

Platinum Group Metals Recovery Using Secondary Raw Materials (PLATIRUS): Project Overview with a Focus on Processing Spent Autocatalyst

Novel pgm recycling technologies ready for demonstration at next scale

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PLATInum group metals Recovery Using Secondary raw materials (PLATIRUS), a European Union (EU) Horizon 2020 project, aims to address the platinum group metal (pgm) supply security within Europe by developing novel and greener pgm recycling processes for autocatalysts, mining and electronic wastes. The initial focus was on laboratory-scale research into ionometallurgical leaching, microwave assisted leaching, solvometallurgical leaching, liquid separation, solid phase separation, electrodeposition, electrochemical process: gas-diffusion electrocrystallisation and selective chlorination. These technologies were evaluated against key performance indicators (KPIs) including recovery, environmental impact and process compatibility; with the highest scoring technologies combining to give the selected PLATIRUS flowsheet comprising microwave assisted leaching, non-conventional liquid-liquid extraction and gas-diffusion electrocrystallisation. Operating in cascade, the PLATIRUS flowsheet processed ~1.3 kg of spent milled autocatalyst and produced 1.2 g palladium, 0.8 g platinum and 0.1 g

rhodium in nitrate form with a 92–99% purity. The overall recoveries from feedstock to product were calculated as $46 \pm 10\%$, $32 \pm 8\%$ and $27 \pm 3\%$ for palladium, platinum and rhodium respectively. The recycled pgm has been manufactured into autocatalysts for validation by end users. This paper aims to be a project overview, an in-depth technical analysis into each technology is not included. It summarises the most promising technologies explored, the technology evaluation, operation of the selected technologies in cascade, the planned recycled pgm end user validation and the next steps required to ready the technologies for implementation and to further validate their potential.

1. Introduction

The pgms comprise six chemically similar elements: iridium, osmium, palladium, platinum, rhodium and ruthenium. The primary use of pgms is for their catalytic properties with applications in the automotive, chemical manufacture and petroleum refining industries. The pgms have been denoted by the European Commission as critical raw materials with their significant economic importance and potential supply risk (1). The EU supply stability of primary source pgms is uncertain given the market dominance by a small number of non-EU countries, the ongoing political, economic and social factors in these regions and the EU's reliance on imports. Between 2017–2019, recycling only provided 25–33% of the global demand for palladium, platinum and rhodium. Recycling can further mitigate the supply risk and ensure the future pgm demand is met both in the EU and globally (2), while also dramatically reducing the environmental impact of pgms when compared with primary sources: high energy use, large amounts of waste from mines and significant CO₂ emissions.

There are several pgm refining facilities across Europe but almost all rely on pyrometallurgical processes, including smelting, as the precursor to hydrometallurgical chemical separation and purification processes. Using these existing smelting-based recycling routes provided by primary producers or refining companies such as Anglo American Platinum, Impala Platinum, Umicore, Johnson Matthey, Heraeus and BASF is conventionally how autocatalysts are recycled in the EU (3–7). Though the pyrometallurgical processes are effective at upgrading the pgm content and hence reducing the levels of impurities, they

are high temperature processes requiring large amounts of energy.

During the past two decades, alternative technologies to the pyrometallurgical processes, more specifically smelting, have been evaluated for autocatalysts recycling with the focus on reducing the environmental impact of pgm recycling (8, 9). The hydrometallurgical dissolution of the spent autocatalyst using aqua regia, cyanide or strong acids (HCl, HNO₃ or H₂SO₄) usually in presence of an oxidising agent is the most commonly used dissolution process (8–12). Among these, cyanide leaching was widely implemented for its high dissolution efficiency (13, 14). However, due to the severe toxicity and energy consumption, it has been replaced with safer methods. The achieved recovery, efficiency and purity of the proposed alternative hydrometallurgical methods are still insufficient to compete with the results obtained from industrially employed pyrometallurgical methods.

Of the techniques reported to separate and purify pgms from the dissolution or leach liquor irrespective of the selected upstream processes (8, 9, 15–17), the most employed by global refineries are solvent extraction (18, 19) and multi-stage precipitation techniques (20). Although solvent extraction is one of the preferred methods because of its high efficiency and selectivity, effort continues to find greener and safer organic extractants and diluents without compromising the efficiency already achieved (21–25). Opportunities for process modifications and improvement sit not only with solvent extraction but with other industrially employed processes all the way through the pgm recycling flowsheet.

To the present there are few examples of complete flowsheets, from feed to product, for the recycling of pgms that do not involve a pyrometallurgical pre-concentration step followed by a smelting process (26–29). PLATIRUS is an EU Horizon 2020 project that brings together companies from the pgm supply chain alongside research organisations to foster the development and upscaling of novel and greener pgm recycling technologies. This project brings a complete feed to product flowsheet for the separation and purification of pgms without the use of smelting whilst using novel as well as modified traditional processes.

This paper provides an overview of the project summarising the most promising technologies explored in the research and innovation phase, the technology selection, operation of the selected

technologies, planned recycled pgm end user validation and the next steps for the PLATIRUS flowsheet. To the best of our knowledge, the selected PLATIRUS technologies provide a novel flowsheet for the separation and purification of pgms which could open new insights for future pilot scale plants.

2. Overview of Technologies Explored

The project is split into three phases (Figure 1): (a) research and innovation (R&I) into leaching, separation and recovery technologies; (b) selection of the best technologies for validation supported by economic and environmental assessment; and (c) upscaling of the selected PLATIRUS technologies and operation in cascade in an industrially relevant environment.

During the R&I phase, partners investigated their respective technologies (Figure 1). Key

results are presented based on processing the same waste feedstock, namely milled spent autocatalyst feed containing palladium, platinum and rhodium (Table I). This feed comprises over 100 different de-canned and milled autocatalysts from the open market. The grain size was <2 mm. The feed contained 1588 ± 18 ppm palladium, 912 ± 5 ppm platinum and 327 ± 9 ppm rhodium as characterised using X-ray fluorescence spectral analysis. Other feeds have been investigated (Figure 1) but are considered outside of this paper’s scope.

Collaboration between the project partners on analytical methods was key to ensure consistency of the project results between them; a standard sample with a known and certified concentration of each pgm was used by each partner to evaluate different analytical methods to ensure accuracy and repeatable results. All results presented, unless otherwise stated, are experimental results.

