duration. Concerning CuCl$_2$ engagement, leaching is conducted at relatively low acid and high cupric ion concentrations; otherwise, lower Rh yields (20–38%) were achieved (Nogueira et al., 2014). As for NaCl source, H$_2$SO$_4$ (60%)-NaCl (0.1 M) at 125 °C for 2 h, where leaching residue was filtered and washed with bi-distilled water acidified with 5% aqua regia, leaded to promising results (95% Pt, 85% Rh, 85% Pd). It is remarkable that leaching order

Table 5
Sources of chloride ions Cl$^-$ in leaching systems.

Leaching system	Source of Cl$^-$ ions	Extraction	Reference
HCl(5 M)-NaClO(3%)-H$_2$O$_2$(1%) at 65 °C, 3 h	NaClO	Pt 88%, Pd 99%, Rh 77%	Harjanto et al. (2006)
HCl(5%)-AlCl$_3$(0.33 M)-NaOCl(4%), at 70 °C, 1 h	AlCl$_3$ & NaClO	90–99% Rh, Pt	Angelidis (2001)
HCl(6 M)-CuCl$_2$(0.3 M) at 80 °C, 4 h.	CuCl$_2$	95% Pd, 86% Rh	Nogueira et al. (2014)
H$_2$SO$_4$ (60%)-NaCl (0.1 M) at 125 °C, 2 h	NaCl	95% Pt, 85% Rh, 85% Pd	Mahmoud (2003)

Table 4
PGM leaching systems from spent automotive catalysts.

Leaching system	Reagents and processing	pretreatment	extraction	aspects	Reference
Acid leaching	HCl(12 M)-H$_2$SO$_4$(18 M)-H$_2$O$_2$ at 90 °C, 6 h	Thermal treatment (250 °C, 22 h)	95% of PGMs	H$_2$O$_2$ implies reduction of pollutant gases	(J. de Aberasturi et al., 2011)
Chlorine leaching	HCl(2 M)-H$_2$O$_2$(1 M) at 25 °C, separate Pd (II) from Al (III)	No pretreatment	90% Pd	Al (III) shows a harmful effect on the solvents	Paiva et al. (2017)
Chlorine leaching	HCl(5 M)-NaClO(3%)-H$_2$O$_2$(1%) at 65 °C, 3 h	Hydrogen reduction	Pt 88%, Pd 99%, Rh 77%	Lower acidity	Harjanto et al. (2006)
Chlorine leaching	HCl– H$_2$O$_2$–O$_3$ system at 60 °C for 0.5–4 h and residue aqua regia leaching	No pretreatment	48% Pt (3 g/h O$_3$ flow)	Alternative oxidizing agent O$_3$	Fornalczyk et al. (2018)

varies, by changing the acid concentration, namely Pd > Pt > Rh using 50% H_2SO_4, but Pt > Rh > Pd for higher acid concentrations (Mahmoud, 2003).

Leaching in Iodide-iodide media is used for gold extraction, but researchers have also dissolved PGMs into iodine-based leaching media (Dawson and Kelsall, 2007). In the study of Dawson et al. (Dawson and Kelsall, 2007), dissolution of Pt from into iodine leaching achieved under milder conditions, recovering >99% of Pt content on graphite spheres. Moreover, Pt, Pd iodo-complexes were dissolved under high pH conditions preventing the stabilization of oxide phases; thus, it is suggested that iodide/tri-iodide species could be used as oxidizing agents, where triiodide (>1 M) can effectively dissolve Pd under mild conditions.

It has been demonstrated that pre-treatment is widely used affecting acidity requirements and acting synergistically to the final purification yields. On the other hand, pre-treatments are, most of the times, costly and time consuming procedures incorporated reduction of the catalytic powder in controlled nitrogen atmosphere and/or high temperature operations. Yakoumis et al. (2020) recently proposed a state-of-the-art industrial one-step leaching process. The leaching rates presented are 100%, 92% and 61% for Pt, Pd and Rh, respectively. The leaching system proposed is HCl–H_2O_2–NaCl media under mild conditions (70 °C, 2 h), while the extremely high solid per liquid ratio (S/L 70%), provides very promising ground for upscaling in industrial conditions.

2.1.2.4. Kinetic studies. Crucial parameters that affect the leaching kinetics refer to reagents' acidity, S/L ratio, leaching temperature and leaching time. As for the mainstream system for PGMs leaching, namely H_2O_2–HCl, various studies have been carried out. As proved in the work of A. M. Yousif et al., HCl–H_2O_2 leaching system depends on HCl–H_2O_2 ratio, leaching temperature and contact time. By increasing the HCl–H_2O_2 up to 0.8/100 v/v (H_2O_2 vol%/HCl vol %), the PGM-complexes dissolution raises sharply, while afterwards leaching yields for Pt, Pd, Rh do not further alter. The optimum HCl–H_2O_2 ratio has been evaluated under different temperature conditions (20°C–80 °C) as well, revealing the optimized kinetic behavior at 60 °C. As for the parametrization of contact time (0.5–3 h), the system H_2O_2(0.8 vol%)/HCl(9 M) at 60 °C reached an equilibrium at 2 h, while Rh-complex dissolved at the highest level (86%) after 2.5 h contact time (Yousif, 2019). The leaching system H_2O_2(0.8 vol%)/HCl(9 M) at 60 °C for 2.5 h resulted in leaching yields 98%, 96%, 86% for Pd, Pt and Rh, respectively.

In the recent study of Yakoumis et al., the kinetic conditions of HCl–NaCl–H_2O_2 system for the PGMs recovery have been evaluated (Yakoumis et al., 2020). The optimized leaching system HCl (3 M) -NaCl (4.5 M)-H_2O_2 (1% v/v) at 70 °C for 2 h resulted in 100%, 92% and 61% recovery yields, for Pt, Pd and Rh, respectively. According to the kinetic study (Fig. 6), PGM chlorides formation sharply increases up to 0.5 h, while 2 h leaching duration is the optimized one for the Pt, Pd, Rh

Fig. 6. PGMs kinetic behavior for 0.5, 1, 2 and 3 h s leaching time (Yakoumis et al., 2020).

dissolution. After 2 h leaching time, recovery yield does not further alter. Comparing Pt and Pd dissolution, a plateau is reached after 0.5 h in case of Pd, while Pt plateau appears between 1 h and 2 h. As for the leaching order Pt > Pd > Rh, Rh exhibits the slowest kinetics, due to its' stereo tactical structure and passivation layer formed in acid conditions.

