

Recovery of noble metals from spent catalysts: a review

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Abstract

During several past decades, plenty of technologies for platinum group metals (PGM) and rhenium (Re) recovery from electronic wastes and spent catalysts have been developed and published. The reasons for the rising interest in this area are:

- The abundance of these elements in the earth's crust is less than 10^{-3} ppm (~6.6 10^4 t all over the world);
- global demand for PGMs is over 590 t;
- electronics and catalysts industry consumes over 90% of precious metals (about 65% of Pd, 45% of Pt and 84% of Rh are consumed in catalytic converters);
- properties of PGMs and Re (resistance towards corrosion and oxidation, high melting temperatures, electrical conductivity, and catalytic activity) are of great commercial interest.

Even though several comprehensive reviews on the recovery of precious metals from spent catalysts have been recently published, several developments were out of the attention of the scientific community. The reviews divide the technologies into hydro- and pyrometallurgical ones. However, the variety of different approaches requires a more detailed classification. This article is an overview of the recently reported works and the comparison of different technologies in terms of extraction efficiency, environmental friendliness, and capital and operational expenditures. The new electrochemical method, which is now under development, is also presented.

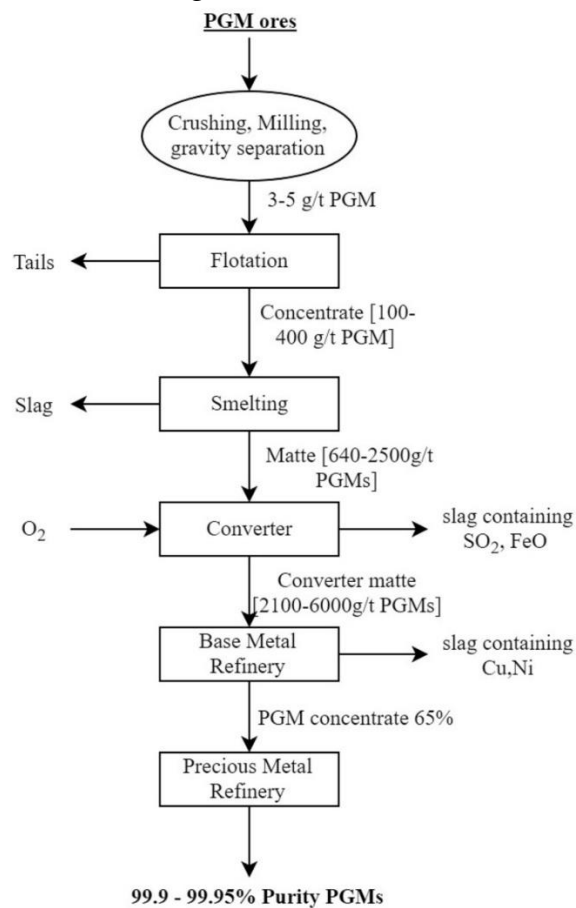
Keywords: spent catalysts processing, platinum group metals, hydrometallurgical process, pyrometallurgical process, electrochemical process, magnetic separation

1. Introduction

Platinum group metals incorporate six noble metals namely, platinum (Pt), palladium (Pd), iridium (Ir), osmium (Os), rhodium (Rh), and ruthenium (Ru). All the metals from this group possess more or less identical physical and chemical properties. PGMs are chemically inert, highly resistant against corrosion, electrically and thermally stable, shows high mechanical strength [1–3]. The properties possessed by them are highly desirable and over 90% of overall PGMs are used by electrical and catalyst industries. PGMs are limited natural resources with only 66000 tons available across the earth. Only 2–10 g/t of PGM content is present in its natural ores. The recovery of the PGM as a co-product or a by-product depends upon their percentage in the ore. Recent advancements in the technologies for the extraction and recovery of PGM have

51 enhanced its application in the chemical industry, oil refining, medical practices, vehicle and
 52 equipment construction, jewelry making, etc. [4, 5].

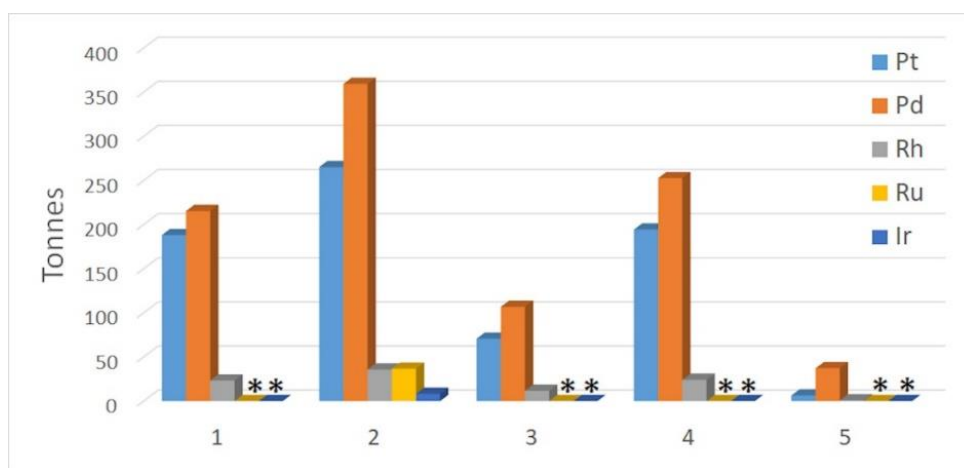
53 Production of 73% of primary PGMs in the world is associated with the Bushveld
 54 Complex of South Africa, while the rest of the PGMs reserves are mainly concentrated in Russia,
 55 Zimbabwe, the United States, and Canada [6]. The PGM ores are mainly in the form of sulfide
 56 and arsenide materials like $PtAs_2$, $Pt(AsS)_2$, PtS , $(Pt, Pd)S$, $(Pt, Pd, Ni)S$, Pd_3Sb and RuS_2 along
 57 with elemental ruthenium [7]. Fernandez [8] presented comprehensive data related to the
 58 amounts of PGMs in different forms. PGMs are recovered from the high-grade concentration
 59 ores (200 to 2000 g/t of PGM and 0.3 to 2.5% Cr_2O_3) by matte-smelting-refining technique.
 60 Initially, the PGM ores are crushed and ball-milled to make them fine particles. This ore in the
 61 form of particles is treated in the gravity separators and transferred to the flotation cells to
 62 produce a sulfide-rich PGM concentrate, where reagents like dithiophosphate and xanthate
 63 collectors are used for flotation process at pH of 7.5 to 9 [9]. Smelting is performed on the
 64 sulfide-rich PGM concentrates to remove feldspar, plagioclase, pyroxene, and biotite gangue
 65 materials. The matte is treated in converters where the slag containing SO_2 , FeO is removed. The
 66 converter matte is transferred to a base metal refinery where Cu, Ni, and other metals are
 67 removed. The PGM concentrate with more than 65% PGM is refined in precious metal refinery
 68 and high-quality PGMs are recovered (see figure 1).



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 70

Figure 1. PFD of the PGM extraction from ores

71 The demand for PGMs is increasing due to its various applications in the industries.
 72 Figure 2 shows the demand and recycling of PGM for the year 2019. The demand for Pt, Pd, and
 73 Rh is around 660.305 tons but the recycling only provides 189.02 tons. This shows that the
 74 future acquirement of these metals would highly depend on the recycling of the secondary source
 75 due to its lack of availability as a natural resource. Concentrations of PGMs are higher in spent
 76 catalysts than in ore deposits. For example, an automotive catalytic converter contains about
 77 2000 g/t of PGMs in a ceramic block while an average PGMs concentration is less than 10 g/t in
 78 most of PGM ores [10].



79

80 **Figure 2.** The total supply and demand for PGMs in 2019 (in tons) [11]. 1– Total supply, 2– Gross
 81 demand, 3– Total recycling, 4– Total net demand, 5–Movements in stocks. **Note:** *– No available data

82 Spent catalyst is one of the sources for the PGM recovery. The catalyst used in the
 83 refining and petrochemical industries constitutes of Al₂O₃-based carrier with 0.05 – 1% of noble
 84 metals (PGM and rhenium) as the active components. The catalyst loses its catalytic properties
 85 after a certain time (3 to 5 years), technology to regenerate and reactivate the metal fouled
 86 catalyst is not available at present and are discarded as the solid wastes [12,13]. The spent
 87 refinery catalyst amounts only 4% of the total refinery wastes but still is considered to be the
 88 most hazardous waste generated in the petroleum industry [14, 15].

89 The catalyst industry heavily depends on PGMs, which act as active components. The oil-
 90 refining, automobile emission purification, chemical engineering industries are the main
 91 consumers of PGMs in the form of the catalyst [16]. Immense research has been conducted by
 92 researchers to replace the PGMs with fewer abandon materials but no significant results were
 93 attained. About 45% of platinum (99.82 tons), 65% of palladium (186.5 tons) and 84% of
 94 rhodium (24.07 tons) were used in catalytic converters in the year 2018. The recycling of PGMs
 95 from the spent catalyst is difficult as it is used for different purposes and varying proportions of
 96 PGMs from 200 ppm to 100% in an entire catalyst material. Table 1 elaborates on the
 97 information of catalysts used in automobiles and chemical industries.

98

99 **Table 1.** PGMs used for applications in industries [17].

Application areas	Application	Catalyst type support	PGMs	PGMs loading/ %	Life span (year)
Fine chemicals	Hydrogenation Oxidation Debenzylation	Activated carbon	Pd; Pd/Pt Rh; Ir	0.5–10	0.1–0.5
Automotive	Catalysts Diesel particulate filter	Cordierite monolith ceramic pellets Metallic monolith SiC or cordierite	Pt/Rh Pt–Pd– Rh Pt	0.1–0.5	>10
Oil-refining	Reforming Isomerization Hydrocracking Gas to liquid	Al ₂ O ₃ Al ₂ O ₃ , zeolites SiO ₂ , zeolites Al ₂ O ₃ , SiO ₂ , TiO ₂	Pt/Pd Pt; Pt/Re, Pt/Ir Pt; Pt/Pd Pd; Pt Co+(Pt; Pd; Ru; Re)	0.02–1	1–12
Chemical engineering	Nitric acid H ₂ O ₂ PTA* HCN* VAM* KAAP*	Gauzes Powder (black) Carbon granules Al ₂ O ₃ or gauzes Al ₂ O ₃ , SiO ₂ Activated carbon	Pd Pd Pd Pt; Pt/Rh Pd/Au Ru	100 100 0.5 0.1; 100 1–2	0.5 1 0.5–1 0.2–1 4
Homogeneous	Oxo Alcohols Acetic acid	Homogeneous	Rh Rh; Ir/Ru	100–500 ppm in the process solution	1–5

100 **Note***: PTA - Purified terephthalic acid, HCN - Hydrogen cyanide, VAM - Vinyl Acetate Monomer, KAAP - KBR
101 Advanced Ammonia Process.

102

103 Effective recovery of PGMs and extraction from spent catalysts are environmentally and
104 economically desirable. Three factors are influencing the recyclability of spent catalysts: (1) the
105 composition of the spent catalyst, (2) the intrinsic metal value, and (3) the associated lifecycle
106 structure and the application segment, including the turnaround speed (catalyst life), recycling
107 chain and business model.

108 In this paper, the methods implemented to recover the PGMs from the spent catalyst are
109 discussed. The advantages and disadvantages associated with the various recycling methods will
110 be mentioned. This topic is particularly important, as in the future the industries will be relying
111 on recycling processes to obtain PGMs. Recycling should be efficient and environmentally
112 friendly. The recovery of PGMs from the spent catalyst is important because of:

113 □ simple catalyst composition with carriers being Al₂O₃, activated carbon, cordierite, and so
114 on;

115 □ high PGM proportion of about several kilograms per ton.

116 Therefore, the recovery of PGMs from the spent catalysts should be economically
117 advantageous, small scale, simple, and environmentally friendly process. Techniques like non-
118 cyanide leaching, smelting in the furnace, mild leaching, and physical separation pre-treatment
119 cause less pollution and have been developed in the last two decades. Nevertheless, even with
120 many advantages, they show negative effects on the environment and recovery process [18, 19].