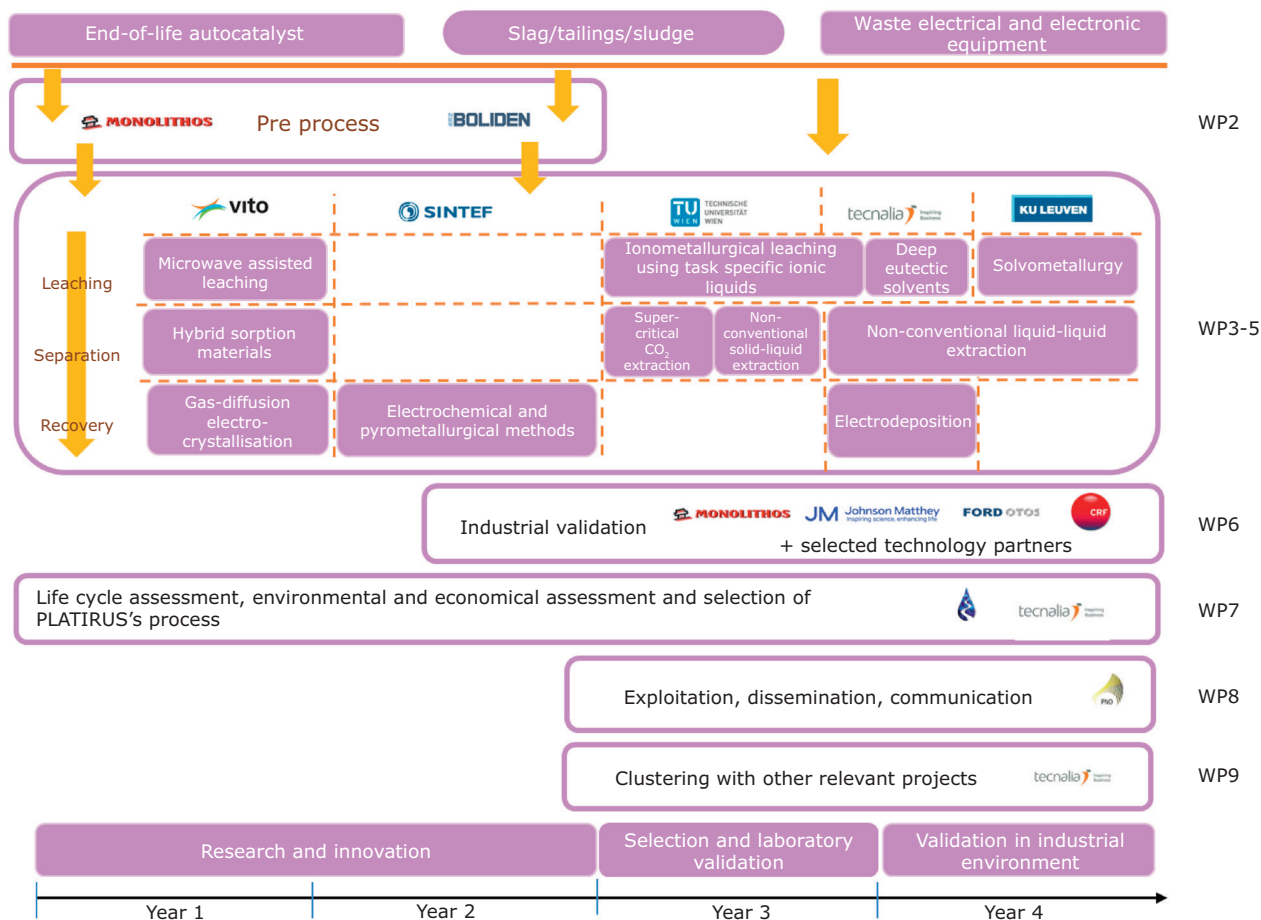


Fig. 1. PLATIRUS project overview. As of April 2020 Env-Aqua Solutions Ltd is not involved in the project activities

2.1 Ionometallurgical Leaching and Reduction Using Deep Eutectic Solvents

TECNALIA developed a two-stage leaching and reduction process using deep eutectic solvents (DES), comprising choline chloride and oxalic acid (Figure 2). The solvent is first used to leach the pgms from the solid feedstock at a temperature $<90^{\circ}\text{C}$, followed by a reduction of the pgms to their metallic form, by heating the solution to $>100^{\circ}\text{C}$. Centrifugation was employed at this laboratory scale based on equipment availability, separately both for the removal of the depleted autocatalysts substrate and the pgm product. Recovered DESs can be recycled for the next leaching batch.

The solvents used are readily prepared from renewable, non-toxic and naturally occurring chemicals when compared to traditional hydrometallurgical processes that employ strong acids (15, 31). Another advantage is that it is a one-pot leaching and reduction process where no additional reducing agent is required. An increase in the pgm purity is achieved from the selective reduction process with a highly pure (90–95%) pgm solid generated, a significant improvement from the low content feedstock. Therefore, it is a simple process for the concentration of pgms, with reduced costs and wastes generated, compared with the cementation process (31–33) and with

a very low energy consumption compared to existing pyrometallurgical processes (15). Further separation steps are needed to separate the three pgms from each other. The DES must be kept close to the leaching operation temperature to avoid handling issues arising from DES solidification.

2.2 Microwave Assisted Leaching

An advanced leaching process using microwave (MW) technology has been developed by VITO using a laboratory MW digester (flexiWAVE, Milestone Srl, Italy). The feedstock is contacted with 6 M HCl and H_2O_2 , as an oxidising agent, before being heated using MW radiation (2.45 GHz) to the reaction temperature of 150°C . MW heating allows short leaching times, consisting of 15 min heating with 10 min dwell time at the reaction temperature (34). The resultant leachate, containing the pgms, is filtered, to remove the undissolved catalyst substrate, leaving an aqueous solution containing the pgms in a chloride matrix.