The leaching kinetics of HCl–H_2O_2–NaClO system have been evaluated by Harjanto et al. (2006), where HCl (11.6 mol/L)–H_2O_2 (1 vol%) at 65 °C for 3 h has been proved the optimum one. A significant result refers to 0.5%vol H_2O_2 addition, which lead in a sharply dissolution increase. Moreover, the addition of NaClO (3 vol%) into HCl (5 mol/L)–H_2O_2 (1 vol%) improved the dissolution of PGMs about 3–5%.

As for different leaching systems, NaCl–HCl–$FeCl_3$ media has been evaluated for Pd leaching, indicating that the Pd dissolution is controlled by surface chemical reactions, by following a shrinking-core model. Different leaching temperatures (40°C–80 °C), leaching durations (10–360min), under the stable ratio concentrations of HCl (2.0 mol/L)-NaCl (4.0 mol/L)- Fe^{3+} (0.67 mol/L) have been investigated. The leaching efficiency of Pd increased significantly at 60 °C, while elevated temperatures at 80 °C further promoted the dissolution. Under conditions of leaching between 30 and 60min at 80 °C, Pd dissolution sharply raised, reaching the optimized recovery yield (99.5%Pd) for 90min leaching duration (Ding et al., 2019a).

In another study of Nogueira et al. (2014), leaching yield of 95%Pd and 86%Rh has been achieved, by following the system HCl (6 M)/Cu^{2+}(0.3 M) at 80 °C for 4 h. Different leaching temperature range (25 °C–100 °C), different concentrations of HCl (up to 6 M) and Cu^{2+} (up to 0.3 M) and leaching time (5min to 4 h) have been evaluated. As for temperature parameter, Rh recovery yield increased constantly by increasing the temperature, while Pd yield was affected more at lower temperature rates (>60 °C). Leaching efficiency at several HCl concentrations has been evaluated for the temperatures 60 °C and 80 °C. According to the kinetics of 2 M HCl leaching solution, almost 70–80% of Pd and 35–40% of Rh have been dissolved within 1 h. After the leaching duration of 1 h, dissolution increased in a lower extent, resulting in 88% and 50% recovery yields for Pd and Rh, respectively. Concerning Cu^{2+} concentrations factor, it is expected that Cu^{2+} addition enhanced both Pd and Rh extraction, but no significant variation was observed in case of Rh. The leaching time of 0.5–1 h was proved to be adequate for the Pd yield to be stabilized, while Rh yields increased slowly at different durations.

2.1.2.5. Leaching stimulation techniques. Additional methods to meliorate PGM-complexes dissolution refer to microwave-assisted leaching, pressure-assisted leaching and electro-generated chlorine recovery. By following these leaching stimulation techniques, the solvents' acidity can be adjusted.

According to the study of Spooren et al. PGMs were recovered from spent catalyst using a two-step microwave assisted extraction. The first step refers to microwave sulfation roasting in the presence of NaH-SO_4·H_2O or $KHSO_4$ and $NaClO_3$; then, a second short (30 min, 105 °C) microwave acidic leaching at a liquid to salt ratio of 10 leads to Pd 96%, Pt 85% and Rh 96%, respectively. It was also demonstrated that sulfation roasting attacks both the cordierite material and rare earth elements, which are present in the washcoat, in order to form sulfate salts (Spooren and Abo Atia, 2020).

Regarding pressure-assisted leaching, which is commonly applied for primary PGMs production, soluble minerals are dissolved under pressure conditions (>20 atm). This technique is widely used in industry over the last 75 years, offering promising leaching results for a variety of minerals. Pressure-assisted leaching is used in Kell process, in order for the base metals to be removed from the PGM-rich material (Liddell and Adams, 2012), as well as in cyanide leaching systems (Sibrell et al., 1994). A novel method for spent automotive catalyst recycling refers to two-step pressure cyanide leaching (Chen and Huang, 2006), where catalyst feed is pretreated to remove carbon and fuel contaminants; then
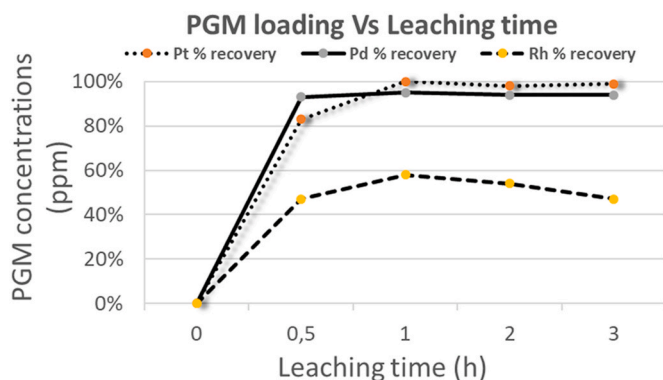
PGMs are dissolved twice into pressure cyanide leaching media, resulting in 95–96% and 90–92% recoveries for Pt, Pd and Rh, respectively.

Regarding electro-generate chlorination, the leaching efficiency depends on S/L ratio, current density, leaching temperature and stirring speed. PGMs deriving from spent catalysts were dissolved into HCl media with the stimulation of electro generated chlorine as an oxidant (K. Upadhyay et al., 2013). Under the optimized conditions of 6.0 mol/L HCl, 714 A m^{-2} current density, 363 K, 20 g L^{-1} pulp density and 700 rpm agitation speed, 71% Pt, 68% Pd and 60% Rh were leached. Though this eco-friendly method, chlorine gas is bubbled into the leaching media, and the process takes place into an autoclave.

2.1.3. Biometallurgy

As for the biometallurgical contribution to PGMs recovery, biometallurgical techniques, such as bioleaching and biosorption, are applied in lab scale by this time. According to Segneri et al. (Zhuang et al., 2015), the three major PGMs streams comprise end of life products, manufacturing residues and urban, industrial wastewater. PGMs can be recovered from metal refining residues (Gauthier et al., 2010) and spent catalytic converters (Mabbett et al., 2006) via the interaction between microorganisms and metal-bearings. As for the wastewater resource, the precious metal content is quite low, but the waste volume generated from industrial, pharmaceutical, chemical, geothermal (Segneri et al., 2014), municipality water, electrochemical sector is enormous. Thus, the aforementioned waste streams are considered as potential PGMs resources. Research attention is focused on the biometallurgical recycling of wastewater streams, in order to contribute to urban waste management and CRMs recovery.

Several advantages are provided via biometallurgy recovery methods, such as lower carbon footprint, utilization of greener than in hydrometallurgy solvents, less energy consumed and absence of hazardous gases. However, the non-biocompatible nature of PGMs, in combination with a variation of multiple parameters to be controlled should be considered as challenges. Effective control of pH, leaching temperature, ionic strength, as well as the reduction of PGMs salts, play a crucial role in both PGM leaching and extraction. In addition, PGMs appear into waste streams in a mixed complex form, requiring an extensive research on proper extraction methodologies. Generally, a scale-up investigation is critical, in order for biometallurgy to become industrially established (Juvonen et al., 2002).