121

122 **2. Techniques used for the PGMs recovery from spent catalysts**

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124 The supply of spent catalysts to the recycling process is a crucial step as it is a decisive factor
125 in the recovery of the PGMs. The spent catalyst should undergo (1) dismantling, (2) size
126 reduction, and (3) physical separation before the start of the main process [20]. The selection of
127 the recycling technique mainly depends on three factors: (1) type of catalyst's supporter, (2)
128 PGM (loading) content, and (3) presence of other base metals. Finally, recycling of spent catalyst
129 to extract PGMs can be distinguished into five basic steps: sampling/homogenization, pre-
130 concentration, dissolution, enrichment, and purification. Several recovery techniques have been
131 introduced for the past 20 years and few of them are already employed at the industrial level [21,
132 22]. The below techniques are a few of them, which will be discussed briefly.

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134 **2.1. Hydrometallurgy**

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136 In the hydrometallurgical process, the spent catalysts are dissolved in the aqua regia,
137 cyanide, or strong acids like HNO₃, HCl, and H₂SO₄. The leaching efficiency is enhanced by
138 adding oxidizing agents like O₂, H₂O₂, Cl₂, and I₂. Before the leaching process, the PGMs should
139 be reduced to the metallic state as they turn into the inert state due to the sulfuration or oxidation.
140 In this process, Pd is leached easily while Rh cannot be leached for more than 90%. Cyanide
141 leaching is a more efficient recovery process but as this method is performed at high
142 temperatures, cyanide is highly toxic.

143

144 **2.1.1. Hydrochloric acid + oxidant system leaching**

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146 In this process, PGMs are leached in HCl medium with oxidizing agents such as Cl₂,
147 H₂O₂, HNO₃, and NaClO₃, etc. [23–25]. The PGMs form the soluble chloro-complexes when
148 reacted with HCL and the oxidizing agent, according to the following reactions:

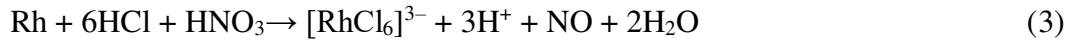
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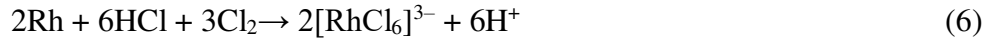
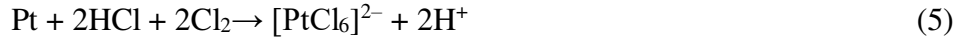
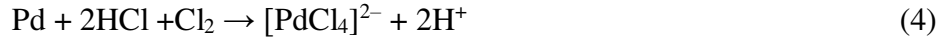
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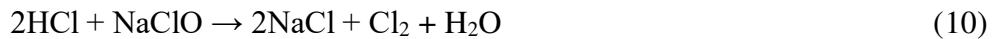
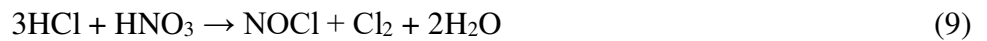
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The above reactions (1) – (3) show the formation of the complex PGM ions when HNO₃ oxidizing agent is used and similar ions are obtained when Cl₂ is used as an oxidizing agent and can be seen from the reactions [26]:



Decomposition of Hydrochloric acid when oxidizing agents are added occurs according to the reactions (7)–(10). Obtained Cl₂ react with the PGMs, leading to the formation of soluble PGM chloro-complexes and reduces the processing time.

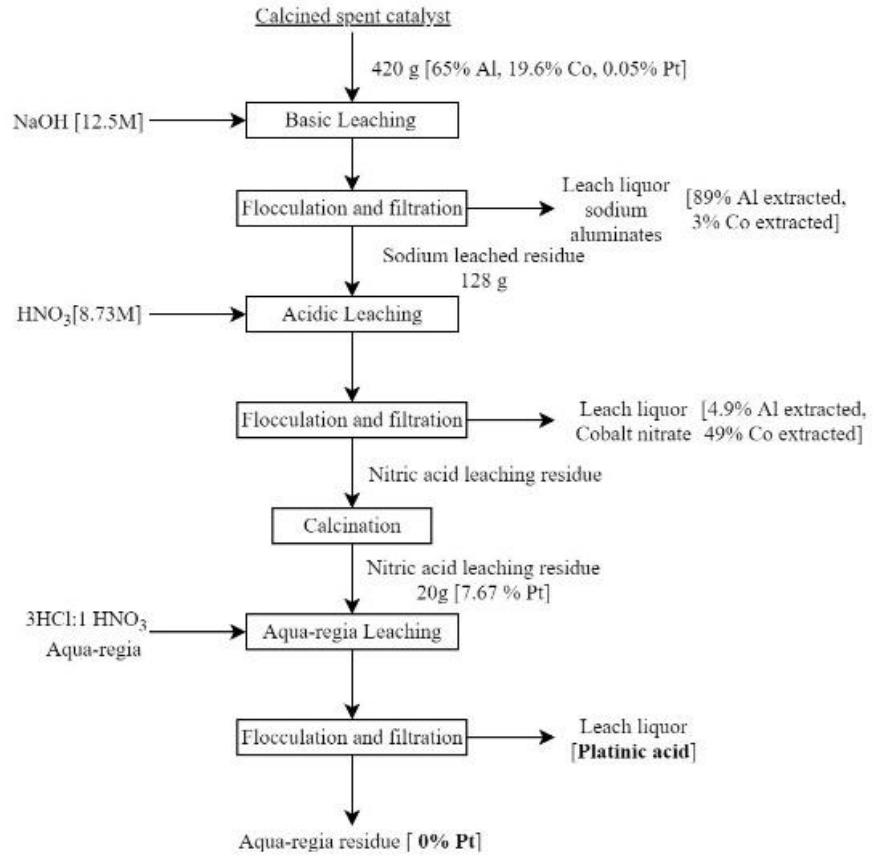


The extraction of PGMs highly depends upon its dissolution and the formation of chloride complexes, which are stable at pH < 1, whereas at high pH values, the chloride complexes are hydrolyzed forming hydroxy complexes [27]. To avoid slow leaching the pre-treatment should be performed on the PGMs as their surface is covered with many organic substances. Processes such as pre-leaching, reduction roasting, and oxidation roasting are suggested [28].

Shams et al. [29] conducted a study where 280 g of spent dehydrogenation catalyst was decoked at 400–450 °C and then crushed to a particular size required. Leaching of the particles was then made with a mixture of 3850 gm of concentrated hydrochloric acid (5 mol. L⁻¹) and nitric acid (HNO₃ – 0.2 vol.%) solution which is used as a leaching agent in a 5000 cc container. The recovery process is followed by the ion exchange of the metallic complexes with the help of strong base ion exchange resin (AMBERTJET 4200 Cl, industrial grade). The replacement of chloride anion by hydroxyl group ion to treat the strong basic anionic resin by using a sodium hydroxide solution. It was observed that the PGM recovery increased with the increase of HCl concentration in the solution. At 9 mol.L⁻¹ HCl concentration, the results were excellent. This process is temperature-sensitive with the best extraction obtained at 100 °C. This states that the recovery of PGMs from spent catalyst while using HCl requires less leaching severity reactions. The process is also not time-efficient (slow) as studies show that after 24 hours of leaching, no further recovery of PGMs was possible. Angelidis et al. [30] developed a laboratory-scale hydrometallurgical process for the recovery of Pt and Rh from the spent catalyst. The process constitutes oxidation leaching (NaClO, HCL, and AlCl₃), reduction leaching (H₂SO₄ and N₂H₆SO₄) and final leaching with HCl followed by the neutralization of the metal. About 94% of Pt and 89% of Rh were recovered. Similar results were obtained in a process where CeO₂ was used as an additive to increase the recovery rate of the PGMs, although while separating the PGMs from the residue, a significant amount of Ce was leached along with the PGMs [31].

Matjie et al. [32] reported that the spent catalyst was first calcined at around 800 °C to remove the wax present in it to heighten the extraction efficiency during the leaching process.

205 The calcined spent catalyst containing 7.67 % of Pt was then dissolved in 1000 ml aqua regia
 206 (3HCl:1HNO₃) at 90 °C for 240 mins at atmospheric pressure to attain chloroplatinic acid
 207 species. Then filtration is carried out to separate the metal from the insoluble aqua regia residue.
 208 The XRD was performed on aqua regia residue to find the Pt content and only traces of Pt were
 209 seen, stating that almost all the Pt present in the calcined catalyst was dissolved (see figure 3).
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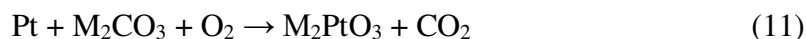


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Figure 3. PFD of aqua-regia leaching process [32]

213 The HCl leaching was performed on spent activated carbon-supported Pd catalyst with
214 hydrogen peroxide as a leaching agent for the Pd recovery. The leaching process was carried out
215 for 90 mins at 90 °C. A maximum leaching rate of 99% was attained for Pd when the solution
216 mixture contained 10 vol. % HCl and 5 vol. % H₂O₂. The increase in temperature and time
217 improved leaching efficiency. The optimum conditions to recover Pd were when the solution
218 with 10 vol. % HCl and 5 vol. % H₂O₂ was used at 90 °C for 180 mins [33]. Paiva et al. [34]
219 investigated the hydrometallurgical process to extract Pd from the spent alumina catalyst, where
220 the HCl solution is used for the leaching. The main task of this investigation was to achieve a
221 promising recovery of Pd with minimal Al contamination. H₂O₂ was used as an oxidizing agent,
222 which improved the Pd leaching in HCl to above 90%, the ideal conditions were being (2.0 mol.
223 L⁻¹) HCl, (1.0 mol. L⁻¹) H₂O₂ at 25 °C and reaction time is 10 – 15 mins. The Al contamination
224 can be decreased by reducing the acidity, a mixture of HCl, H₂O₂, and additives like NH₄Cl or
225 MgCl₂ were tested and high Pd leaching was obtained for long periods (30 – 60 mins) with low
226 Al contamination.

227 Kasuya et al. [35] introduced a novel method for the recovery of the Pt, where the PGMs
228 are dissolved in the HCl using complex oxides. Platinates were produced by calcining the
229 mixture of Pt/Al₂O₃ and alkali metal salts. The formation reaction of platinates includes O₂ and
230 CO₂ (equation 11, where M = Li & Na). At 600 °C, Pt is converted into Li₂PtO₃ when reacted
231 with Li₂CO₃. This promotes the fact that alkali metal salts enhance the oxidation of Pt.



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235 The platinates obtained are leached in HCl (12 mol. L⁻¹) at 180 °C for 120 mins, the
236 solubility of Pt was nearly 100% with proper dissolution conditions. The PGMs recovery
237 through the leaching process from the spent catalyst is adopted widely due to its simple
238 technique. The disadvantage with the process is the low recovery of PGMs, especially rhodium,
239 also it is a difficult process to extract PGMs from low grade spent catalysts.

240 A microwave (MW) assisted PGMs extraction process was performed by Spooren and
241 Atia [36]. The spent catalyst of about 1 g was initially milled and mixed with the sulfate salt (7.5
242 g NaHSO₄·H₂O, 8.37 g KHSO₄ or 0.5 g H₂SO₄ solution) and oxidation agent (2.5 g NaClO₃, 5
243 ml NaOCl or 5 ml H₂O₂). They were well mixed by pestle and mortar, transferred to the ceramic
244 crucible and MW roasted at 750 W for 30 mins. The roasted mixture was leached using 100 ml
245 of de-ionized water for 30 mins at 60 °C. The slurry was cooled at room temperature and the
246 solid residue was separated and dried at 105 °C. The remaining leachate was analyzed to
247 determine the presence of PGMs (see figure 4).