The MW heating promotes fast, homogeneous volumetric heating enhancing leaching reproducibility and efficiency, with a positive impact on the energy efficiency. Optimisation of the leaching process has resulted in a significant reduction in the HCl acid concentration (i.e. 6 M HCl) required compared to previous results reported in literature (i.e. 12 M HCl) (34). The necessity of

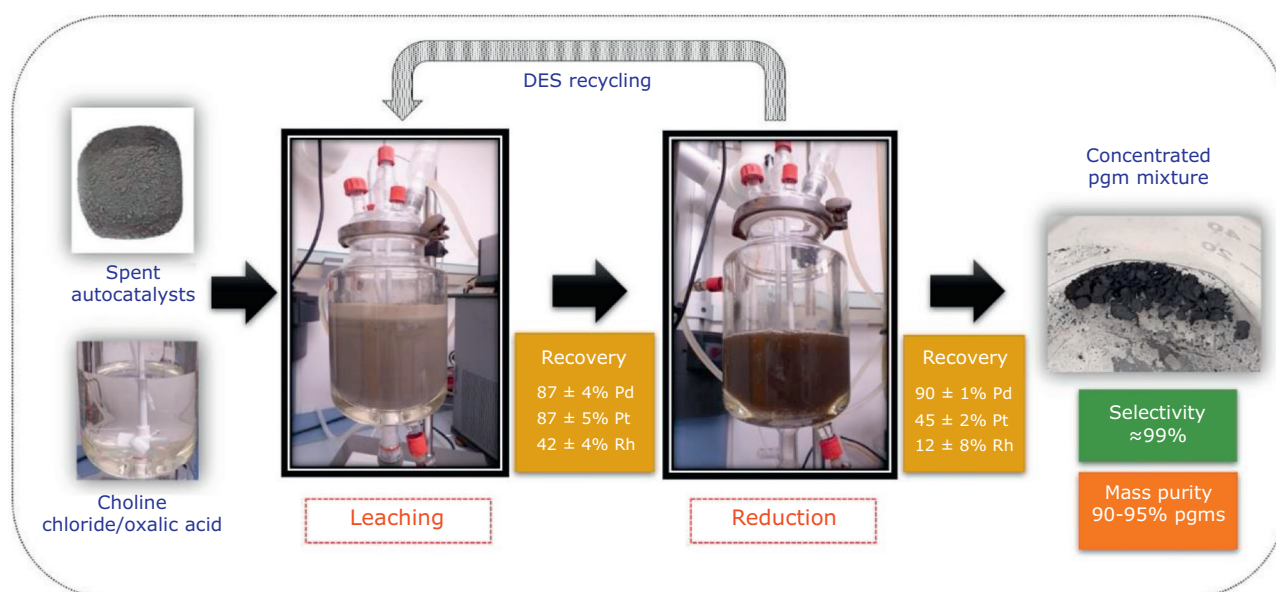


Fig. 2. Diagram of TECNALIA's leaching process using DESs (selectivity is recovery of pgm divided by recovery of impurities)

the H₂O₂ addition is dependent on the feedstock (Table I, data provided in presence of 10 v/v% H₂O₂ (31%)). In some circumstances its addition has been shown to have a significant impact on the pgm leachability. Through modelling and analyses of the reactor head-space gas, it was shown that H₂O₂ addition increased the formation of Cl₂ and H₂ gas, which must be considered in the process safety assessment.

2.3 Solvometallurgical Leaching

Solvometallurgy is an alternative branch of metallurgy that uses non-aqueous solutions (35). KU Leuven investigated the oxidative dissolution of pgms from the feedstock using two different solvometallurgical approaches. In

the first, an innovative method for the selective leaching of palladium from the feedstock was developed, avoiding the co-extraction of platinum and rhodium whose recovery can be achieved from the palladium depleted feedstock by varying the process conditions. Dilute and concentrated solutions of FeCl₃ in acetonitrile are used for the selective dissolution of palladium and the dissolution of platinum and rhodium, respectively. This solvometallurgical approach provides a preconcentration of the pgms after which further purification is needed to separate platinum and rhodium. In the second approach, highly concentrated solutions of AlCl₃·6H₂O and Al(NO₃)₃·9H₂O were used to dissolve palladium selectively from spent autocatalysts; 95% palladium was leached in only 15 min at 80°C (36).

Table I Summary of Technologies Investigated in the PLATIRUS Project and Experimental Results

	Owner	Technology	Recoveries, %	Output Form
Leaching	TECNALIA	Ionometallurgical leaching and reduction	79 ± 4 Pd 39 ± 5 Pt <10 Rh	One solid stream containing palladium, platinum, rhodium
	VITO	MW assisted sulfation roasting followed by microwave assisted leaching (30)	96 ± 1 Pd 85 ± 5 Pt >96 Rh	One aqueous chloride + sulfate matrix leachate containing palladium, platinum, rhodium
	VITO	MW assisted leaching	91.8 ± 0.1 Pd 96 ± 4 Pt 89.9 ± 0.2 Rh	One aqueous chloride matrix leachate containing palladium, platinum, rhodium
	KU Leuven	Solvometallurgical leaching	90 ± 4 Pd 76 ± 2 Pt 45 ± 2 Rh	Two organic streams <ul style="list-style-type: none"> • palladium • platinum/rhodium
Separation	VUT	Ionometallurgical leaching using ILs	100 ± 3 Pd 98 ± 4 Pt 43 ± 4 Rh	One ionic liquid stream containing platinum, palladium, rhodium
	VUT	Non-conventional liquid-liquid extraction	100 ± 0.1 Pd 100 ± 0.3 Pt 99 ± 2 Rh	One ionic liquid stream containing palladium, platinum, rhodium
	VUT	Non-conventional solid-liquid extraction	96 ± 3 Pd 86 ± 2 Pt	One ionic liquid stream containing palladium, platinum (no rhodium)
	KU Leuven	Non-conventional liquid-liquid extraction	81 ± 3 Pd 62 ± 2 Pt 54 ± 5 Rh	Three aqueous streams <ul style="list-style-type: none"> • palladium • platinum • rhodium
	VITO	Hybrid sorption material	97 ± 6 Pd 0 Pt 0 Rh	Two aqueous streams <ul style="list-style-type: none"> • palladium • other metals
Recovery	SINTEF	Electrodeposition	Close to 100 ± 10 for Pd, Pt and Rh	One solid stream containing palladium, platinum, rhodium
	SINTEF	Selective chlorination	35 ± 10 Pd 40 ± 10 Pt 25 ± 10 Rh	One solid stream containing palladium, platinum, rhodium
	VITO	Gas-diffusion electrocrystallisation	70 ± 2 to close to 100 ± 2 for all pgms	One solid stream of nanoparticles or colloidal dispersions pellets

2.4 Ionometallurgical Leaching Using Ionic Liquids

Ionic liquids (IL) are perceived as 'green solvents', mainly due to their low volatility, which signifies a reduction in the degree of negative environmental impact and health hazards, low toxicity and non-flammability (37). In metal extraction applications, they have provided dramatically higher extraction efficiencies than commonly used solvents. They can act either as solvents in the presence of an extracting agent or as selective extractants, since *via* modifications in their anion or cation their selectivity towards a certain metal can be tuned (38, 39).