Biometallurgical recovery of spent catalytic converters through bioleaching (leaching step) and bio-absorption (extraction step) (Fig. 7) involves the PGMs interaction with biomaterial substances (e.g. bacteria), and PGMs absorption by various media, such as NaCN, NaOH, HCl. Bacteria such as *Chromobacterium violaceum, Pseudomonas fluorescents, Acidithiobacillus thiooxidans* have metal-sequestering properties, sequestering the dissolved noble metal ions from dilute complex solutions (e.g. cyanide complexes). As for biosorption, various techniques can be followed, such as absorption precipitation, solvent extraction, ionic exchange that should promote the interaction of target metal ions and charged surface microorganisms. Common bio-absorbents for Pt and Pd refer to bacteria *Desulfovibrio desulfiricans, Desulfovibrio vulganis* (de Vargas, Inmaculada, Macaskie, Lynne E, Guibal, 2004), chitosan derivatives (Chassary et al., 2005) and collagen fiber membranes (Nikoloski and Ang, 2014).

According to Das et al., utilization of *Chromobacterium violaceum* (pBAD) under glycine concentration (11.81 g L^{-1}), ultrasound power, pH (10.73), agitation speed (150 rpm) and pulp density (2%) results in promising PGMs extractions, namely 63.1% of Pt, 38.4% of Pd and 99.3% of Rh. Moreover, it is proved that ultrasound pretreatment acts synergistically in PGM cyanide-complexes formation, by removing the base metals (S. DAS, K.N. GOH, 2017). Factors that affect ultrasound pretreatment are ultrasound power, sonication frequency, acid concentration and pulp density and ultrasound duration. According to Hosseinkhani et al. bacteria, such as *Halomonas* and *Vibrio*, can be
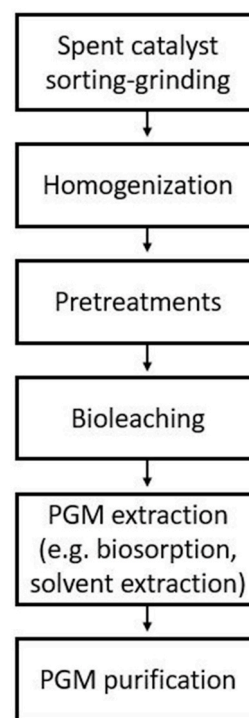

Fig. 7. Biometallurgy steps for the PGMs recovery.

incorporated for Pd reduction in saltwater, offering perspectives for PGMs recovery (Hosseinkhani et al., 2014).

3. Analysis

Among all technologies described above, pyrometallurgy dominates in industry, by offering high recovery yields and is being further improved by effective smelting processing. However, pyrometallurgy requires high energy consumption, equipment investment and purification achieved is average leveled. In this respect, hydrometallurgy that offers high selectivity, purification, better process control, promising recovery yields, should be applied in plant scale recycling. Bioleaching and biosorption techniques offer eco-effectivity, as non-toxic reagents are utilized, and less energy is required. Nevertheless, research and scale up trials should be conducted in case of biometallurgy, in order to be a commercial alternative for PGMs recovery. Highlighting the hydrometallurgical routes, it is perceived that leaching efficiency, purity of the leachate, liquid waste management and S/L ratio leached are to be monitored and examined.

3.1. Discussion on proposed leaching systems

Regarding to the green chemistry principles, state-of-the-art leaching systems are based on mild solvents, lower temperatures and direct processing. In several studies, chlorine system seems favorable, as PGMs chloro-complexes are quite stable under acidic conditions. The beneficial methodology of PGM-complexes dissolving is being improved, by balancing the acidity of chlorine media (e.g. HCl aqua media) with the addition of chloride anion sources (e.g. NaCl, NaClO, AlCl$_3$, CuCl$_2$) (Harjanto et al., 2006) (Angelidis, 2001) (Nogueira et al., 2014) and oxidizing agents (e.g. H$_2$O$_2$, ozone, NaClO) (Fornalczyk et al., 2018) (Yakoumis et al., 2020). By utilizing milder solvents, less waste is produced than in high chloride acidity (e.g. HCl 12 M, aqua regia), preventing further waste management procedures.

The single (without pre-treatment) step leaching process proposed by Yakoumis et al. [52] is very promising for industrial upscaling, since it incorporates mild acidic environment in accordance with high solid to

liquid ratio. The recoveries utilized, namely 100%Pt, 92%Pd and 61% Rh, are very promising. Though, extensive scale-up testing should take place before the proposed process could be characterized as industrial, taking care of waste management, solvent re-use issues and controlled washing conditions.

Special treatments before leaching could meliorate the leaching effectivity, resulting in better kinetic behavior, especially in the case of Rh complex. Pretreatments, such as reduction, calcination and re-concentration, affect strongly the final PGMs-complex dissolution, by removing impurities and destroy the passivation layer of PGMs (Sibrell et al., 1994) (J. de Aberasturi et al., 2011). However, the procedure cost increases, due to the labor time and the energy consumption required; thus, it is debatable whether pretreatments should be applied in industrial scale. As for alloying pretreatment, the dissolution rate of PGMs is accelerated, but more energy is consumed relating to the alloying stage, increasing the industrialization cost (Saguru et al., 2018). On the other hand, direct leaching processing offers a simple, cost-efficient alternative for PGMs recovering; thus, should be preferred for upscaling recoveries, being further optimized.

Other leaching trends refer to leaching assistance by microwave heating, pressure conditions, generated chlorination that undoubtedly improve the leaching kinetics. Although kinetics is improved, microwave leaching is applied in lab-scale by the time. Various parameters are to be considered, such as high energy consumption, feed material composition and better process control, in order to be upscaled. Concerning generated chlorination process, both process safety and environmental footprint should be addressed.

3.2. Feed material identification

Spent automotive catalysts are the PGM-richest secondary feedstock material. Spent catalytic monoliths, containing high PGMs concentrations, should be characterized to define bulk composition, surface morphology, impurities, and any contamination that deteriorates the leaching procedure (J. de Aberasturi et al., 2011) (Yakoumis et al., 2020) (Trinh et al., 2019). The mechanically processed (milled) spent monoliths, that are received in a powder form, have to be analyzed by elemental analysis methods, such as X-ray Fluorescence (XRF), Inductively coupled plasma spectroscopy (ICP) to define elements involved, such as base metals, cordierite elements (MgO, SiO_2, Al_2O_3) washcoat materials (CeO_2, ZrO_2, Al_2O_3, TiO_2) and poisoning elements (e.g. As, Cr_2O_3, CaO, Cd, C, S, BaO, ZnO). Moreover, Scanning Electron Microscopy (SEM) in conjunction with Energy-dispersive X-ray spectroscopy (EDS) evaluates the catalyst size, morphology, composition and distribution on the carrier. Shoot and unburned hydrocarbons' deposition should be detected and removed; otherwise, catalyst surface area is not properly reactive to chemical reagents.