248 It was observed that the leachability rate of PGMs while using 1M HCl instead of de-
249 ionized significantly improved. The ideal parameters suggested for the recovery of the PGMs
250 after the studies were as follows:

- 251 □ the salt: spent catalyst ratio of 5
- 252 □ NaClO₃: NaHSO₄·H₂O molar ratio of 0.05
- 253 □ the liquid to a salt ratio of 10 and HCl = 1 M,

254 At the above conditions the leachabilities for Pd, Pt, and Rh of 96 ± 1%, 85 ± 5%, and
255 >96% were achieved respectively. The concentration of Pd, Pt, and Rh in the solid residue of
256 0.34 g were measured to be 97 ± 18 mg/kg, 207 ± 66 mg/kg and <20 mg/kg, respectively. It can
257 be highlighted that when leaching the mixture without NaClO₃, the leaching efficiency for Pd
258 and Rh was low, and it was 0% for Pt. Although using KHSO₄ salt resulted in a slightly higher
259 leachability rate of Pt, using NaHSO₄ was considered economically friendly.

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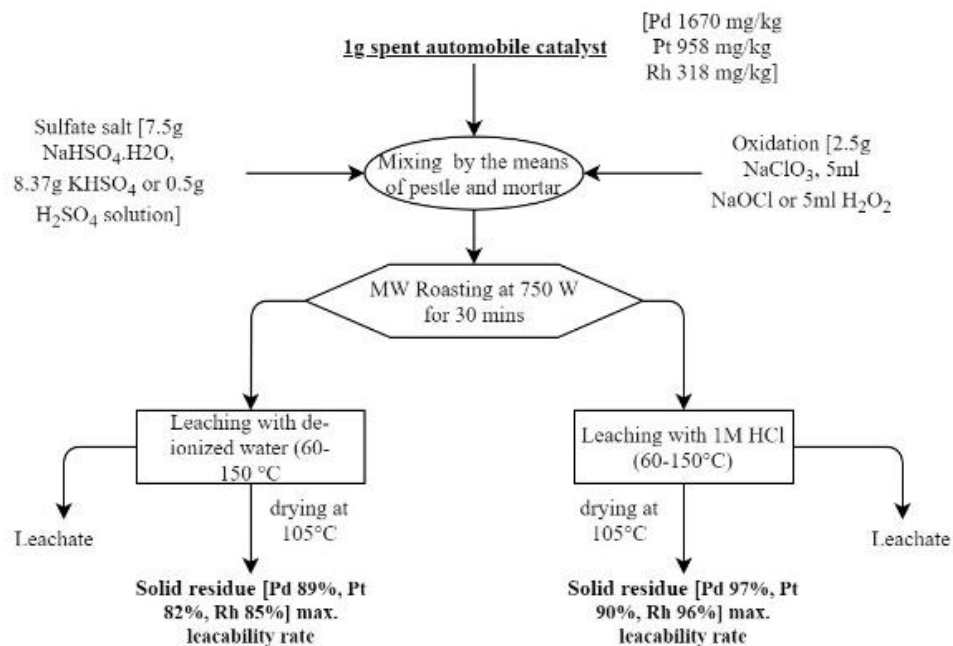


Figure 4. PFD of microwave-assisted extraction process [36]

In [37, 38], novel Phosphonium ($P_{8,8,8,12}Cl$)-based ionic liquid was used to separate the PGMs from the automobile leach liquor. Initially, 570 g of the spent catalyst was mechanically crushed followed by ball milling for 30 to 300 mins until the particle size of 75 μm is attained. The leaching process was performed using HCl with 5 mol. L^{-1} concentration for 2 days at 70 $^{\circ}C$. The $P_{8,8,8,12}Cl$ was added to the leachate and centrifuged at 8000 rpm for 5 min. The Pd was extracted (reaction 12) within 5 mins while the extraction of Rh from the raffinate to $P_{8,8,8,12}Cl$ is performed after the removal of Pd and Pt. The process is highly efficient in the extraction of PGMs. Scrubbing of Fe is performed using 1.2M Na_2SO_3 while the PGMs stripping (back extraction) from the complex ion is performed by the required solutions accordingly (see figure 5).

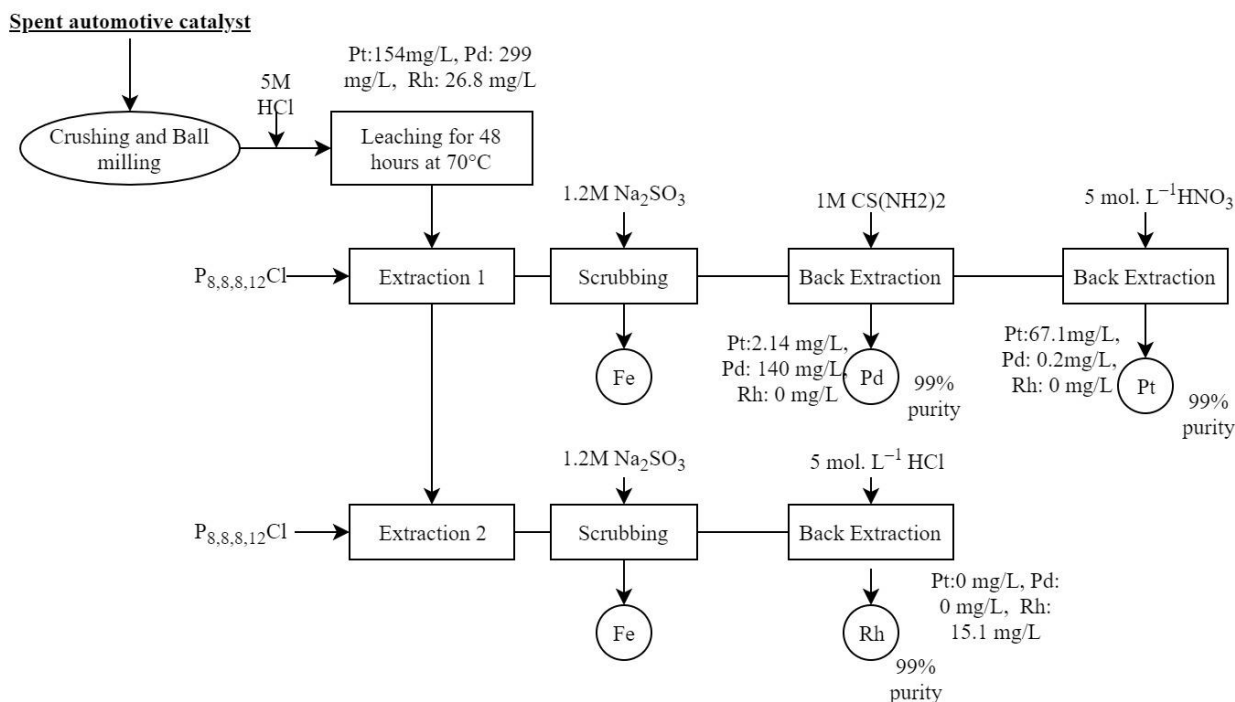
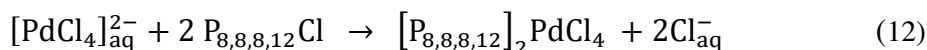
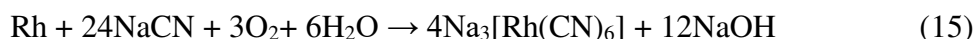
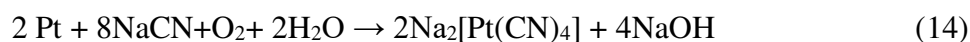
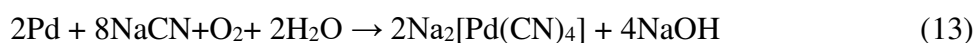


Figure 5. PFD of novel separation method [37, 38]

2.1.2. Cyanide solution leaching

Industries have desired to recover PGMs by using cyanide-leaching technology for decades [39–41]. The following equations are the dissolution reactions occurring while using cyanide solution:



The decomposition of cyanide occurring while reacting with the oxidizing agent is as follows:



Shams et al. [42] reported a process where the spent catalyst was first crushed into small particles while its size was determined by a mesh size sieved to find the dependency of the particle size with the recovery of PGMs. The spent catalysts are leached with 1 wt.% of NaCN at 160 – 180 °C at a pressure between 618 and 1002 kPa for an hour. The weight ratio between the sodium cyanide solution and the spent catalyst is 2:1. To prevent sintering, the spent catalyst was decoked at a temperature range of 450–480 °C. Pt in the form of anion $\text{Pt}[\text{CN}]_4^{2-}$ is replaced by anion Cl^- in an ion exchange reaction with the resultant being $\text{N}^+(\text{CH}_3)_3)_2 \text{Pt}[\text{CN}]_4^{2-}$ (Styrene divinylbenzene copolymer) formation. It was observed that the decoking of the coked catalyst is not required at high-temperature cyanide leaching. With the decrease in the particle size of the catalyst, the Pt recovery increases. At 2:1 weight ratio of NaCN and catalyst and temperature between 140 and 180 °C, optimum results were attained.

Chen et al. [41] investigated the recovery of PGMs from spent catalyst with NaCN leaching. The recovery of Pt is 96%, Pd is 98% and Rh is 92% with an oxygen pressure of 1.5 MPa, NaCN 0.1275 mol. L⁻¹, NaCN to catalyst ratio of 4:1 at around 160 °C. The cyanide leaching order was Pt > Pd > Rh, due to the complex ions metal bonding strength. The cyanide leaching process is highly toxic at high temperatures and still difficult to be implemented at the industrial level. The optimization of the method is still highly considered.

2.1.3. Bioleaching

In bioleaching, the microorganisms with their metabolites are used to extract metals from the spent catalyst. This process is eco-friendly and cost-efficient when compared to other leaching techniques [43]. The bioleaching method can be in two ways, direct (one or two-step process) or an indirect two-step process. In the one-step process (direct), fermentation and leaching take place at the same time, which means that the metal leaching and microorganism cultivation happen at the same time. In the two-step (direct) process, the cultivation takes place before the leaching even though both the processes takes place in the same container. In an indirect process, the leaching process takes place in the spent medium (microorganism free medium obtain through fermentation) [44,45].

Malekian et al. [46] conducted an experiment for the Pt recovery through bioleaching, (Aspergillus niger produced oxalic acid solution) was investigated, where direct (one-step, two-step) and indirect (spent medium bioleaching with and without pH control) process were performed. It was observed that the production of oxalic acid and Pt recovery were higher with the pH-controlled process. The optimal conditions were: 0.5 pH, 1 wt. % of pulp and bioleaching

330 temperature of 70 °C, which resulted in 37% recovery of Pt. By replacing HNO₃ with HCl, the
331 pH value was adjusted resulting in the increase of Pt recovery to 41%. The bioleaching process is
332 extensively used at industrial scale to recover metals like Ni, V, and Mo but is still under study
333 for the PGMs recovery. The recovery of the PGMs by using bioleaching is low when compared
334 with the conventional methods, but still the former is environmentally friendly, energy-efficient
335 while the latter is hazardous, and energy-consuming process. Improvements can be made to
336 increase the PGM recovery percentage by optimizing the process accordingly.