VUT explored the properties of ILs for both leaching and separation processes (for separation see Section 2.5). Leaching of the pgms from the feedstock was performed using hydrophilic and low cost choline-based ILs. The choline-based IL leaching process was selected as the optimum due to its high extraction efficiency and selectivity. The process operates at mild conditions in the presence of an oxidising agent: <100°C for 4 h in a sealed vessel with continuous stirring (**Figure 3**).

This process leaches the pgms, but further separation steps are needed to separate the three pgms from each other. Depending on the feedstock, the loaded IL can be re-used for subsequent leaching batches until the IL capacity is reached. Of note is the mild process conditions used.

The major drawback is the high IL viscosity, making implementation on an industrial scale challenging. Nevertheless, dilution of the IL with water is feasible without compromising the pgm extraction efficiencies. Furthermore, larger scale system design and operation must ensure the

violent exothermic reaction between the feedstock and oxidising agent is managed safely.

2.5 Non-Conventional Liquid-Liquid and Solid-Liquid Extraction

Due to the increased interest in ILs, a new concept surfaced: IL immobilisation on solid support materials, which is the deposition of a fine IL layer on a solid surface. Use of supported IL phases (SILPs) is an ideal strategy in order to make use of the benefits of IL and simultaneously avoid the inherent complications of IL-based separations such as mass-transport limitations and excessive usage of the IL (40).

VUT exploited the properties of hydrophobic ILs in both liquid and solid extraction processes; this was employed in conjunction with the VUT ionometallurgical leaching process (Section 2.4). In the liquid-liquid extraction process, a solution comprising 50 wt% phosphonium-based IL in *n*-heptane was used to extract palladium, platinum and rhodium from the loaded pgm hydrophilic leachate (generated from ionometallurgical leaching) to the hydrophobic IL phase. Quantitative extraction is obtained after continuous stirring for 2 h at room temperature. The pgm-free hydrophilic IL phase can be recycled to perform the next batch of IL leaching. No significant performance loss of the hydrophilic ILs was observed between the different cycles; only five cycles have been tested to date. This is particularly attractive to minimise environmental impact and operating costs.

The alternative approach, solid extraction, relied on SILPs using hydrophobic phosphonium-based ILs (**Figure 4**). The pgms are adsorbed onto the



Fig. 3. Up-scale of VUT's leaching process (100 g catalyst)

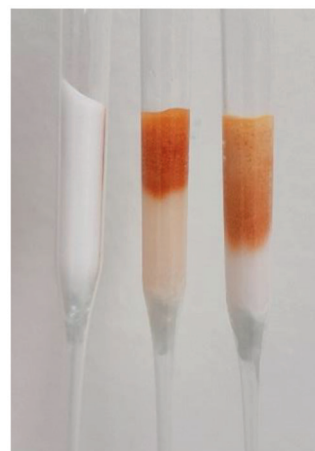


Fig. 4. VUT's pure SILP (left - white) and SILPs loaded with pgms (middle and right - orange)

solid enabling their one-step separation from the main impurities of aluminium, iron and cerium due to their low retention on the solid material.

The stripping is a two-step process: (a) an acidified thiourea solution strips the impurities retained on the SILP; (b) a more concentrated acidified thiourea solution strips palladium and platinum (rhodium is retained on the solid).

The use of SILPs allows fast and simple separation of the pgms from other metals with reduced chemical reagent consumption compared to liquid-based separations. There is the possibility to re-use the solid material for further separations without any loss in its retention and separation performance, to date one recyclability experiment has been conducted. An advantage of SILPs compared to most commercially available resins is no pre-equilibration is required; this could have significant impact on cycle times and effluent generation if re-equilibrium is necessary, as part of the load-elution cycle. A drawback of the process is the retention of rhodium alongside chromium on the SILP and the removal requires a suitable stripping agent not yet identified.

2.6 Non-Conventional Liquid-Liquid Extraction

A split-anion solvent extraction process has been developed by KU Leuven for the separation of

an aqueous mixture of pgms into their individual elements (**Figure 5**) (41). Generally, the split-anion extraction relates to the solvent extraction process where different anions are present in the aqueous and organic phases and the distribution of the IL anions strongly favours the IL phase. The pgms are extracted from the chloride leaching solution using the iodide form of the quaternary ammonium IL Aliquat® 336, [A336][I], dissolved in *p*-cymene. The iodide anions, which have a strong affinity for the organic phase, coordinate with pgms to form stable iodo-complexes that can be extracted to the ionic liquid phase (42, 43). The split-anion extraction allows not only efficient extraction of pgms without changing from a traditional chloride feed solution, but also the selective recovery of the extracted metal complexes from the loaded organic phases. The organic is scrubbed and stripped of its pgms, as detailed in **Figure 5**.

The ionic liquid-based split-anion extraction process is simple, selective and effective for the sustainable separation of pgms, using only one ionic liquid [A336][I] as the extractant, which can be regenerated for consecutive extraction-stripping cycles. The high viscosity of [A336][I] is a drawback, which has shown, during its pilot scale application in mixer-settlers, to slow the mass transfer. Some measures have been identified to reduce the IL viscosity, such as the use of water-