The assaying of secondary resources is crucial for the process' design, since the material's characteristics could lead to the selection of the proper leaching system. Characterization of both leach residue and leachate is crucial for the further extraction of PGMs and the co-extraction of rare earths, in case of spent catalyst resource.

Compared to hydrometallurgy, pyrometallurgical routes involve slag production, where PGMs are combined with various elements, challenging their further purification. On the other hand, material composition during hydrometallurgy can easily be controlled and monitored, by performing mass balance assessments, chemical characterization, as well as monitored by further post-leaching treatments.

3.3. Input material preparation

Concerning spent catalysts, the material to be leached should be in a fine and homogenous granulometry, meliorating the chemical reactions within the leaching system. As described in the work of Yakoumis et al. (2018), spent catalysts should be sorted (e.g. DOC, TWC, SCR) in separate batches and processed individually to achieve higher recovery

yields. The sorted batches are de-canned, in order all metallic parts to be removed facilitating the leaching/smelting of spent catalytic monoliths. Thereafter, the broken catalytic monoliths are crushed, milled and sieved <2 mm), obtaining a fine granulometry. By downsizing material grain dimensions, specific surface area is increased, playing a crucial role in the reactivity of the feed material (Sarıoğlan, 2013). Regarding the impurities, the catalyst powder is thermally treated, in order for the humidity and contaminations to be removed and surface interaction with the leachate media to be eliminated. Proper sampling and assaying of the feed is possible to determine the leaching efficiency and define material losses, which affect even more the refining stage.

3.4. Economic & environmental perspectives

Concerning the economic aspect, hydrometallurgical methods that add value to process monopolize the involved incorporations' interest. The number of the recovery steps incorporated is directly related to the waste produced, affecting the cost of the process. Thus, breakthrough hydrometallurgical procedures focus on green solvents, mild temperatures, process duration, and high recovery yields for PGMs.

As for the leaching route, which is the most important stage in hydrometallurgy, mild leaching systems prevent liquid waste; otherwise, extensive waste management raises the total cost. Furthermore, non-toxic reagents utilization benefits both environment and working conditions. Compared to common cyanide and aqua regia systems, mild chloride solvents do not emit poisonous gasses or by-products. Direct leaching refers to another adding value technique, where the mechanical processed PGMs resource is fed into the leaching media without any pre-concentration or thermal reduction (Yakoumis et al., 2020). The simplicity of direct leaching methods offers cost effectivity in upscaling recycling processes, as pretreatments are energy intensive and require special equipment.

As for state-of-the-art recovery techniques, solvents used in solvent extraction are toxic, flammable and expensive, tending to be replaced with biological reagents (biometallurgy), inorganic reagents (precipitation methods), ionic liquids, switchable solvent systems, and surfactant micelles (cloud-point extraction). As for ion exchange technology, large equipment used, time consuming processing required and low mass transfer rates achieved are considerable limitations (Rovira, 1998). Ionic liquids are expensive, complex solvents, being used only for lab-scale recoveries. Deep eutectic solvents (DES) refer to a new class of ionic liquids, exhibiting limited environmental impact, less expensive and easily produced in scale-up batches (Zhang et al., 2012). As for metals extraction, by following electrochemical methods, DES are promising electrolytes, proper for electrowinning/electrodeposition extraction techniques. Molecular recognition technology (MRT) seems the latest big trend in noble metals recovery, due to its time- and cost effectiveness, green technology, high purification achieved, high selectivity and scalability (Izatt et al., 2015).

3.5. Industrial aspect

Secondary PGMs sources' recycling should be designed to achieve sustainability and high recovery yields, in order to be technoeconomically feasible. In terms of cost effectivity, pyro-based recovery consumes high amount of energy, while metal purity is on average level. In the case of catalytic converters, washcoat materials such as alumina are hardly recovered (Saguru et al., 2018), due to the high temperature smelting stage, as support materials are driven to the slag phase. Although pyrometallurgical processes dominate in industrial application, it is a common trend that hydrometallurgy gains the foothold over the years. Hydrometallurgical extraction is favorable, due to lower temperature conditions required, less energy consumed, higher purity achieved, potential co-extractions, and better process control. However, the afore-mentioned factors are not adequate for hydrometallurgy to be adopted in plants, as further requirements should be fulfilled and

studied. In terms of industrialization, hydrometallurgical processes should focus on higher solid to liquid (S/L) ratio dissolution, under milder leaching conditions. By using additional chloride salts and oxidizing agents, the media acidity can be minimized.

It is vital that new business models are established for noble metals' recovery, in order to decouple Europe from PGM imports (Gaustad et al., 2018). An effective circular economy model for PGM sustainability requires the continuous engagement of PGM producer companies, service providers, consumers and recycling companies (Moschovi et al., 2018). Some hydrometallurgical routes have been proposed for recovering PGMs from secondary sources. Some of the reported methods have been commercialized, while others are still under examination, in order to overcome issues that have already been elaborated by pyrometallurgical methods. Most common technologies and their technological readiness are presented in Table 6.

The major mining companies refer to IMPALA, ANGLO PLATINUM, NORTHAM PLATINUM LIMITED, NORNICKEL, while PGM' refiners include BASF, UMICORE, JOHNSON MATTHEY (Jha et al., 2013). In general, suppliers of primary and secondary PGM resources, manufacturers of automotive catalytic converters, integrators of exhaust systems, recycling companies, even automotive companies should collaborate for PGM recovery, following green chemistry principles and cost-effective solutions. Furthermore, the implementation of an innovative

Table 6
Technological readiness level for PGMs leaching/extraction.