337 338 **2.1.4. Supercritical fluids oxidation**

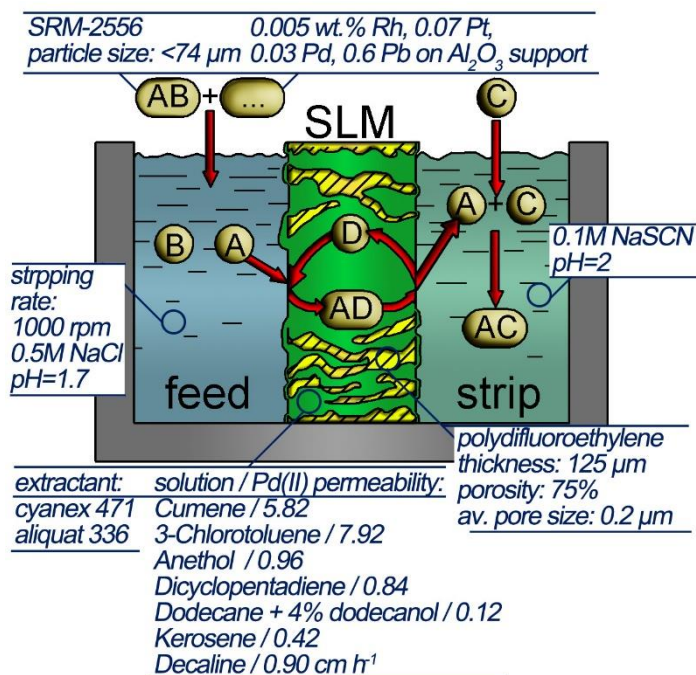
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340 The use of supercritical fluids (SF) is an alternative method of PGMs extraction, which is
341 eco-friendly, low energy, easy recycling, good sensitivity and facile. SFs are used for different
342 types of reactions as unique solvents [47]. It is known that creating an SF is simple: by moving
343 the substance beyond its critical point (critical temperature, critical pressure) with increasing the
344 temperature and pressure, supercritical fluids are obtained. Due to its relatively low critical
345 temperature and pressure ($T_c = 31.1^\circ\text{C}$, $P_c = 7.38\text{ MPa}$), CO₂ is considered as the best substance
346 to make supercritical fluid. CO₂ is low in cost, reactivity, and toxicity and also widely available.
347 Supercritical CO₂ can be used to extract nonpolar and slightly polar substances such as
348 aldehydes, alkanes, terpenes, esters and alcohols [48].

349 By using the modifiers (polar: acetone, methanol & nonpolar: propane, octane), the
350 solubility of polar and nonpolar solids in SF CO₂ can be enhanced. In the SF solution, low
351 concentrations (5 vol. %) of modifiers are added. As SF CO₂ possesses low polarizability, the
352 addition of modifiers improves this property and the same was stated in the papers [49,50].
353 Faisal et al. [51] conducted an experiment to determine the extraction of PGMs using the
354 supercritical CO₂ in combination with tributyl phosphate, no extraction of PGMs was observed.
355 HNO₃ ligand was introduced into the system and above 96% of Pd extraction was attained. It is
356 also stated that the present process is not suitable for the recovery of Pt and Rh (as less than 3%
357 of these metals are recovered). The optimal conditions for the extraction process are when it is
358 performed at 60 °C, 20 MPa for 60 min of static extraction time. Supercritical water was used for
359 the recovery of PGMs from the homogeneous precious metal catalysts by Collard et al. [52]. At
360 500 to 600 °C with 30 MPa and oxygen injection (0–15%), over 95% of leaching rates for Pt, Pd
361 and Rh from organic catalyst was attained. The process has been effective but limited to only
362 certain types of catalysts.

363 364 **2.1.5. Supported liquid membranes**

365
366 The possibility of utilizing thin layers of organic solutions (supported liquid membranes,
367 **SLM**), immobilized on microporous inert supports interposed between two aqueous solutions
368 (**feed** and **strip**), for removing selectively metal ions (**A**) from a mixture (**AB+...**) was first
369 proposed more than 55 years ago [53]. The schematic representation of the process is shown in
370 Figure 6. In some processes, the addition (**C**) is added to the strip to form the insoluble
371 compound (**AC**).

372 The general problems of using this technique are connected with the membrane
373 instability due to the pressure difference, the carrier and membrane dissolution, the presence of
374 osmotic pressure, and other issues described in [54]. Since it was first proposed, supported liquid
375 membrane technology has been used for the separation of a wide range of metals ions [55].
376



377
378 **Figure 6.** Schematic representation of supported liquid membrane [55, 56]

379 Fontas et al. [56, 57] described the new system combining two hollow-fiber-supported
380 liquid membranes for the separation and concentration of platinum, palladium, and rhodium
381 from spent automotive catalytic converters. Selective separation of these metals was achieved
382 when the feed solution (to which a small amount of thiocyanate had been added) was first
383 introduced into the HFLM system containing Cyanex 471 (triisobutylphosphine sulfide) as the
384 extractant and then passed through the second liquid membrane system consisting of Aliquat 336
385 (Tricaprylmethylammonium chloride) as the carrier. Only an insignificant amount of aluminum
386 was co-transported. In the later work [57], palladium separation and concentration was achieved
387 in a single step when using the liquid membrane system in hollow fiber geometry. Its efficiency
388 has been demonstrated working with real solutions of PGMs obtained from the leaching of
389 automotive catalysts, where palladium has efficiently been separated and concentrated, while no
390 platinum extraction was observed. More developments of supported liquid membranes technique
391 are described elsewhere [58].

392 393 2.2. Pyrometallurgy

394
395 In the pyrometallurgical process, the spent catalyst is transformed physically and
396 chemically by performing a thermal treatment. Calcination, chlorination, and PGM smelting
397 collection are considered as the three kinds of pyrometallurgical technologies [59, 60]. These
398 technologies can be performed at a higher rate compared to the hydrometallurgical processes, as
399 in the latter case there is no geometrical significance for the scrap materials used in the
400 extraction of PGMs. In this process, a high amount of energy is consumed and leads to the
401 emission of SO₂, which is an environmental hazard [61].

402 403 2.2.1. Sintering process

404
405 The sintering process was performed by Bronshtein et al. [62] to extract the PGMs with
406 high efficiency by mixing the spent catalyst with the metal chloride salts including (for Pd
407 extraction)/ excluding (for Pt extraction) fumed silica powder. Two procedures were followed: in
408 procedure #1, CaCl₂ was mixed with the crushed catalyst materials under dry conditions and in
409 procedure #2, the spent catalyst was immersed in the aqueous calcium chloride solution followed
410 by drying. An optimal chloride salt to catalyst ratio was 6.7:2.5 for procedure #2. During the

411 experiment, continuous airflow was provided into the reactor. In procedure #1, the sintering
412 process was performed for 120 mins and Pt extraction efficiency did not exceed $63 \pm 3\%$ for the
413 temperatures between 500 to 1000 °C. The calcium hypochlorite addition (20% w.r.t. catalyst
414 wt.%) to the dry mixture improved the extraction efficiency to $74 \pm 4\%$. In procedure #2, the
415 extraction efficiency of Pt was up to $80 \pm 4\%$, the addition of ammonium chloride and sodium
416 chloride salts as a supplement to the mixture to enhance the Pt extraction did not show any
417 positive effect. At 1100 °C, Pt was 100% extracted from the catalyst mixture using the procedure
418 #2.

419 The Pd extraction by using procedures #1 and #2 was poor ($< 3\%$), fumed silica paste
420 was used as an additive and a significant improvement in the extraction efficiency was observed
421 ($76 \pm 4\%$) when sintered between 1000 to 1100 °C. The addition of silica paste leads to a
422 significant negative Gibbs energy for the reaction to form CaSiO_3 from CaO and SiO_2 (equation
423 18) ($\Delta G^0 = -220 \text{ KJ/mol}$ at $T = 1100 \text{ °C}$) and without the silica paste addition, the $\Delta G^0 = -45$
424 KJ/mol .



426
427
428 The primary advantage of the process is that it does not use strong acids or bases, no
429 corrosive gases, and no hazardous chemicals. It produces nontoxic silicate waste as a by-product,
430 which is minimal.

431 **2.2.2. Chlorination process**

432
433
434 In this process, the PGMs from the spent catalysts are transformed into their respective
435 chlorides at high temperatures [63]. The PGMs are then separated based on the difference
436 between the metal chlorides or by adsorption on an activated carbon bed or by repulp washing
437 [40]. Murray et al. [64] in his patent mentioned that the PGMs in the spent catalyst are converted
438 into chlorides in a chlorine gas/fluid field at 600 to 1200 °C. The separation is then carried out by
439 absorption of PGM chlorides by ammonium chloride liquor or water. The recovery of Pd, Pt, and
440 Rh were up to 80–90%, 80–90%, and 85–90% respectively.

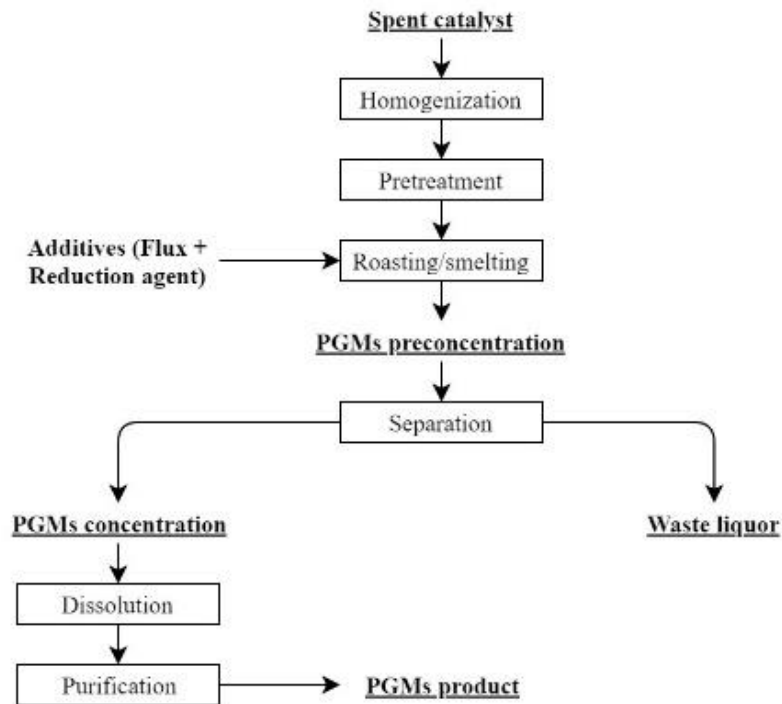
441 Horike et al. [65] proposed a chlorination process for an efficient Pt recovery. CuCl_2 was
442 used as a chlorine solution for the chlorination of Pt at 400 to 600 °C. Due to high chemical
443 stability, pure Pt was insoluble in HCl (aq), scrap containing Pt was then alloyed with Mg and
444 physically mixed with CuCl_2 at 500 °C and then dissolved in HCl (aq). The solubility of Pt in the
445 HCl (aq) improved after the chlorination process. The recovery of Pt through this process can be
446 environmentally friendly.

447 Xu et al. [66] proposed a method where the spent catalyst was pre-treated by crushing,
448 roasting, and reducing. Then NaCl was added to it to perform chlorination at 600–700 °C. The
449 mixture was then dealt with by the hot water and steam, resulting in PGM chloride salt solution.
450 The recovery of Pd, Pt, and Rh was up to 90%. This process is not adaptable to the industrial
451 scale as it results in the emission of toxic gases, high equipment requirement, and is performed at
452 high temperatures.

453 **2.2.3. Metal smelting collection**

454
455
456 In this process, the spent catalysts are mixed with flux, collector and reducing agent and
457 then smelted in a high-temperature electric arc or plasma furnace or induction furnaces at around
458 1000 °C (Figure 7). PGMs are converted into easily treatable complex ions and later refined to
459 recover the PGMs. The pre-treatment processes such as the dismantling of non-metallic
460 components, calcination or reduction are performed before the smelting, which is done at high
461 temperatures with the addition of collectors (with high specific gravity) such as lead, iron,
462 copper. The PGMs form an alloy with the collectors; at the same time catalysts, carriers are

463 melted in the presence of flux to form a slug with the low viscosity. Then the separation
 464 procedure is performed where the PGM enriched alloy is separated from the slag and the
 465 purification process is done. High recovery rates of PGM are expected from this process [67].



466
 467

Figure 7. Flowsheet illustrating the PGMs recovery by the pyrometallurgical process

468 The lead collection is the oldest method used to recover PGMs from the spent catalyst
 469 [68]. In this process, the spent catalyst is crushed and then added to a mixture containing PbO,
 470 anhydrous borax, sodium carbonate, and potassium bitartrate, which is then smelted for 2h at
 471 1100 °C. The PbO is reduced to Pb, forming an alloy with the PGMs while SO₂ from the catalyst
 472 is oxidized to form a slag namely borosilicate, which floats on top of the molten lead layer. The
 473 borosilicate slag is removed and molten Pb containing PGMs is left for purification. This process
 474 is easy to operate and Pt recovery is highly efficient but also has disadvantages: the Rh recovery
 475 being less than 80% and the emission of toxic PbO gas.