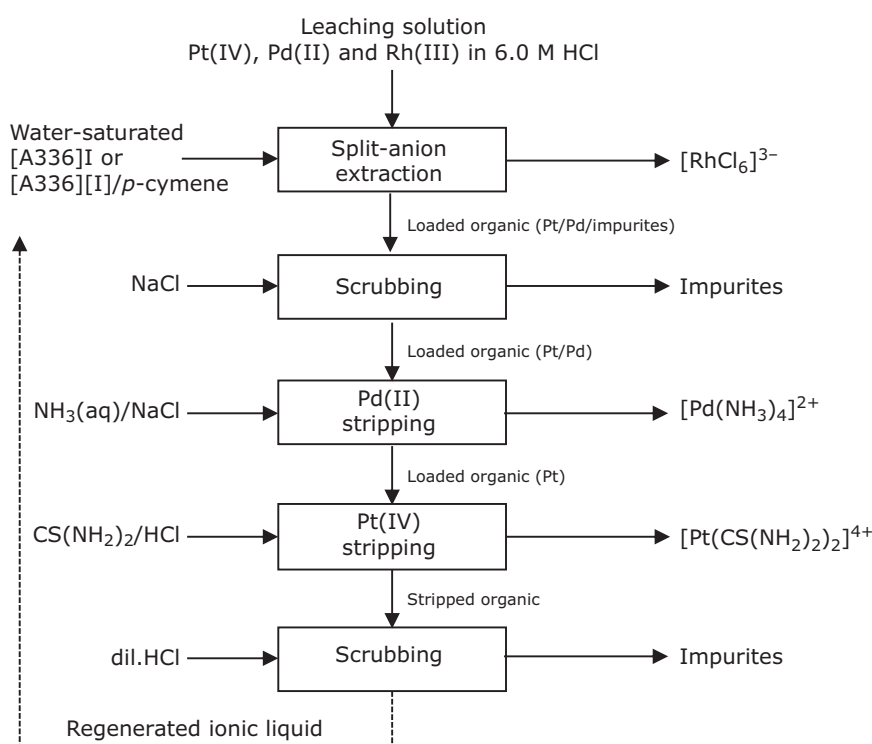


Fig. 5. KU Leuven's proposed flowsheet for the extraction and separation of pgms from spent automotive catalysts

saturated ionic liquid or use of green diluents (i.e. *p*-cymene), but the measures can only partially resolve the problem. To the best of our knowledge this is the first time that a process based on IL for the separation of pgms is tested in continuous mode using real pregnant leach solutions as feed. Other separations using IL have been developed and show good performance but have been only tested with synthetic solutions and not in continuous mode (44, 45).

2.7 Hybrid Sorption Material

Sorbents are an established method to selectively recover palladium and other noble metals for acidic aqueous streams such as leachates (16, 46–48). Many materials have been developed by different groups and their performance tested in powder form. However, to be applied in a continuous way, the shape has to be optimised to avoid clogging and pressure build-up in a column or the material has to be modified for easy recovery afterwards with for example a magnetic core (49, 50). Therefore, VITO has developed solid sorbents by first selecting or forming a suitable solid backbone before grafting active organic scavenging groups onto the support using a green aqueous synthesis method. Two types of regenerable three-dimensional (3D) structured metal oxide supports (**Figure 6**) have been investigated: monodisperse microspheres and 3D printed monoliths. These types of supports have the advantage of reducing mass diffusion limitations, optimising packing density and decreasing pressure drop while allowing fast adsorption and desorption cycling times.

The functionalised microspheres show good selectivity for palladium over other pgms and impurities giving a method to remove palladium from acidic solutions. The adsorbed palladium can be easily recovered by stripping with concentrated HCl acid resulting in a concentrated acidic solution of palladium. The sorbents have a palladium capacity of 0.33 mmol g⁻¹ from acidic solutions (pH 2). When stripped with 3 M HCl, a seven-fold increase in the palladium concentration between the feed (100 mg l⁻¹ palladium) and stripping solution was observed. No significant performance loss of the sorbents was observed between the different cycles; only seven cycles have been tested to date.

The developed material is a hybrid (ceramic-organic) adsorbent selective to palladium over the rest of the pgms with good hydrolytic stability that can be regenerated and reused. If a degradation of the organic scavenging groups and hence, decreased performance is observed over a higher number of cycles, the metal oxide support can be recovered and refunctionalised. The biggest drawback is the limited sorbent capacity, but more developments to improve this are ongoing by increasing the specific surface of the supports and optimising the grafting conditions.

2.8 Electrodeposition

SINTEF investigated extracting pgms from the feedstock using pyrometallurgy, employing copper as the pgm collector, followed by a molten salt electrolysis process (**Figure 7**).

The pyrometallurgical process was investigated at two laboratory scales (10 g and 5 kg). The pgm recovery rates, in the alloy phase, were close to

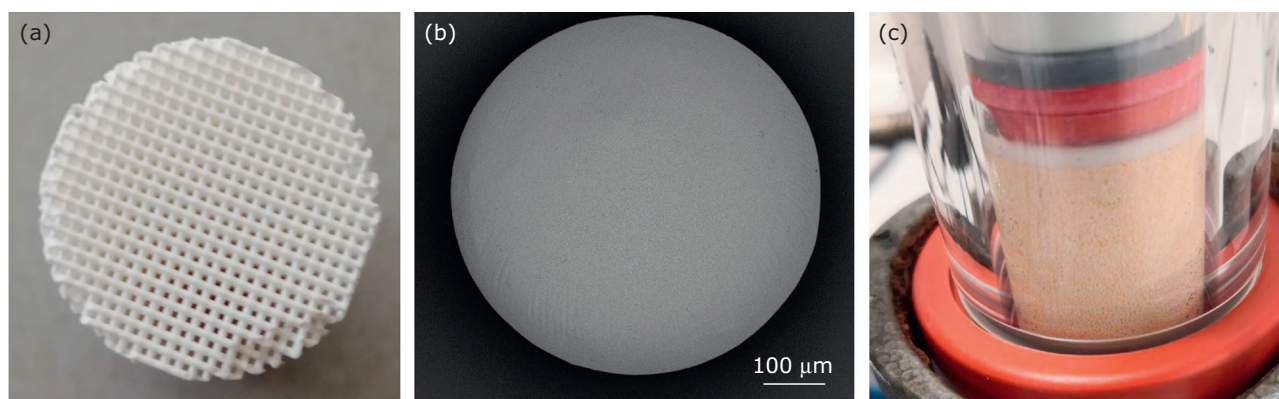


Fig. 6. (a) Image of VITO's 3D-printed titania monolith with a diameter of 17 mm; (b) scanning electron microscopy (SEM) image of the titania microsphere support; (c) a column loaded with the developed microsphere sorbents in operation adsorbing palladium from an acidic solution