Technology	Application	TRL	Reference
Pyrometallurgy	British Petroleum Co P (UK) company for the separation of PGM from a graphite base	9	(A Devyatykh et al., 2018)
Pyrometallurgy PGM-Pb recovery	JM PGM extraction	9	(Benson et al., 2000) (Keyworth, 1983)
Rose Process (PGM-Cu-collection)	Nippon PGM Co., Ltd.	9	Hagelüken (2012)
Plasma arc smelting and mineral phase reconstruction	Umicore S.A.	9	(Hai-Zhao Zhao, 1998) (Hagelüken, 2006)
Pyrometallurgy and electrolytic refining	Institute for Mining and Metallurgy Bor, Serbia	7	Ivanović et al. (2011)
Hydrometallurgy	British Petroleum Co P (UK) company for the separation of PGM from a graphite base	9	(A Devyatykh et al., 2018)
Hydrometallurgy Anglo American Corporation/ University of British Columbia Process	(low grade ores)	6	Panda et al. (2018)
Hydrometallurgy -Albion process	(low grade ores)	9	
Hydrometallurgy -Galvanox™ process	(low grade ores)	6	
Hydrometallurgy - Total pressure oxidation process	(low grade ores)	9	
Hydrometallurgy -Hydro copper process	(low grade ores)	9	
Hydrometallurgy -Kell process	(low grade ores)	6	
Hydrometallurgy -Nitrogen species catalyzed process	(low grade ores)	9	
Solvometallurgy	PGM extraction	3–4	(Binnemans and Jones, 2017) (Nguyen et al., 2021)
Cyanide leaching process	PGM extraction	3	Wadsworth et al. (2000)
Magneto-hydrodynamic (mhd) pump	PGM extraction	3–4	Saternus et al. (2020)
Bioleaching-bioprocessing	PGM extraction	3–4	Hedrich et al. (2020)

hydrometallurgical technology will further assist in raising public awareness and implementing a local PGM circular value chain.

3.6. Challenges for future research

Future research should focus on high solid to liquid ratio leached along with green reagents utilization, minimizing liquid waste production and shortening the leaching process in time and number of processing steps. Future work should be carried out to develop new leaching methods, where eco- and cost-leaching efficiency not only refers to the PGMs recovery, but offers the possibility of co-extraction, relating to base metals and rare earths. Moreover, the re-use of leach residue for less-demanding applications is going to further improve process economics, establishing a circular economy model. Multiple waste streams could be managed in a recycling plant, whereas agile production will further improve the recycling process the next few years (de Almeida and Borsato, 2017).

Concerning the adoption of non-toxic, one-step leaching systems, extensive assaying is required to determine feed material composition and impurities. Impurities limit the surface reactivity during the leaching, playing a critical role in final PGM recovery. It is true that pre-treatment steps tend to remove such contaminations and impurities, but should be performed in a limited extent, aiming to minimize energy consumption. Post-treatments, such as precipitations and re-dissolving of PGM feed, might remove impurities more efficiently, by avoiding energy consuming pretreatments, such as reduction roasting. In case of post-treatments after leaching procedure, careful process design and pilot trials are required.

4. Conclusion

The demand of low-carbon energy technologies, as well as the considerable gap between supply and demand, create an imperative need for PGMs recycling. Regarding the pyrometallurgy's drawbacks, hydrometallurgy has been developed, offering promising recovery yields for PGMs, as well as higher purity' level achieved. Compared to pyrometallurgy, less energy is consumed, and lower temperature process is required, affecting both the process cost and environmental footprint. The most crucial stage in hydrometallurgy, namely leaching process, is being further improved, by adopting green chemistry requirements. The following statements are highly recommended, in order for the hydrometallurgy to be industrially adopted:

1. State-of-the-art leaching systems refer to chlorine solutions, where milder acidity is achieved by adding chlorine ion sources and oxidizing agents. Mild leaching temperatures contribute to ecological protection as well.
2. The optimized leaching systems should dissolve even greater amount of noble metals (high S/L ratio) into less leachate volume, generating less liquid waste. Moreover, by increasing S/L ratio smaller plant installations may be required. Although liquid waste from leachate volume is minimized, washing stage must be controlled; otherwise, considerably wastewater produced will increase process expenses. Real time analysis is required to prevent pollution and reduce process cost.
3. Co-extraction of rare earths, in the case of spent automotive catalyst recycling, could add higher value to the industrial process. Agile production design is being further developed; thus, many opportunities of easier, parallel waste steams management will be provided the next few years.
4. Direct leaching seems beneficial, minimizing energy consumed. Undoubtedly, feed material composition, as well as contaminations should be defined and validated, in order to choose the most appropriate leaching and extraction method. Post-treatments, such as PGM salt re-dissolution and purification, may be required.

5. Future research shall focus on high S/L ratio leached, co-extraction techniques, multiple waste streams management and replacing of pretreatments by post-treatments.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

A Devyatykh, E., O Devyatykh, T., N Boyarsky, A., 2018. Overview of technologies for extraction of platinum group metals from poor raw materials. In: KnE Engineering, p. 154. https://doi.org/10.18502/keg.v3i5.2664.

Angelidis, T.N., 2001. Development of a laboratory scale hydrometallurgical procedure for the recovery of Pt and Rh from spent automotive catalysts. Top. Catal. 16, 419–423. https://doi.org/10.1023/A:1016641906103.

Baghalha, M., Khosravian, Gh.H., Mortaheb, H.R., 2009. Kinetics of platinum extraction from spent reforming catalysts in aqua-regia solutions. Hydrometallurgy 95, 247–253. https://doi.org/10.1016/j.hydromet.2008.06.003.

Barakat, M.A., Mahmoud, M.H.H., 2004. Recovery of platinum from spent catalyst. Hydrometallurgy 72, 179–184. https://doi.org/10.1016/S0304-386X(03)00141-5.

Benson, M., Bennett, C.R., Harry, J.E., Patel, M.K., Cross, M., 2000. The recovery mechanism of platinum group metals from catalytic converters in spent automotive exhaust systems. Resour. Conserv. Recycl. https://doi.org/10.1016/S0921-3449(00)00062-8.

Bernardis, F.L., Grant, R.A., Sherrington, D.C., 2005. A review of methods of separation of the platinum-group metals through their chloro-complexes. React. Funct. Polym. 65, 205–217. https://doi.org/10.1016/j.reactfunctpolym.2005.05.011.

Bezuidenhout, G.A., Eksteen, J.J., Akdogan, G., Bradshaw, S.M., De Villiers, J.P.R., 2013. Pyrometallurgical upgrading of PGM-rich leach residues from the Western Platinum base metals refinery through roasting. Miner. Eng. 53, 228–240. https://doi.org/10.1016/j.mineng.2013.04.002.

Binnemans, K., Jones, P.T., 2017. Solvometallurgy: an emerging branch of extractive metallurgy. J. Sustain. Metall. https://doi.org/10.1007/s40831-017-0128-2.

Birgersson, H., Eriksson, L., Boutonnet, M., Järås, S.G., 2004. Thermal gas treatment to regenerate spent automotive three-way exhaust gas catalysts (TWC). Appl. Catal. B Environ. 54, 193–200. https://doi.org/10.1016/j.apcatb.2004.09.001.

Chassary, P., Vincent, T., Sanchez Marcano, J., , E. Macaskie, L., Guibal, E., 2005. Palladium and platinum recovery from bicomponent mixtures using chitosan derivatives. Hydrometallurgy 76, 131–147. https://doi.org/10.1016/j.hydromet.2004.10.004.