476 The copper collection process is recommended for the spent catalyst containing cordierite
 477 carriers [69–71]. The copper collectors are CuCO₃, CuO, or Cu with the flux being SiO₂, CaO,
 478 and the reducing agent is usually powder coke. The collector, the flux, the reducing agent and the
 479 spent catalyst mixture is placed in an induction furnace and smelted at 1400 °C. PGMs are
 480 collected at low temperature under ambient atmosphere. The ceramic carriers of the PGMs form
 481 a slag on the top of the molten copper, which can be poured out easily. The PGM contained
 482 copper is cast into anodes and electrolysis is performed. A slime containing 25% of PGMs is
 483 obtained after the electrolysis, 99% of PGMs can be recovered overall through this process.

484 Using iron as a collector is economically beneficial. Fe shows a strong chemical affinity
 485 towards the PGMs [72]. The crushed spent catalyst mixed with the flux (CaO), Fe powder, and
 486 reducing agent (powder coke) is smelted in a plasma arc furnace at 1500 – 2000 °C. The PGM
 487 enriched Fe alloy and the carrier slag can be easily separated because of their large densities
 488 differences (density ratio = 2:1). The recovery rates of Pd, Pt, and Rh were over 98%, 98%, and
 489 97%, respectively [73].

490 The matte collection is a relatively new method used for the recovery of PGM from spent
 491 catalyst [74, 75]. When the spent catalyst is smelted, a matte type substance is formed, which
 492 acts as a collector of PGMs. PGMs enriched matte is obtained at 1000 to 1450 °C by adding Ni
 493 or NiS and the flux (Na₂B₄O₇, Na₂CO₃, CaO). You et al. [76] reported that nickel and sulfur can
 494 be used as collectors in the smelting of spent catalyst in the presence of borax and sodium

495 carbonate for 30 min at 1050 °C. The recoveries of Pd, Pt, and Rh were 93%, 90%, and 88%
496 respectively for this process.

497 A novel Pd recovery method was proposed by Zhang et al. [77] where the eutectic copper
498 is used to capture Pd from the spent automobile catalyst. The recovery of Pd is difficult
499 compared to the rest of the PGMs, as the element possesses inert behavior [78]. Cu is used as a
500 capture agent, where Pd forms an alloy with Cu at a temperature above 1250 °C. The studies
501 were conducted at temperatures between 1200 and 1400 °C. The spent catalyst mainly comprised
502 of cordierite ($2\text{MgO}:2\text{Al}_2\text{O}_3:5\text{SiO}_2$), aluminum oxide, and 1650 mg/kg of Pd. The spent catalyst
503 sample was transferred to a crucible along with CuO, 5wt % C, 30 wt.% CaO, 20 wt % SiO_2 , 10
504 wt.% borax, and 8 wt.% Na_2CO_3 , where borax and Na_2CO_3 enhances the melting of the slag. The
505 $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ glass phase, which plays a key role in the formation of Cu-Pd alloy, is expected
506 to formed. At 1200 °C, the recovery of Pd was 0% as the spent catalyst was not in the molten
507 form. At 1250 °C, the Pd recovery reached 90% and was up to 100% when the operating
508 temperature reached 1400 °C. The authors suggested the optimal temperature to be 1350 °C
509 where the Pd recovery rate was 97%.

510 The metal smelting collection process can be implemented on a wide range of secondary
511 materials, especially low grade, and refractory spent catalysts. Factors like collector materials,
512 flux, reducing agents, operational conduction affect the efficiency of the process. Copper
513 collection technology has relatively low cost, high efficiency, and low smelting temperature. The
514 collector material can be re-used. Therefore, this method can be easily adapted to an industrial
515 scale. It is also worth mentioning that adding metal collectors to the briquettes increases the
516 PGM yielding and significantly decrease the dust-gas emission [79].

517

518 **2.3. Physical separation**

519

520 In the spent catalyst, the catalyst carriers are honeycomb-structured items with the porous
521 catalyst layers on its surface. The PGMs are only present on these porous layers where a simple
522 low-energy-consuming and low-cost process like physical separation can be implemented to
523 separate the PGMs or PGM containing layer from the carrier would be significant to eliminate
524 the toxic gases usually released from the regular recycling process. By pulverizing the spent
525 catalyst, a magnetic separation technique can be employed to physically separate the PGMs from
526 the catalyst carriers. The magnetic separation can be performed only on old catalysts with nickel
527 content. Techniques like selective grinding followed by size separation [80, 81] and selective
528 grinding followed by quenching/heat treatment [82] can enhance the PGM-containing catalyst
529 layer concentration.

530 Taninouchi et al. [83] came up with a new process (Figure 8), where a magnetic
531 separation technique is used to recover the PGMs from spent catalysts.

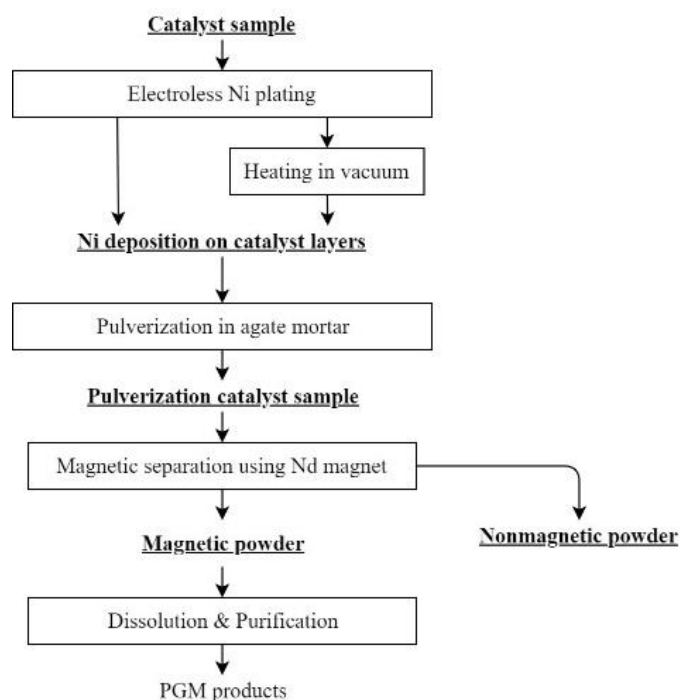


Figure 8. Flowchart illustrating physical concentration technique [83]

In this process, the Ni deposition on the PGMs is done by using an electroless-plating bath along with a complexing agent and reduction agent, which are glycine and sodium hypophosphite respectively. The composition of electroless plating bath ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O} = 35.6 \text{ c}^i/\text{g} \cdot \text{L}^{-1}$, glycine = $22.0 \text{ c}^i/\text{g} \cdot \text{L}^{-1}$, $\text{NaHPO}_2 \cdot \text{H}_2\text{O} = 24.1 \text{ c}^i/\text{g} \cdot \text{L}^{-1}$ and $\text{PbCl}_2 = 0.004 \text{ c}^i/\text{g} \cdot \text{L}^{-1}$). The pH value was adjusted to 7.7 ± 0.4 at room temperature ($25 \text{ }^\circ\text{C}$) by using $\text{NaOH}(\text{aq.})$. The catalyst sample is immersed in the plating solution (40 ml) at room temperature. The container with the catalyst sample and plating solution is then heated to $70 \text{ }^\circ\text{C}$ for 15 mins. The ferromagnetic nickel was plated on the surface of the porous catalyst layer successfully without additional steps like sensitization or activation. Crushing and pulverization were performed on catalyst samples. Neodymium magnet (Nd–Fe–B alloy) was used for the magnetic separation process under dry conditions. Results from the separation process showed that this process can be further developed and can be adapted to the industrial scale.

The recovery of PGM by treating the spent catalyst with FeCl_x ($x= 2, 3$) was tested by Taninouchi et al [84, 85]. The idea was to convert Pt into the Pt–Fe alloy, which exhibits ferromagnetic behavior. The FeCl_2 vapor reacted with Pt samples under the coexistence of Fe metal at $927 \text{ }^\circ\text{C}$ for 60 mins, resulted in the formation of the γ_2 –FePt ferromagnetic phase. Fe was transported from metallic Fe to Pt sample due to the disproportionation of FeCl_2 vapor and the gaseous phase FeCl_x acted as a mediator between the metals. When the γ_2 –FePt alloy was exposed to FeCl_3 , Fe was removed from the alloy resulting in the loss of the magnetic property. It can be stated that Pt can be only treated with FeCl_2 but not with FeCl_3 . Further tests were conducted on the rest of the PGMs and the result was the same. Pd and Rh formed alloys with Fe showing strong ferromagnetic character. The carriers like Al_2O_3 did not react with the FeCl_2 but La_2O_3 and CeO_2 were converted into their respective oxychlorides. Magnetic separation was effective on the PGMs after the FeCl_2 vapor treatment. These processes showed promising results and have the potential to be used at a higher level. The process can be performed at a low cost with a quick pace and is environmentally friendly.

2.4. Electrochemical techniques

High-temperature electrochemical treatment can be applied to extract precious metals from spent catalysts. In general, the electrochemical methods are easy to arrange, can be

566 performed with low waste emission and with low energy and reactant consumption. The major
 567 disadvantage is that these methods are not universal. They can be applied for the treatment of
 568 catalyst based on γ - Al_2O_3 carrier with a minor content of other oxides (SiO_2 , Fe_2O_3 , MgO , TiO_2 ,
 569 CeO_2 , etc.), however automotive exhaust gas convertors, which are catalysts with the highest
 570 annual amount can barely be successfully treated by electrochemical process due to their
 571 complexity. They generally have cordierite ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) as a substrate coated with γ -
 572 Al_2O_3 wash-coat where precious metals (basically Pt, Pd, Rh) are placed. Each of the oxide
 573 components requires separate treatment and adjustment of the technology.

574

575 2.4.1. Two-step method

576

577 Belov et al. [86, 87, 88] proposed an electrochemical method for the extraction of Pd
 578 from spent Al_2O_3 -based catalysts, which was carried out in several stages, based on the Hall-
 579 Heroult process for the primary aluminum production and the three-layer refining process for the
 580 high-purity aluminum production (shown in Figure 9). These stages are:

581

1. Calcination of the catalysts at $800\text{ }^\circ\text{C}$ under air (or oxygen) atmosphere to remove
 582 organic impurities and partially transform PGMs into oxides;

583

2. Dissolution of the catalysts in the molten fluoride system (Na_3AlF_6 - AlF_3 - CaF_2),
 584 electrodeposition of aluminum and PGM on the cathode alloy with the simultaneous evolution of
 585 carbon dioxide on the carbon anode according to the reaction:

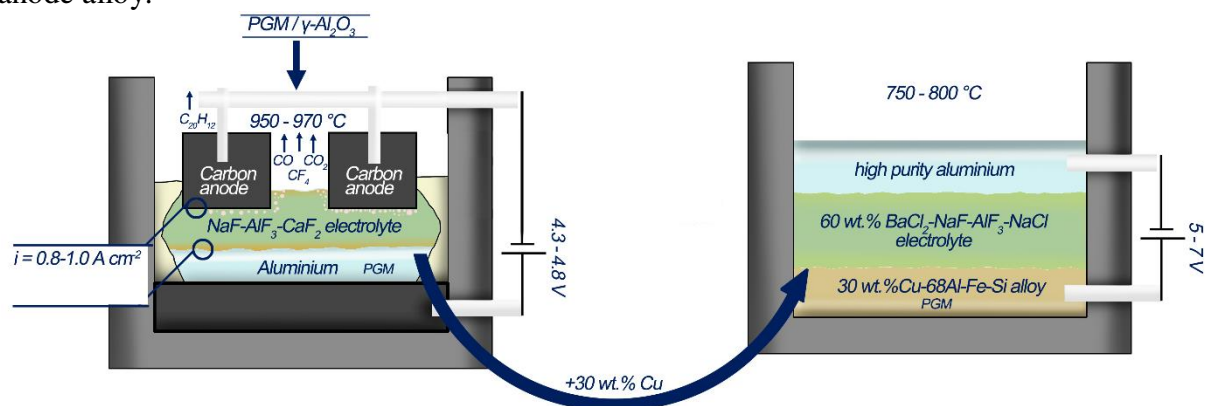
586



588

3. Electrolytic refining of the Al-Cu-PGM alloy (Cu is added to heighten density) with
 589 electrodeposition of high-purity aluminum at the cathode and concentration of PGMs in the
 590 anode alloy.