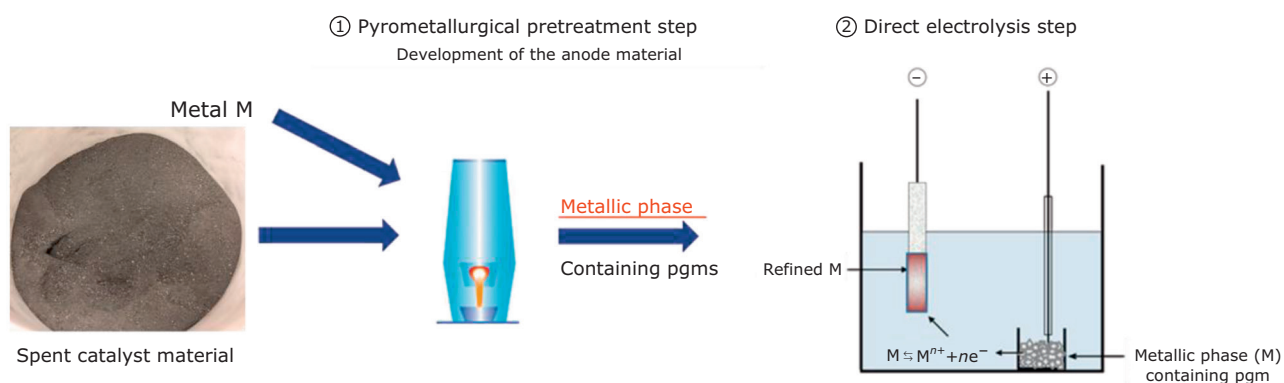


Fig. 7. Schematic representation of the process carried out by SINTEF

100%, and the copper-collector recovery rates were in the range 82–100%, when using the optimised parameters: 10 wt% copper-collector, 10–15 wt% calcium oxide, 1600–1650°C and 1–1.5 h holding time. This pyrometallurgy step pre-concentrated the pgms by ~10 times from feedstock to the generated metallic phase.

In the electrolysis step, the copper-pgm alloy is used as anode in an electrorefining cell with the eutectic LiCl-KCl as electrolyte at 450°C. The experiments demonstrated the selective extraction of the metal phase (copper), which was recovered at the cathode with a current efficiency of *ca.* 70%. Under these conditions, the pgms (and other impurities) remain in the anode residue giving a solid with >99.9% purity. Further separation steps are needed to separate the three pgms from each other.

One significant advantage of pyrometallurgical over hydrometallurgical processes is the lower reagent use in relation to the feedstock pgm content (kilograms of reagent per kilogram of pgm) (51). As such, it provides attractive conditions for preconcentrating pgms from very dilute wastes, such as the PLATIRUS feedstocks; the optimised conditions of the SINTEF process showcase that. High recovery rates of the copper collector at the electrolysis cathode have been achieved and it can be recycled for the next pyrometallurgical step.

The electrolysis process allows the extraction of copper from the pgm-containing copper anode in a molten salt electrolyte with better selectivity and kinetics as well as lower energy consumption than in state-of-art copper-refining processes using aqueous solutions (52). Cu(I) species are stable in the molten salt electrolyte, thus the voltage (and energy) needed in the electrorefining process is lower than in an analogous aqueous solution process where Cu(II) are the solely stable species.

In general, the kinetics of the electrode charge-transfer reaction in molten salts are considered faster due to the high operational temperature (53).

The challenges of operating the SINTEF pyrometallurgical step are the same as those found in industry. The separation of pgm microparticles from the molten slag phase is impacted by the slag viscosity and metal-to-slag interfacial tension and in turn affect the pgm extraction efficiencies. The energy consumption was *ca.* 5.5 kWh kg⁻¹ copper recovered in the pyrometallurgical step and *ca.* 7 kWh kg⁻¹ pgm recovered in the electrolysis step (equal to 0.3 kWh kg⁻¹ copper refined) under optimised experimental conditions. Energy consumption can be challenging to extrapolate from laboratory to industrial scale. Due to the energy intensiveness of pyrometallurgical processes, energy consumption and associated cost must be evaluated at larger scale.

2.9 Selective Chlorination

Molten chloride mixtures can be used as a reaction media in the chlorination of oxide mixtures, ores or industrial byproducts. The dissolution reaction generates chloride compounds at much lower temperatures (*ca.* 450°C) than those needed in solid-gas chlorination reactions (*ca.* 1000°C). This is due to significant solvation effects of the dissolved metal cation with the chloride ions of the molten chloride media.

SINTEF investigated the selective recovery of the pgms using molten salts and chlorine gas as an oxidiser and chlorination agent, followed by an electrolysis process (Figure 8). LiCl-KCl eutectic mixture was chosen as the best candidate. The feedstock was fed into the reactor at 450°C without any pretreatment or up-concentration steps, resulting in a single step pgm extraction

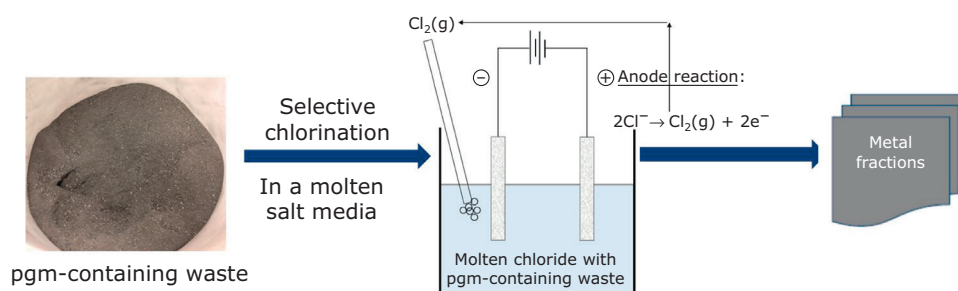


Fig. 8. Diagram representing the selective chlorination process carried out by SINTEF