Chen, J., Huang, K., 2006. A new technique for extraction of platinum group metals by pressure cyanidation. Hydrometallurgy 82, 164–171. https://doi.org/10.1016/j.hydromet.2006.03.041.

Cole, S., 2002. A Review of the Beneficiation and Extractive Metallurgy of the Platinum Group Elements. Highlighting Recent Process Innovations [WWW Document]. L. J. Cabri. https://www.sgs.com/-/media/global/documents/technical-documents/sgs-technical-papers/sgs-min-tp2002-03-beneficiation-and-extractive-metallurgy-of-pge.pdf.

Das, S., Goh, K.N., Ting, Y.P., 2017. BIOLEACHING OF PLATINUM GROUP METALS (Pt, Pd, Rh) FROM SPENT AUTOMOTIVE CATALYTIC CONVERTERS USING GENETICALLY MODIFIED BACTERIA. In: Sixteenth International Waste Management and Landfill Symposium. Sardinia.

Dawson, R.J., Kelsall, G.H., 2007. Recovery of platinum group metals from secondary materials. I. Palladium dissolution in iodide solutions. J. Appl. Electrochem. 37, 3–14. https://doi.org/10.1007/s10800-006-9218-8.

de Aberasturi, D.J., Pinedo, R., R deLarramendi, J.I., Rojo, T., 2011. Recovery by hydrometallurgical extraction of the platinum-group metals from car catalytic converters. Miner. Eng. 24, 505–513. https://doi.org/10.1016/j.mineng.2010.12.009.

de Almeida, S., Borsato, M., 2017. Exergetic analysis as an agile approach to recycling processes: a literature review. Int. J. Agile Syst. Manag. 10, 137. https://doi.org/10.1504/IJASM.2017.086157.

de Sá Pinheiro, A.A., de Lima, T.S., Campos, P.C., Afonso, J.C., 2004. Recovery of platinum from spent catalysts in a fluoride-containing medium. Hydrometallurgy 74, 77–84. https://doi.org/10.1016/j.hydromet.2004.01.001.

Inmaculada, de Vargas, Macaskie, Lynne E., Guibal, E., 2004. Biosorption of palladium and platinum by sulfate-reducing bacteria. J. Chem. Technol. Biotechnol. 79, 49–56. https://doi.org/10.1002/jctb.928.

Ding, Y., Zheng, H., Li, J., Zhang, S., Liu, B., Ekberg, C., 2019a. An efficient leaching of palladium from spent catalysts through oxidation with Fe(III). Materials 12, 1205. https://doi.org/10.3390/ma12081205.

Ding, Y., Zheng, H., Li, J., Zhang, S., Liu, B., Ekberg, C., Jian, Z., 2019b. Recovery of platinum from spent petroleum catalysts: optimization using response surface methodology. Metals 9. https://doi.org/10.3390/met9030354.

Dong, H., Zhao, J., Chen, J., Wu, Y., Li, B., 2015. Recovery of platinum group metals from spent catalysts: a review. Int. J. Miner. Process. 145, 108–113. https://doi.org/10.1016/j.minpro.2015.06.009.

Ficeriová, J., Baláž, P., 2010. Leaching of gold from a mechanically and mechanochemically activated waste. Acta Montan. Slovaca 15, 183–187.

Fornalczyk, A., Saternus, M., 2009. Removal of platinum group metals from the used auto catalytic converter. Metalurgija 48.

Fornalczyk, A., Willner, J., Gajda, B., Sedlakova-Kadukova, J., 2018. Influence of H2O2 and O3 on PGM extraction from used car catalysts. Arch. Metall. Mater. 63, 963–968. https://doi.org/10.24425/122428.

Gaustad, G., Krystofik, M., Bustamante, M., Badami, K., 2018. Circular economy strategies for mitigating critical material supply issues. Resour. Conserv. Recycl. 135, 24–33. https://doi.org/10.1016/j.resconrec.2017.08.002.

Gauthier, D., Søbjerg, L.S., Jensen, K.M., Lindhardt, A.T., Bunge, M., Finster, K., Meyer, R.L., Skrydstrup, T., 2010. Environmentally benign recovery and reactivation of palladium from industrial waste by using gram-negative bacteria. ChemSusChem 3, 1036–1039. https://doi.org/10.1002/cssc.201000091.

Glaister, B.J., Mudd, G.M., 2010. The environmental costs of platinum–PGM mining and sustainability: is the glass half-full or half-empty? Miner. Eng. 23, 438–450. https://doi.org/10.1016/j.mineng.2009.12.007.

Gouldsmith, A.F.S., 1963. Extraction and Refining of the Platinum Metals [WWW Document]. https://www.technology.matthey.com/article/7/4/136-143/.

Hagelüken, C., 2006. Recycling of electronic scrap at Umicore's integrated metals smelter and refinery. World Metall 59, 152–161.

Hagelüken, C., 2012. Umicore: precious refining-the power of integration [WWW Document]. https://www.serdc.org/Resources/Documents/Summit Presentations/SERDC Summit Presentation - Mark Caffarey.pdf.

Harjanto, S., Cao, Y., Shibayama, A., Naitoh, I., Nanami, T., Kasahara, K., Okumura, Y., Liu, K., Fujita, T., 2006. Leaching of Pt, Pd and Rh from automotive catalyst residue in various chloride based solutions. Mater. Trans. 47, 129–135. https://doi.org/10.2320/matertrans.47.129.

Hedrich, S., Kraemer, D., Junge, M., Marbler, H., Bau, M., Schippers, A., 2020. Bioprocessing of oxidized platinum group element (PGE) ores as pre-treatment for efficient chemical extraction of PGE. Hydrometallurgy. https://doi.org/10.1016/j.hydromet.2020.105419.

Hosseinkhani, B., Hennebel, T., Van Nevel, S., Verschuere, S., Yakimov, M.M., Cappello, S., Blaghen, M., Boon, N., 2014. Biogenic nanopalladium based remediation of chlorinated hydrocarbons in marine environments. Environ. Sci. Technol. 48, 550–557. https://doi.org/10.1021/es403047u.

Ivanović, S.Z., Trujić, V.K., Gorgievski, M.D., Mišić, L.D., Božić, D.S., 2011. REMOVAL OF PLATINUM GROUP METALS (PGMs) FROM THE SPENT AUTOMOBILE CATALYST BY THE PYROMETALLURGICAL PROCESS. In: 15th International Research/Expert Conference "Trends in the Development of Machinery and Associated Technology".