591



592

593 **Figure 9.** Schematic representation of the commercial Hall-Heroult Cell and the aluminum
 594 refinery cell [89]

595 This process requires high (950 – $970\text{ }^\circ\text{C}$) temperature and should be operated within a
 596 narrow window of catalysts concentration to prevent the sludge formation and the emission of
 597 perfluorocarbons during low- or high-voltage anode effect that in case of slow dissolution can be
 598 a difficult problem to overcome.

599 Despite the mentioned considerations, several experimental facts confirm the
 600 perspective of the electrochemical extraction method [86–88]:

- 601 with the introduction of palladium oxide into molten cryolite, palladium is sufficiently fully
 602 reduced and dissolved in aluminum, while the addition of finely dispersed palladium to the
 603 melt leads to its appreciable distribution between aluminum and cryolite (in the latter,
 604 palladium forms suspension);
- 605 palladium from the catalysts is dissolved and almost completely concentrated in primary
 606 aluminum (98 – 99%);

- 607 □ replacing smelter grade alumina with the catalyst in the Hall-Heroult process has virtually no
- 608 effect on the performance of the aluminum production;
- 609 □ the presence of palladium in the anode alloy in the three-layer refining process has almost no
- 610 effect on the current efficiency of the aluminum refining;
- 611 □ high palladium extraction degree (>98%) and the simultaneous production of high-purity
- 612 aluminum (A97, A99) were achieved.

613

614 2.4.2. One-step method

615

616 The cost of noble metals extraction from spent catalysts can be significantly reduced by

617 using a one-step electrochemical method. Moreover, the temperature of the process can be

618 lowered to 700–850 °C by replacing sodium cryolite with low-temperature fluoride or chloride

619 melts with considerable solubility of Al₂O₃. The promising option, the molten 1.3KF–AlF₃

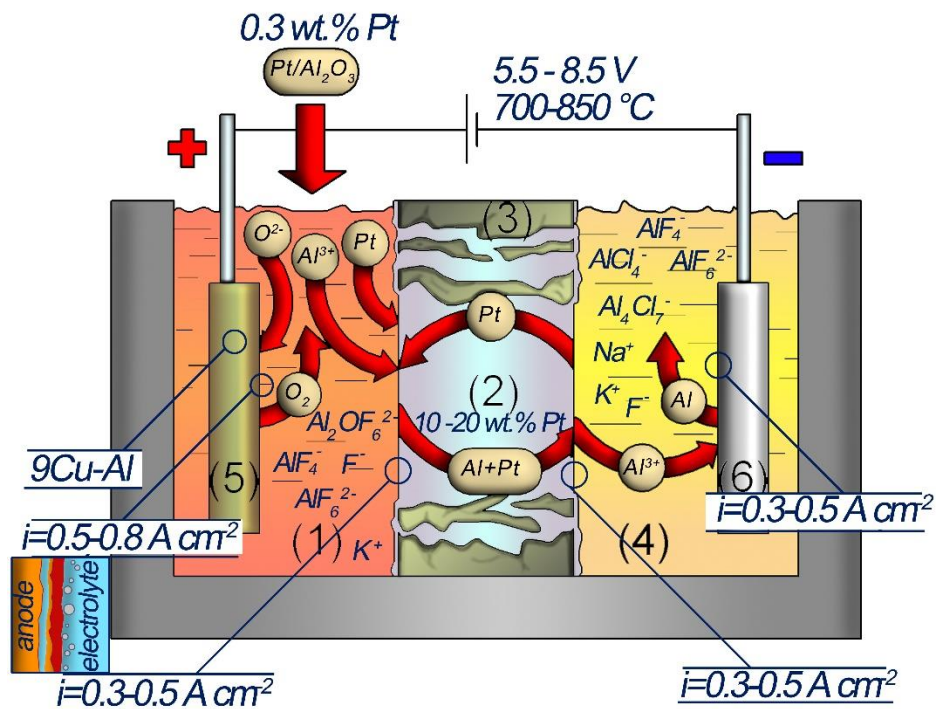
620 system has been studied elsewhere [89–91]. Dividing the cell into two parts (half-cells) by

621 supported vertical or unsupported horizontal liquid Al membrane (bipolar electrode) can be a

622 beneficial solution for one-step extraction. The first half-cell acts as the aluminum reduction cell,

623 the second one plays the role of the aluminum refinery cell. The schematic representation of the

624 cell is shown in Figure 10.



625

626 **Figure 10.** Concept of one-step electrometallurgical process, (1) KF–AlF₃ electrolyte for catalyst

627 decomposition, (2) Al-based bipolar electrode, (3) wettable substrate TiB₂ or W – optional, (4) NaCl–

628 KCl–AlF₃ (+optional BaCl₂) electrolyte for removing Al from the bipolar electrode, (5) oxygen-evolving

629 anode, (6) cathode for high-purity aluminum evolution

630

631 This process is patented [92] and now is under the laboratory scale studies [93] with the

632 spent Pt(+Re)/γAl₂O₃ catalysts from the petrochemical industry with 0.35 wt.% Pt and 0.2 wt.%

633 Re (optional). The catalysts were calcined under air atmosphere in the electrical furnace at 800

634 °C for 30 mins with the manual stirring, ground and treated with mechanical activation for 10 s

635 for better performance in terms of dissolution rate. The 24-hours experiment showed that Pt

636 extraction reaches 99%. This value obtained by comparing the Pt concentration in the bipolar

637 electrode and high-purity aluminum. The detailed description of these results is a subject of

638 further publications. The spent catalyst used by the authors for the recovery of Pt is shown in
 639 Figure 11.



640
 641 **Figure 11.** Spent catalyst Pt/ Al₂O₃: a) before sintering, b) after 10 minutes of calcining at 800 °C, c) after
 642 30 minutes of calcining at 800 °C with manual stirring

643
 644 While Pt is successfully concentrated in the alloy, Re requires additional effort to be
 645 extracted as it is oxidized in a wide range of temperatures. The boiling temperatures of rhenium
 646 oxides are lower than 620 °C that makes it difficult to extract it to the alloy. This is another
 647 drawback of this process when the catalyst contains Re.

648 The catalysts based on the cordierite can also be dissolved in molten cryolite. In that case,
 649 silicon (and iron) will be collected in the alloy along with precious metals. Magnesium will be
 650 collected in the refinery electrolyte in the form of MgCl₂ due to the significant differences
 651 between the electrode potentials of Al and Mg. The same is true for cerium, which will also be
 652 collected in the electrolyte in an oxidized form.

653 The complexity of cordierite (and another mineral supports as zeolites) makes the
 654 possibility of using the electrochemical technology for the treatment of spent catalysts other than
 655 Al₂O₃-based questionable. Major changes should be made to adjust this technology for different
 656 types of catalysts.

657 2.5. Comparative analysis of the technologies

658
 659
 660 The comparison between different approaches for the extraction of metals from spent
 661 catalysts is presented in table 2.

662 **Table 2.** The comparison of different technologies for catalysts processing

Generic composition (wt. %)	Recycling technology	Operating condition	Recovery effect	Advantages and disadvantages of the recycling process	Impact on environment and pollutants released	Extraction %	Application scale	Ref.
Pt/Al ₂ O ₃ Pt- 0.35, Al- 52.80, Fe- 0.02, C- 0.35	HCl + Cl ₂ /NaClO/NaClO ₃ leaching	Low operating temperature (60-150 °C), Emission of SO ₂ , Cl ₂	High Pt, Pd and Rh recovery rate	+High recovery efficiency, +mature technology, +low toxicity, +low investment and cost	Wastewater pollution (heavy metal ions); Cl ₂ emission	Pd: 99%, Pt: 94% Rh:89%	Commercial level	23-31
Pd/Al ₂ O ₃ PdO ₂ - 0.03% CrO ₃ - 0.03% Al ₂ O ₃ matrix – 99.94%	HCl + H ₂ O ₂ leaching	Low operating temperature (60-150 °C), Low emission of Cl ₂	High Pt, Pd and Rh recovery rate	+High recovery efficiency, + mature technology, +negligible toxicity, +low investment and cost, short process	Low environmental pollution due to the low emission of Cl ₂	Pd: 97%, Pt: 90% Rh:>97%	Commercial level	32-36
Pt/Al ₂ O ₃ PtO ₂ - 0.56% CdO- 0.44% SiO ₂ - 0.17%	Cyanide leaching	Low operating temperature (60-150 °C), Hazardous gases	High Pt, Pd and Rh recovery rate	+Low recovery efficiency, +low investment and cost	Wastewater pollution (CN ⁻); HCN emission	Pd: 98%, Pt: 96% Rh:92%	Laboratory level	39-41

Al ₂ O ₃ - 96.09% rest of the matrix < 1%		emission		–immature technology, –high toxicity,				
Pt/Al ₂ O ₃ Pt- 0.307% Cl- 1.43% Fe ₂ O ₃ - 0.343% Al ₂ O ₃ - 92.15% Loss of ignition- 4.95%	Bioleaching	Low operating temperature, No harmful gases emitted	moderate Pt, Pd and Rh recovery rate	+moderate recovery efficiency (relatively new process for the recovery of PGMs), +non-toxicity, +low investment and cost, +low energy consumption, –immature technology –low extraction rate	Environmentally friendly, no chemical emission	Pt: 41%	Laboratory level (Industrial level while extracting metals like (Ni, V, Mo, etc)	43-46
Pt,Pd, Rh/carbon Pt- 1.3% Pd- 0.8% Rh- 0.973% C- rest of the % with respect to the PGM	Supercritical fluids oxidation	Low operating temperature	The high Pd recovery rate	+High recovery efficiency (only Pd), +low investment and cost –Low Pt and Rh recovery, –immature technology,	Waste gas and waste oil pollution	Pd: 96%, Pt: 95% Rh:95%	Laboratory level	47-52
Pt,Pd/Al Pt- 0.15% Pd- 0.07% Pb- 1.56% Al- 98.21%	Supported liquid membrane	High operating temperature	High selectivity	+High selectivity –Low extraction rate –High wastes	wastes	No reliable data available	Laboratory level	53-58
Pt,Rh/slug Pt- 0.23% Rh- 0.053% Ce- 6.153% Zr- 1.437% Ba- 1.15% Mg- 5.893% Al- 20.27% O- 64.814%	Pyrometallurgical process	High operating temperature (750 – 1500 °C)	High Pt, Pd and Rh recovery rate	+High recovery efficiency, +Mature technology, –high investment, –high energy consumption	Large volumes of slags and air pollution	Pd: 98%, Pt: 98% Rh:97%	Industrial level	59-78
Pt,Pd,Rh/ Mg ₂ Al ₄ Si ₅ O ₁₈ Pt- 0.0056% Pd- 0.0062% Rh- 0.0019% Al ₂ O ₃ - 42.0% SiO ₂ - 32.9% MgO- 8.2%	Separation process (magnetic)	High operating temperature (800 – 1300 °C), low pollutants	Moderate Pt, Pd and Rh recovery rate (experimental stage)	+Moderate recovery efficiency, +low investment, +low energy consumption –immature technology	Environmentally friendly, negligible Cl ₂ emission	No reliable data available	Laboratory level	80-85
Pd/Al base metal Pd- 1.2% Al- 98.80%	Two-steps electrochemical process in molten salts	High operating temperature (950-970 °C), emission of greenhouse gases	The concentration of metals in Al alloy	+High recovery efficiency – Two steps	Greenhouse gasses emission	Pd: 98-99%	Laboratory level	86-88
Pt(+Re)/γAl ₂ O ₃ Pt- 0.35% Re-0.2% Al ₂ O ₃ - 99.45%	One-step electrochemical process in molten salts	High operating temperature (700-850 °C)	The concentration of metals in Al alloy	+High recovery efficiency +Low waste emission +Co-production of high-purity aluminum +O ₂ production – Under study	Under study	Under study	Laboratory level	92

663 **Note:** Generic composition of the feed mentioned in this table is only for one particular study with a high recovery
664 rate, the composition varies with studies and can be found in the references mentioned.
665

666 The methods can be united into several groups according to the diagram presented in the
667 figure. 12; however this classification is rather suppositive as combined approaches are often
668 used in practice.