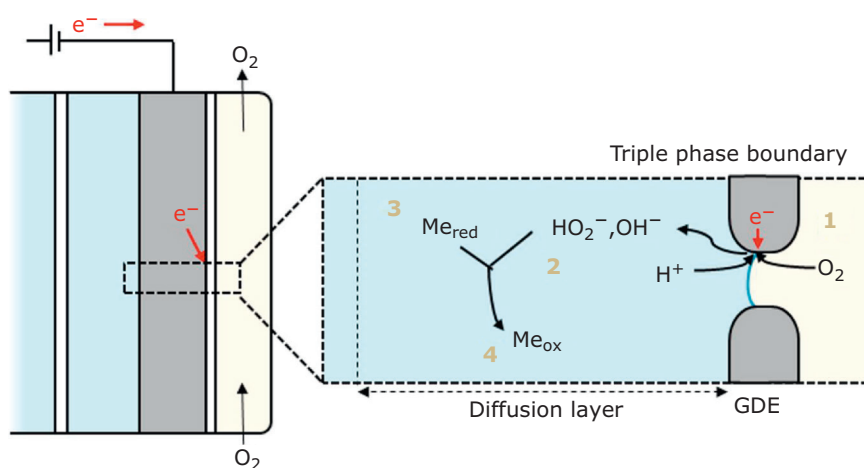


Fig. 9. Schematic representation of the VITO's GDEx process operating with O_2 . This represents the presumptive mechanism, which may be revised as we gain further understanding of the process

process. Silicon, magnesium and aluminium were not dissolved thus remain as a solid sludge at the bottom of the reactor. The analysis of the residue shows that, after 3 h, the total chlorination and therefore dissolution of the pgms is close to 50%. The dissolved pgms are recovered in an electrolysis process as a metallic-pgm alloy at the cathode resulting in chlorine evolution at the anode. Only 80% of the dissolved pgms can be accounted for in the molten chloride as pgm-chlorocomplexes; it is believed unaccounted pgm mass corresponds to formed volatile pgm-chlorocomplexes that could be recovered from the off-gas system by condensation; estimates calculated from a mass balance suggested a feed volatilisation of *ca.* 10% palladium, 10% platinum and 20% rhodium.

This chlorination process presents clear advantages in terms of rate, conversion and selectivity when compared with traditional gas-solid reaction systems. In the latter, the rate and conversion are limited by the contact of the gaseous chlorinating agent and the material to be chlorinated, and the reaction occurs non-selectively

as, at the much higher temperature, chlorination of all other elements contained in the material occurs, not only pgms.

Though faster than gas-solid reactions, the kinetics are still slow when using chlorine gas and the use of other gaseous chlorination agents, such as HCl, should be tested. Further optimisation of the process is required to achieve competitive pgm recovery rates, including recovery of the volatile pgm-chlorocomplexes.

2.10 Gas-Diffusion Electrocrystallisation

GDEx is defined as the reactive precipitation between metal precursors in solution and intermediates from the reduction of gases at a gas-diffusion electrode. When the gas is air or O_2 , the O_2 reduction reaction leads to hydroxyl ions and hydrogen peroxide being formed in the pgm solution, which react, forming oxides or hydroxides (**Figure 9**). Alternatively, the process can run with other gases. The GDEx process

is enabled by VITOCORE® multi-layered gas-diffusion electrodes (54).

GDEx uses the cleanest possible reagent, the electron, and it is highly versatile, as it can be used to recover many different metals. The process uses an inexpensive reactor. As it operates in a flow-cell configuration, it is easily up-scalable by stacking multiple individual cells, without a reduction in performance. The process is highly reproducible, involves mild operation conditions (room temperature and atmospheric pressure). The process has a low energy consumption, for example ~2-6 kWh kg⁻¹ of materials recovered, when compared with electrowinning platinum from chloride media reported at 21 kWh kg⁻¹ platinum (55). Finally, it is efficient, i.e. 50% current efficiency for the formation of the reactive intermediates that fully react with the metal precursors to achieve the targeted recovery.

Notably, the recovery of dilute metals and simultaneous synthesis of nanostructures with GDEx is fast, with rates approaching ~3–15 kg per day, using a single, inexpensive, electrochemical reactor under flow regime.

The best results were achieved with dilute metal concentrations, and significant optimisation is required for solutions with metal concentrations above 10 g l⁻¹. Especially with high metal concentrations, it is expected that, after a period of operation, the electrode would become clogged and require an acid treatment to regenerate the

electrode porosity. The recovery of the precipitated materials is impacted by the unoptimised downstream separation and drying processes. Some reagents, such as sulfur-based compounds, are known to interfere with the process under defined processing conditions, coprecipitating with the pgms.

3. Selection Criteria for Industrial Validation

A key aim of the PLATIRUS project was to develop technology that could be applied at scale to bridge the supply gap of pgms in Europe. Novel and sustainable technologies are unlikely to be commercialised if the economics are not competitive. The KPIs were chosen as selection criteria to align with these project objectives, namely, to develop novel sustainable pgm recovery processes. Dimension reduction, employing traditional processes of multicriteria decision analysis (MCDA), was used to reduce the number of KPIs to a practical range (Figure 10).

The KPIs identified for PLATIRUS were quantified and added to an MCDA model. The results were then scored and normalised to present all KPIs on the same scale and range. At this point, the KPIs were all considered to be of equal importance and contribute the same impact to the overall technology rating. Whilst reaching this point is enough to deliver a review score, the model

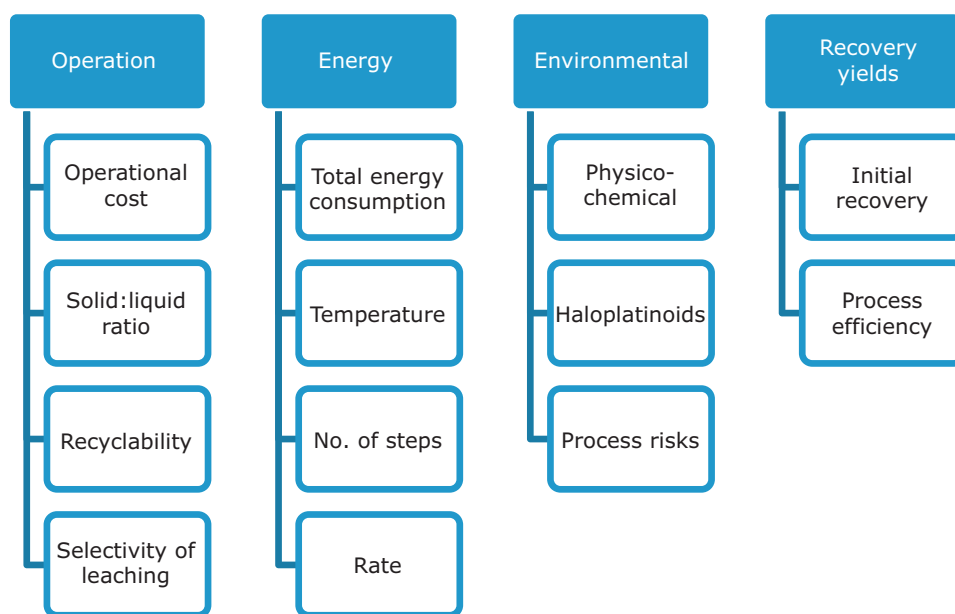


Fig. 10. Key performance indicators used by Env Aqua to enable the selection of the best (combination of) pgm recovery technologies