Izatt, R., R Izatt, S., E Izatt, N., L Bruening, R., Navarro, L., Krakowiak, K.E., 2015. Industrial applications of molecular recognition technology to separations of platinum group metals and selective removal of metal impurities from process streams. Green Chem. 17 https://doi.org/10.1039/C4GC02188F.

Jafarifar, D., Daryanavard, M.R., Sheibani, S., 2005. Ultra fast microwave-assisted leaching for recovery of platinum from spent catalyst. Hydrometallurgy 78, 166–171. https://doi.org/10.1016/j.hydromet.2005.02.006.

Jamsa-Jounela, S.-L., Saloheimo, K., Marttila, T., 2003. A Monitoring System for the Copper Solvent Extraction - Electrowinning Process. https://doi.org/10.1016/S1474-6670(17)37639-5.

Jha, M.K., Lee, J., Kim, M., Jeong, J., Kim, B.-S., Kumar, V., 2013. Hydrometallurgical recovery/recycling of platinum by the leaching of spent catalysts: a review. Hydrometallurgy 133, 23–32. https://doi.org/10.1016/j.hydromet.2012.11.012.

Juvonen, R., Lakomaa, T., Soikkeli, L., 2002. Determination of gold and the platinum group elements in geological samples by ICP-MS after nickel sulphide fire assay: difficulties encountered with different types of geological samples. Talanta 58, 595–603. https://doi.org/10.1016/S0039-9140(02)00330-2.

Kasuya, R., Miki, T., Morikawa, H., Tai, Y., 2014. Synthesis of sodium platinates and their dissolution behaviors in hydrochloric acid: effects of lithium carbonate addition on platinate formation. Int. J. Miner. Process. 128, 33–39. https://doi.org/10.1016/j.minpro.2014.02.005.

Keyworth, B., 1983. ROLE OF PYROMETALLURGY IN THE RECOVERY OF PRECIOUS METALS FROM SECONDARY MATERIALS. https://doi.org/10.1016/b978-0-08-025396-1.50044-0.

Kim, C.-H., Woo, S.-I., Jeon, S.H., 2000. Recovery of platinum-group metals from recycled automotive catalytic converters by carbochlorination. Ind. Eng. Chem. Res. 39, 1185–1192. https://doi.org/10.1021/ie9905355.

Lee, J.-M., 2012. Extraction of noble metal ions from aqueous solution by ionic liquids. Fluid Phase Equil. 319, 30–36. https://doi.org/10.1016/j.fluid.2012.01.033.

Liddell, K., Adams, M., 2012. Kell hydrometallurgical process for extraction of platinum group And base metals from flotation concentrates – an update presenter and corresponding author. J. South. Afr. Inst. Min. Met. 112.

Mabbett, A.N., Sanyahumbi, D., Yong, P., Macaskie, L.E., 2006. Biorecovered precious metals from industrial Wastes: single-step conversion of a mixed metal liquid waste to a bioinorganic catalyst with environmental application. Environ. Sci. Technol. 40, 1015–1021. https://doi.org/10.1021/es0509836.

Mahmoud, M.H.H., 2003. Leaching platinum-group metals in a sulfuric acid/chloride solution. JOM (J. Occup. Med.) 55, 37–40. https://doi.org/10.1007/s11837-003-0086-y.

Matsumoto, K., Yamakawa, S., Sezaki, Y., Katagiri, H., Jikei, M., 2019. Preferential precipitation and selective separation of Rh(III) from Pd(II) and Pt(IV) using 4-alkylanilines as precipitants. ACS Omega 4, 1868–1873. https://doi.org/10.1021/acsomega.8b03435.

Moschovi, A.M., Souentie, S., Yakoumis, I., Siriwardana, A., 2018. An Integrated Circular Economy Model for Decoupling Europe from Platinum Group Metals Supply Risk in the Automotive Sector. https://doi.org/10.1109/EEEIC.2018.8493824.

Mpinga, C.N., Eksteen, J.J., Aldrich, C., Dyer, L., 2015. Direct leach approaches to Platinum Group Metal (PGM) ores and concentrates: a review. Miner. Eng. 78, 93–113. https://doi.org/10.1016/j.mineng.2015.04.015.

Nguyen, V.T., Riaño, S., Aktan, E., Deferm, C., Fransaer, J., Binnemans, K., 2021. Solvometallurgical recovery of platinum group metals from spent automotive catalysts. ACS Sustain. Chem. Eng. 9, 337–350. https://doi.org/10.1021/acssuschemeng.0c07355.

Nikoloski, A., Ang, K.L., 2014. Review of the application of ion exchange resins for the recovery of platinum-group metals from hydrochloric acid solutions. Miner. Process. Extr. Metall. Rev. 35 https://doi.org/10.1080/08827508.2013.764875.

Nogueira, C.A., Paiva, A.P., Oliveira, P.C., Costa, M.C., da Costa, A.M.R., 2014. Oxidative leaching process with cupric ion in hydrochloric acid media for recovery of Pd and Rh from spent catalytic converters. J. Hazard Mater. 278, 82–90. https://doi.org/10.1016/j.jhazmat.2014.05.099.

Paiva, A.P., Ortet, O., Carvalho, G.I., Nogueira, C.A., 2017. Recovery of palladium from a spent industrial catalyst through leaching and solvent extraction. Hydrometallurgy 171, 394–401. https://doi.org/10.1016/j.hydromet.2017.06.014.

Panda, R., Kumar Jha, M., Pathak, D.D., C., 2018. Commercial processes for the extraction of platinum group metals PGMs. Springer, pp. 119–130. https://doi.org/10.1007/978-3-319-72350-1_11.

Peng, Z., Li, Z., Lin, X., Tang, H., Ye, L., Ma, Y., Rao, M., Zhang, Y., Li, G., Jiang, T., 2017. Pyrometallurgical recovery of platinum group metals from spent catalysts. JOM (J. Occup. Med.) 69. https://doi.org/10.1007/s11837-017-2450-3.

Pitroda, D.J., Memon, A.H., Patel, R., 2017. In: Design for Recovery of Precious and Base Metals from E-Waste Using Electrowinning Process, vol. 4.

Rao, S.R., 2006. Resource Recovery and Recycling from Metallurgical Wastes. Waste Management Series.

Rovira, M., 1998. Contribution to the Development of Hydrometallurgical Separation and Concentration Techniques Focused on Precious Metals Recovery. Universitat Polytecnica de Catalunya.

Rzelewska-Piekut, M., Regel-Rosocka, M., 2018. Wastes generated by automotive industry – spent automotive catalysts. Phys. Sci. Rev. 3 https://doi.org/10.1515/psr-2018-0021.

Saguru, C., Ndlovu, S., Moropeng, D., 2018. A review of recent studies into hydrometallurgical methods for recovering PGMs from used catalytic converters. Hydrometallurgy 182, 44–56. https://doi.org/10.1016/j.hydromet.2018.10.012.