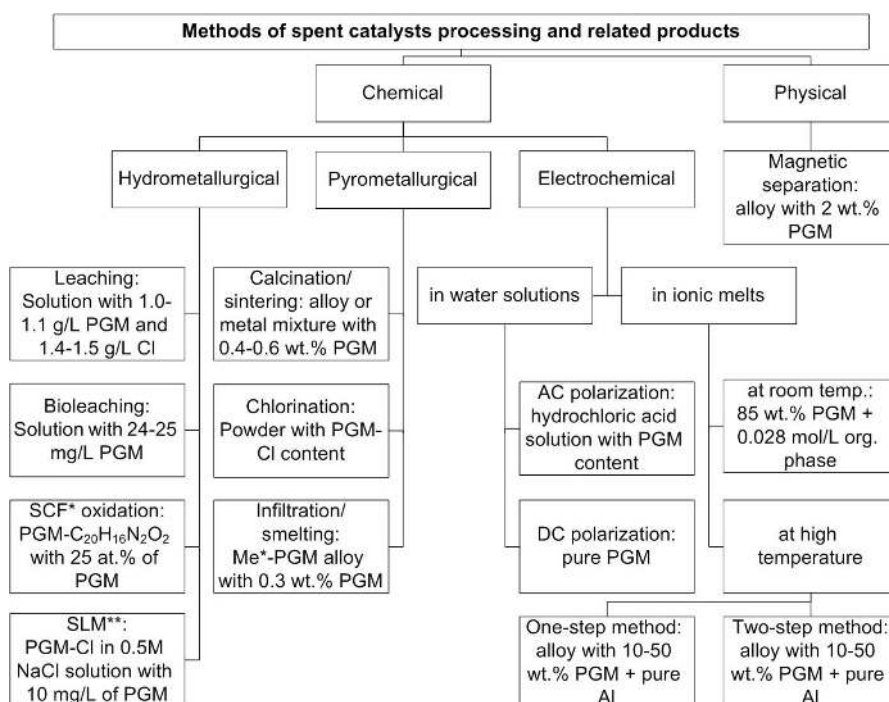


Figure 12. Variety of techniques used for spent catalysts processing and related products (Note: *SCF – supercritical fluid; Me* = Fe, Cu, Pb, Al; SLM – supported liquid membrane) [94–101].

The comparison shows that among the huge variety of technologies several have prospects of further development. Different products of the processes require appropriate treatment to extract valuable metals and purify them. Common significant drawbacks of the methods often are the high cost of equipment and consumables, the high specific energy consumption, and the huge amount of waste.

3. Separation process

In this process, individual PGMs, which are in their chlorocomplex form are separated from the leaching solution. Solvent extraction, ion exchange, and precipitation methods are usually implemented, where the extractants are added to the synthetic solution for individual PGMs separation. Extractants, ion exchange resins, and precipitants play a vital role in the separation behavior of Pt and Pd metals. In this section, the three separation methods mentioned above will be discussed in brief along with the effects of extractants/ion exchange resin/precipitants on the separation behavior of PGMs from the leach liquor. (Note: these separation methods are only used in hydrometallurgical processes)

3.1. Solvent extraction (SX) method

In the SX method, extractants are added to the pretreated leaching liquor where ideal concentrations of PGMs are available for the separation. Three types of extractants added according to the requirements are namely, basic (amine), neutral, and acidic extractants. According to the literature study conducted in Nguyen et al. [102], Pt and Pd can be completely extracted by selective stripping from the leaching solution by using amines, although complications with the formation of the third phase and difficulties in stripping leading to the compulsion in adjusting the stripping solution might occur. By using neutral extractants, selective extraction of Pd

Table 3. Summary of the advantages and disadvantages of extractants in the separation and extraction of Pt and Pd in chloride leaching (adopted from [102]).

Extractants	Aqueous	Advantage	Disadvantage	Ref.
Alamine 300 ^a	0.01 M Pt and Pd	Individual extraction of Pt over Pd	Critical stripping issues. Co-	104

		while using saturated NaCl solution at pH 1.5	extraction of Pd	
Alamine 336 ^a	0.0001 M Pt and Pd	Simultaneous extraction of Pt and Pd from the 1-5 M HCl.	High co-stripping of Pt along with Pd	105
	Pt, Pd	Extraction of both Pt and Pd from HCl with 15% w/w concentration	No data on Pt and Pd separation from stripping	106
TIOA ^a	Pt, Pd, Ru, Ir, Au	Extraction of Pt, Pd, and Au over Pt and Ir from 3.5-6 M HCl.	No data on Pt and Pd separation from stripping	107
DMDCHTDGA ^b	0.1 g/L Pt, Pd	Pd and Pt co-extraction at 8 M HCl. Pd and Pt separation using the stripping step.	Extraction is synthesized. separation efficiency is low	108
DBSO ^b	1000 g/L Pt, Pd	Pd extraction over Pt at 0.1 M HCl	Extraction is synthesized. Usage of 5 M ammonia solution + 3% v/v NH ₄ Cl for metal stripping.	109
Cyanex 923 ^b	50mM of Pd and Pt	Pt extraction over Pd at 5 M HCl	The low separation efficiency of Pd and Pt	110
Cyphos IL 101/104 ^b	2.5 mM of Pd, Pt, Ni, Cu, Ir, Pb, Ir, Ru, Rh	Pd extraction over other metals at 0.1 M HCl	The low separation efficiency of Pd and Pt	111
TBP ^b	Pt-0.55, Pd-0.15, Cr-0.1, Mn-0.5, Ni-1, Fe-1.5 g/L	Pd extraction over other metals at 3 M HCl	Loss of Pt from Fe precipitation	112
PC 88A ^c	0.001 g/L Pt, Pd	Extraction of Pd over Pt from 1 M HCl + 1 M HClO ₄ solution	Low metal concentration and low HCl concentration in the leaching solution	113
N530 ^c	Pt-10.23, Pd-5.95, Au- 5.42 g/L	Extraction of Au over Pt in 5 M HCl. Extraction of Pd over Au and Pt in HCl solution of pH 2.0	Pd stripping only possible at high HCl concentration (6 M)	114
LIX 63 ^c	100 ppm of Pd(II), Pt(IV), Ir(IV) and Rh(III), 6 M HCl	Individual Pd extraction over other metals, easily desorbed by using 0.5 M (NH ₂) ₂ CS stripping reagent	Coextraction of other PGMs occurs at high LIX 63 concentrations (over 0.2 M)	115
LIX 84I ^c	Pt-0.55, Pd-0.15, Cr-0.1, Mn-0.5, Ni-1, Fe-1.5 g/L	Extraction of Pd over other metals at 3 M HCl.	Co-extraction of Fe is high	116
	1 g/L Pt, Pd	Individual extraction of Pd over other metals from the solution with pH values 1-3, Separation factor= 400	Metal stripping from 6M HCl, low HCl concentration in the leaching solution.	117

701 **Note: a-Basic extractants, b-Neutral extractants, c-Acidic extractants**

702 Alamine 300 = tri-n-octyl amine; Alamine 336 = tri-octyl/ dodecyl amine; TIOA = tri-iso-octylamine;
703 DMDCHTDGA = N,N'-dimethyl-N,N'-dicyclohexylthiodiglycolamide; DBSO = dibutyl sulfoxide; Cyanex 932 =
704 the phosphine oxides; Cyphos 1IL 104 = trihexyl(tetradecyl)phosphonium bis-2,4,4-trimethylpentylphosphinate;
705 Cyphos IL 101 = trihexyl(tetradecyl)phosphonium chloride; TBP = tributyl phosphate; PC-88A = 2-ethylhexyl
706 phosphonic acid mono-2-ethylhexyl ester; N530 = 2-hydroxy-4-sec-octanoyl diphenyl-ketoxime; LIX 63 = 5,8 -
707 diethyl-7-hydroxydodecane-6-oxime LIX 84I = 2-hydroxy-5-nonylaceto phenone oxime.

708

709 The separation behavior of Pt(IV) and Ir(III) in three different leaching solutions
710 (HCl/HNO₃/H₂SO₄) between the varying concentrations 0.1-6 mol/L using Cyanex 471X
711 extractant was investigated [118]. Cyanex 471X was diluted with toluene and the concentration
712 of the extractant in this organic solution was 0.1 mol/L. The extraction percentage of Pt(IV) was
713 about 80% at low HCl concentrations of 0.1-0.5 mol/L, and a sudden decrease in the percentage
714 to 50% was recorded at 2.0 mol/L HCl and remained constant on further increase in HCl
715 concentration. The same phenomena were seen while using HNO₃ and H₂SO₄ solutions as the
716 initial recovery rate was 55% and 67% respectively but with the increase in their concentrations
717 reduced that recovery rate. The reason reported was that Pt(IV) could not form an extractable
718 sulphate complex. On contrast to Pt(IV), Ir(III) was easily extracted in HCl solution as it could
719 form extractable chlorocomplexes. Ir(III) from HNO₃ and H₂SO₄ solutions had high recovery at
720 0.1 mol/L concentration and were low when their respective concentrations reached 6.0 mol/L.

721

722 3.2. Ion-exchange method

723

724 In the ion-exchange method, the ion exchange resin is added to the leaching solution,
 725 sometimes combined with the synthetic solution loaded with PGMs in their complex form. Ion-
 726 exchangers play a vital role in the separation process and some of the details on the ion-
 727 exchangers are mentioned in table 4. The PGMs are adsorbed on the resin surface. The elution
 728 process is carried out on loaded organic resins by adding eluents like Na₂CO₃, NaCl, and a
 729 mixture of thiourea and HCl to strip the PGMs. Separation of Pt and Rh from the HCl solution
 730 with varying concentrations of 0.1-5 M using IX technique was investigated in [119]. Three
 731 different ion exchangers were used namely AGMP-1, AG1-x2, and AG1-x8. The adsorption
 732 phenomena of Pt and Rh were similar in all the anion exchangers. Pt showed better adsorption
 733 percentage even at 5M HCl solution while the percentage was less than 20% in the case of Rh
 734 throughout 0.1 to 5 M concentration. It is worth noting that an increase in the concentration of
 735 exchangers in the solution increased the adsorption percentage of both Pt and Rh. Langmuir
 736 isotherm was followed by resins for Pt adsorption. The adsorption percentage of Rh increases
 737 with an increase in the HCl concentration, while the percentage of Pt decreases. AG1-x8 was a
 738 better exchanger compared to the other two, as AG1-x8 had better Pt loading capacity and also a
 739 high separation factor between Rh and Pt. Further continuous column experiment showed that Pt
 740 and Rh can be completely separated using 0.1 HCl solution mixture. Na₂CO₃, NaCl, and a
 741 mixture of thiourea and HCl were used as eluting agents, and thiourea was more effective in
 742 eluting Pt from the loaded organic resin. The process is effective and can be adapted to the
 743 commercial level. The resin used in this process can be regenerated after the desorption of the
 744 PGMs.

745 In [120], the separation behavior of Pt, Pd, and Rh in 2.35 M HCl solution was
 746 investigated where ion exchanger resins namely XUS 43600 (thiuronium functional group),
 747 Lewatit MonoPlus (M+) MP 600 (quaternary ammonium functional group), and Purolite S985
 748 (polyamine functional group) were used. It was reported that Pt and Pd show high adsorption
 749 percentage in the XUS 43600 while Rh had poor adsorption behavior for all three resins. Sodium
 750 thiocyanate (2 mol/L), thiourea (1mol/L) in sodium hydroxide (2 mol/L) thiourea (1 mol/L) in
 751 hydrochloric acid (2mol/L), and hydrochloric acid (2mol/L) were used as an eluting agent.
 752 Desorption of Pt, Pd from the loaded resins was better using acidic thiourea. In both [119] and
 753 [120], it is stated that the adsorption of Rh on the resins and desorption from the loaded resins
 754 using the eluting agent were difficult. Alternative methods need to be used for the recovery of
 755 Rh.

756
 757 **Table 4.** Summary of the advantages and disadvantages of ion-exchangers in the separation and
 758 extraction of Pt, Pd, and Rh in chloride leaching

Ion exchanger	Aqueous	Advantages	Disadvantages	Ref.
AG1-x2	0.001 M Pt, 0.001 Rh, 0.1 to 5 M HCl	High Pt adsorption at 0.1 M HCl	Poor Rh adsorption percentage at all HCl concentrations	119
AG1-x8	0.001 M Pt, 0.001 Rh, 0.1 to 5 M HCl	High Pt and Rh loading capacity, selectivity between (large separation factor) Pt and Rh	Requires high HCl (5 M) and high resin (20 g/L) concentrations separate Rh	119
AGMP-1	0.001 M Pt, 0.001 Rh, 0.1 to 5 M HCl	High Pt separation and extraction	low Rh separation and extraction	119
XUS 43600	Leaching solution (0.000129 M Pt, 0.000125 M Pd, 0.000033 M Rh, 2.35 M HCl), synthetic solution(, 0.000513 M Pt, 0.000470 M Pd, and 0.000194 M Rh, 4.11 M HCl)	High Pt and Pd extraction from both the solution type of around 99.9%	low Rh final elution percentage	120
Lewatit (M+) MP 600	Leaching solution (0.000129 M Pt,	High Pd extraction percentage and high elution	Low Rh recovery and no data on elution data	120

	0.000125 M Pd, 0.000033 M Rh, 2.35 M HCl), synthetic solution(, 0.000513 M Pt, 0.000470 M Pd, and 0.000194 M Rh, 4.11 M HCl)	percentage (using Thiourea 1 M eluant in HCl 2 M)		
Purolite S985	Leaching solution (0.000129 M Pt, 0.000125 M Pd, 0.000033 M Rh, 2.35 M HCl), synthetic solution(, 0.000513 M Pt, 0.000470 M Pd, and 0.000194 M Rh, 4.11 M HCl)	High Rh recovery percentage of 87.8% and 94.8% respectively from leaching and synthetic solution.	Low Pd recovery and low Rh final elution percentage	120
Purolite S920	0.150g/L Pd, 109.5 g/L HCl, 53.5 g/L NH ₄ Cl, 3.2 g/L Cu(II), 3.3 g/L Zn(II), 2.8 g/L Fe(III), 6 g/L Sn(IV)	High Pd adsorption percentage	No elution data	121
Purolite S924	0.150g/L Pd, 109.5 g/L HCl, 53.5 g/L NH ₄ Cl, 3.2 g/L Cu(II), 3.3 g/L Zn(II), 2.8 g/L Fe(III), 6 g/L Sn(IV)	No particular advantages noted in Pd recovery investigation	Adsorption percentage of Pd less than 65%	121
Lewatit TP-214,	0.0011 M Pd(II), 0.1–0.9 M HCl – 0.9–0.1 M HNO ₃ , 0.0011 M Pd(II), 1–2.0 M HCl, 1.0 M NaCl	High ion exchange rate	Difficulty in elution process	122, 123

759 **Note:** AG 1- strongly basic anion exchangers with quaternary ammonium functional groups attached to the styrene
760 divinylbenzene copolymer lattice, XUS 43600- Thiuronium (thiourea) attached to the Styrene-divinylbenzene,
761 Lewatit (M+) MP 600- Quaternary ammonium (type 2) attached to the Styrene-divinylbenzene, Purolite S985-
762 Polyamine attached to the Polyacrylic-divinylbenzene, Purolite S920- thiourea functional group, Purolite S924- thiol
763 functional group, Lewatit TP 214- thiourea or isothiurea functional group attached to Polystyrene–divinylbenzene
764

765 3.3. Precipitation method

766
767 In this method, a suitable precipitating agent is added to the leaching solution containing
768 PGM ions, where the PGMs interact with the agents and form insoluble substances and are
769 individually separated thereafter. The further step involves filtration where their pure metallic
770 forms can be obtained. In [124], selective separation of Rh from the HCl solution containing Pt
771 (IV), Pd (II), and Rh (III) (1 mmol/L) metals was performed using the precipitation method. 4-
772 hexylaniline and 4-butylaniline were used as precipitants in high HCl concentrated solution for
773 Rh separation. Centrifugation was used to separate the metal precipitates from the mixture. The
774 findings showed that while using 4-hexylaniline precipitant, more than 90% of Pt and Pd were
775 precipitated in 1-2 M HCl concentration although a sudden decrease in the precipitation
776 percentage with further increase in HCl concentration. In contrast to that, 85% of Rh was
777 precipitated from the solution at high HCl concentrations (3-8 M). Using 4-butylaniline had
778 poor precipitation percentage of Pt and Pd throughout the (1-8 M) HCl concentration, while Rh
779 was successfully precipitated with an increase in HCl concentration. The color of the Rh
780 precipitate was pinkish, and unique ion-pair complex composed of [RhCl₆]³⁻ /chloride/anilinium
781 ions in a 1:3:6 ratio was found. The process shows promising results for selective separation of
782 Rh and authors claim that the process could influence the PGM recovery process at an industrial
783 scale.

High extraction of Pt from HCl/H₂O₂ leach liquor (9 M HCl and 0.8 vol% H₂O₂) was attained using precipitation technique in [125]. The suitable precipitation concentration of Pt species in the leaching solution is 0.2 g/L, which was attained by heating the solution at 190 °C to make the excess liquid evaporate. NH₄Cl (290 g/L) was added to the solution with simultaneous stirring at 40 °C. The yellowish Pt precipitate in a complex form of (NH₄)₂[PtCl₆] was obtained. The later steps involved washing the precipitate with NH₄Cl solution (140 g/L) followed by the calcination. The Pt recovery rate was 96% and the purity was around 99.6%. This method is simple, energy-efficient, and promising with no harmful gas emission.

792

793 4. Industrial operations

794

On an industrial level, many advancements and optimizations have been made in extracting the PGMs from spent catalysts. Commercial processes for the PGMs recovery from the spent catalyst and used electronic products have successfully been implemented by industries like Engelhard (USA), BASF (USA), Hereaus (Germany), Johnson Matthey (UK), Mitsubishi (Japan), Umicore (Belgium), Nippon (Japan). Table 5 shows the processes already in use commercially.

800

Table 5. Processes used for PGM recovery on a commercial scale [28, 126].

Process	Specification	Industry
ROSETM method	Pyrometallurgy	Nippon PGM Co.
Melting method-1	Pyrometallurgy	
Metal Vapour Treatment	Pyrometallurgy	MatsudaSangyo Ltd
The Plasma arc smelting process	Pyrometallurgy	Texasgulf, USA and Safina, Czech Republic
Chlorination	Hydrometallurgy	Tanaka Kikinzoku
Segregation		N.E. ChemCat
Aqua regia	Hydrometallurgy	
CN extraction	Hydrometallurgy	US Bureau of Mining
HCl leaching	Hydrometallurgy	Heraeus (Germany)

802

A new novel semi-industrial process combining pyrometallurgical treatment and electrolytic refining is been proposed by the Institute for Mining and Metallurgy Bor [127]. They claim that the process is economical, environmental, and highly efficient. A novel membrane electrode assemblies process has been developed by BASF catalysts LLC (USA) to eliminate the emission of highly toxic gas (HF) in the present recycling processes [128]. Cyanide leaching has been extensively used by the industries, although special attention needs to be given on the harmful byproducts released through this process. A novel three-liquid-phase extraction has shown promising results at the laboratory scale and can open a new path in developing an environmentally friendly extraction technique [129,130]. In a novel combination of pyro and hydrometallurgical process, the catalytic converter carrier and Pt-Cu alloy samples acquired from the pyrometallurgical method were treated with aqua-regia (with and without fluoric acid). Solution and solid wastes were by-products of this process making it undesirable, although it has been stated that economical and environmental benefits can be excepted with an adequate combination of pyro and hydrometallurgical methods and can be adopted at commercial scale [131]. Biotechnological recovery where the metal ion-reducing bacterium (Shewanella algae) reduces and deposits the PGMs ions (Pt (IV), Pd (II), and Rh (III)) into metal nanoparticles at neutral pH and room temperature within 60 min using the electron donor formate was successfully developed by Saitoh et al. [132]. The adoption of this technology would be revolutionary and environmentally friendly. Currently, a lot of research is conducted to find the optimal way to recover the PGMs from the spent catalyst and a lot has been achieved at a laboratory scale. Some of them are transferable to the industrial level.

823

824

5. Conclusion

825

826 The platinum group metals are widely used in various industrial applications. The
827 demand for the PGMs is inevitable because of its unique properties and the natural PGM
828 resources are limited, which demands to recycle PGMs spent catalyst. The recycling process
829 satisfies the demand and consumes the leftover catalysts in environmentally friendly way. This
830 paper gives an overview of the processes used for the recycling of the spent catalyst. The
831 processes are distinguished into hydrometallurgy, pyrometallurgy, physical magnetic separation,
832 and electrochemical, which has advantages and disadvantages accordingly. While using the
833 hydrometallurgical process, the by-products like toxic water wastes are released and recovery of
834 Rh is poor when compared with the pyrometallurgical process. The bioleaching process is eco-
835 friendly but the recovery efficiency of PGMs should be improved. The pyrometallurgical process
836 needs huge energy and investments while the process is environmentally friendly compared to
837 the hydrometallurgical process. The process can be economically beneficial when used in the
838 large-scale industrial level. The physical magnetic separation process is relatively new and novel
839 but promising results were attained, nonetheless, the process is still at its beginning stages. The
840 new one-step electrometallurgical process with Pt recovery up to 99% was proposed by the
841 authors of this paper. The process is still under study and major results are expected to be
842 obtained soon. A lot of work has been done in different recycling processes and still, there is a
843 scope of further improvement.

844 **6. Future scope**

845 Hydrometallurgical techniques are highly efficient for Pd extraction and get much more
846 attention in comparison with other ones during recent years; however, Rh cannot be leached for
847 more than 90 %. Strong solvents (aqua regia, cyanide, H₂SO₄, etc.) are used to dissolve the spent
848 catalysts in the leaching process. The PGMs should be reduced to the metallic state before that.
849 Cyanide leaching is a more efficient recovery process but it requires high temperatures, and
850 cyanide is highly toxic. Pyrometallurgical techniques are well studied and applied in industry.
851 The advantage is that calcination, chlorination, and PGM smelting collection (infiltration) can be
852 performed at a higher rate compared to the hydrometallurgical processes. However, in the
853 pyrometallurgical process, a high amount of energy is consumed. The emission of SO₂ is also a
854 significant drawback. Physical separation techniques are more simple, energy-efficient, and low-
855 cost. It also eliminates the toxic gases usually released while using the hydro- and
856 pyrometallurgical methods. Ni deposition on the PGMs is done by using an electroless-plating
857 bath, complexing, and reducing agents. High-temperature electrochemical methods are much less
858 studied. They are easy to set up, can be performed with low waste emission and with low energy
859 and reactant consumption. However, they are not universal as they can only be applied for the γ -
860 Al₂O₃-based catalysts. Complex cordierite-based (or similar) automotive exhaust gas converters
861 can barely be successfully treated by the electrochemical process. Optimization of this
862 technology is required for each of the oxide components. Nevertheless, the one-step
863 electrochemical method appears to be a promising solution. However, it requires further research
864 to be implemented on an industrial scale.

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