Sarıoğlan, Ş., 2013. Recovery of palladium from spent activated carbon-supported palladium catalysts. Platin. Met. Rev. 57, 289–296. https://doi.org/10.1595/147106713X663988.

Sasaki, H., Maeda, M., 2014. Zn-vapor pretreatment for acid leaching of platinum group metals from automotive catalytic converters. Hydrometallurgy 147–148, 59–67. https://doi.org/10.1016/j.hydromet.2014.04.019.

Saternus, M., Fornalczyk, A., Gąsior, W., Dębski, A., Terlicka, S., 2020. Modifications and improvements to the collector metal method using an mhd pump for recovering platinum from used car catalysts. Catalysts. https://doi.org/10.3390/catal10080880.

Schuur, B., Brouwer, T., Smink, D., Sprakel, L.M.J., 2019. Green solvents for sustainable separation processes. Curr. Opin. Green Sustain. Chem. 18, 57–65. https://doi.org/10.1016/j.cogsc.2018.12.009.

Segneri, B., Deprizio, J., Reinhardt, T., 2014. Geologic provenance of rare earth elements in the United States and their potential collocation with geothermal resources. Thirty-Ninth Work. Geotherm. Reserv. Eng. 39, 24–26.

Sibrell, P., Atkinson, G.B., Walters, L.A., 1994. Cyanide Leaching Chemistry of Platinum-Group Metals. Report of Investigations/1994.

Sinisalo, P., Lundström, M., 2018. Refining approaches in the platinum group metal processing value chain—a review. Met. https://doi.org/10.3390/met8040203.

Smith, E.L., Abbott, A.P., Ryder, K.S., 2014. Deep eutectic solvents (DESs) and their applications. Chem. Rev. 114, 11060–11082. https://doi.org/10.1021/cr300162p.

Spooren, J., Abo Atia, T., 2020. Combined microwave assisted roasting and leaching to recover platinum group metals from spent automotive catalysts. Miner. Eng. 146, 106153 https://doi.org/10.1016/j.mineng.2019.106153.

Sun, P., Lee, M.-S., 2013. Recovery of platinum from chloride leaching solution of spent catalysts by solvent extraction. Mater. Trans. 54, 74–80. https://doi.org/10.2320/matertrans.M2012320.

Suoranta, T., Zugazua, O., Niemelä, M., Perämäki, P., 2015. Recovery of palladium, platinum, rhodium and ruthenium from catalyst materials using microwave-assisted leaching and cloud point extraction. Hydrometallurgy 154, 56–62. https://doi.org/10.1016/j.hydromet.2015.03.014.

Swain, B., Jeong, J., Kim, S., Lee, J., 2010. Separation of platinum and palladium from chloride solution by solvent extraction using Alamine 300. Hydrometallurgy 104, 1–7. https://doi.org/10.1016/j.hydromet.2010.03.013.

Thi Hong, N., Kumar B, N., Lee, M.-S., 2016. Selective recovery of Fe(III), Pd(II), Pt(IV), Rh(III) and Ce(III) from simulated leach liquors of spent automobile catalyst by solvent extraction and cementation. Kor. J. Chem. Eng 33 https://doi.org/10.1007/s11814-016-0123-5.

Trinh, H.B., Lee, J., Srivastava, R.R., Kim, S., Ilyas, S., 2017. Eco-threat minimization in HCl leaching of PGMs from spent automobile catalysts by formic acid prereduction. ACS Sustain. Chem. Eng. 5, 7302–7309. https://doi.org/10.1021/acssuschemeng.7b01538.

Trinh, H.B., Lee, J., Srivastava, R.R., Kim, S., 2019. Total recycling of all the components from spent auto-catalyst by NaOH roasting-assisted hydrometallurgical route. J. Hazard Mater. 379, 120772 https://doi.org/10.1016/j.jhazmat.2019.120772.

Tyson, D.R., Bautista, R.G., 1987. Leaching kinetics of platinum and palladium from spent automotive catalysts. Separ. Sci. Technol. 22, 1149–1167. https://doi.org/10.1080/01496398708069004.

K. Upadhyay, A., Lee, J., Kim, E., Kim, M., Kim, B.-S., Kumar, V., 2013. Leaching of platinum group metals (PGMs) from spent automotive catalyst using electro-generated chlorine in HCl solution. J. Chem. Technol. Biotechnol. 88 https://doi.org/10.1002/jctb.4057.

Wadsworth, M.E., Zhu, X., Thompson, J.S., Pereira, C.J., 2000. Gold dissolution and activation in cyanide solution: kinetics and mechanism. Hydrometallurgy. https://doi.org/10.1016/S0304-386X(00)00084-0.

Wei, X., Liu, C., Cao, H., Ning, P., Jin, W., Yang, Z., Wang, H., Sun, Z., 2019. Understanding the features of PGMs in spent ternary automobile catalysts for development of cleaner recovery technology. J. Clean. Prod. 239, 118031 https://doi.org/10.1016/j.jclepro.2019.118031.

Yakoumis, I., Moschovi, A.M., Giannopoulou, I., Panias, D., 2018. Real life experimental determination of platinum group metals content in automotive catalytic converters. IOP Conf. Ser. Mater. Sci. Eng. 329, 12009. https://doi.org/10.1088/1757-899X/329/1/012009.

Yakoumis, I., Moschovi, A., Panou, M., Panias, D., 2020. Single-step hydrometallurgical method for the platinum group metals leaching from commercial spent automotive catalysts. J. Sustain. Metall. 6, 259–268. https://doi.org/10.1007/s40831-020-00272-9.

Yousif, A.M., 2019. Recovery and then individual separation of platinum, palladium, and rhodium from spent car catalytic converters using hydrometallurgical technique followed by successive precipitation methods. J. Chem. 2019, 2318157 https://doi.org/10.1155/2019/2318157.

Zhang, Q., De Oliveira Vigier, K., Royer, S., Jérôme, F., 2012. Deep eutectic solvents: syntheses, properties and applications. Chem. Soc. Rev. 41, 7108–7146. https://doi.org/10.1039/C2CS35178A.

Zhao, Hai-Zhao, 1998. Analysis of Phases in Metallurgical Products of Plasma Treating PGMssecondary Resources. OECD. https://doi.org/10.1787/9789264104976-en.

Zhuang, W.-Q., Fitts, J.P., Ajo-Franklin, C.M., Maes, S., Alvarez-Cohen, L., Hennebel, T., 2015. Recovery of critical metals using biometallurgy. Curr. Opin. Biotechnol. 33, 327–335. https://doi.org/10.1016/j.copbio.2015.03.019.