Table II Evaluation Results of Most Relevant PLATIRUS Process Flowsheets^a

Leaching	MW assisted leaching (VITO)	Solvometallurgical leaching (VUT)	Ionometallurgical leaching using DES (TEC)	Ionometallurgical leaching using DES (TEC)	
Separation	Liquid-liquid extraction (KU Leuven)	Liquid-liquid extraction (KU Leuven)	Liquid-liquid extraction (KU Leuven)	-	Baseline
Recovery	GDEX (VITO)	GDEX (VITO)	GDEX (VITO)	Electrodeposition (SINTEF)	
Sustainability	1	2	8	14	9
Efficiency	2	3	8	14	7
Performance	2	3	10	12	4
Cost	1	3	9	14	5
Environmental	1	4	9	14	8
Weighted position	1	2	8	14	7

^aUnweighted individual KPI position scores and total weighted position (low score is preferred with 1 scored to the best technology and 14 scored to the worse technology)

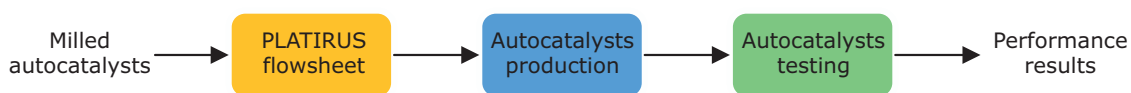


Fig. 11. Key tasks following PLATIRUS flowsheet selection

and the results are not tailored to the specific PLATIRUS objectives. To prioritise the most important factors, weighting of the KPIs was conducted through analytical hierarchical process. In addition, grouping of criteria was conducted to help distinguish components relative to the overall objective using criteria weights.

One critical aspect which is not referenced in the KPIs is the compatibility of each of the individual processes to work in cascade and hence give a complete recycling flowsheet from feed to product. A total of 13 different combinations of the PLATIRUS technologies and the baseline were evaluated. **Table II** shows the evaluation results for the most relevant process combinations; the following three compatible technologies were selected for industrial validation: MW assisted leaching (VITO, Section 2.2), non-conventional liquid-liquid extraction (KU Leuven, Section 2.6) and GDEX (VITO, Section 2.10).

4. Autocatalyst Material Processing

The three selected technologies were demonstrated at the VITO and KU Leuven sites to produce recycled palladium, platinum and rhodium to enable the

manufacture and testing of recycled autocatalysts (**Figure 11**).

The ~1.3 kg feedstock was a mixture of diesel oxidation catalyst (DOC) and three-way catalyst (TWC) from CRF and FORD milled, blended and characterised by MONOLITHOS (56). The resulting powder contained 2066 ± 24 ppm palladium, 2574 ± 15 ppm platinum and 179 ± 5 ppm rhodium.

In addition to the three selected technologies, conventional chemical transformations were employed to convert the PLATIRUS outputs into the correct form for autocatalyst production. Demonstration was carried out using technology and equipment appropriate, available and compatible to process the ~1.3 kg autocatalyst (~15 l pgm solution). Over a six-month period, the PLATIRUS team successfully operated the PLATIRUS flowsheet in cascade and processed the feedstock producing 1.2 g palladium, 0.8 g platinum and 0.1 g rhodium in nitrate form with a purity of 92-99% (as a reference market palladium nitrate solution is sold with a purity of 99.98%) (57) (**Figure 12**). The overall recoveries were calculated as $46 \pm 10\%$ for palladium, $32 \pm 8\%$

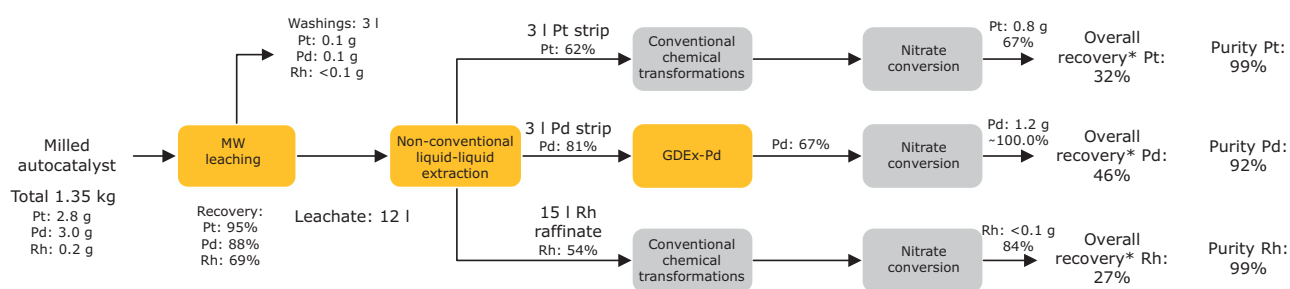


Fig. 12. Overview of the mass balance for autocatalyst processing (*Recoveries include losses for analysis)



Fig. 13. MW system at the VITO laboratory used for leaching process

for platinum and $27 \pm 3\%$ for rhodium, including losses for analysis and equipment start-up which are disproportionately high at this scale of operation. In practice, considering optimisation of auxiliary processes and operating in a manner representative of continued industrial operation, more representative recoveries are estimated, by process modelling, to be between 60–86% from feed to sponge for the three pgms and further optimisation beyond this is possible.

4.1 Leaching–Microwave Assisted Leaching

A laboratory scale MW system (flexiWAVE) equipped with a spinning carousel holding 15 pressure-sealed Teflon-lined reactors was used to process ~ 1.3 kg autocatalyst (Figure 13).

The leaching temperature is measured by a thermowell contained optic fibre, placed in one

of the 15 reactors. Each of the 15 reactors was loaded with 5 g of the feedstock and 50 ml 6 M HCl solution. The MW-assisted reaction took place at 150°C for 10 min, with a heating time to the set temperature of 15 min. Subsequently, the reactor was cooled, opened and the leachate was vacuum filtered. It is noteworthy that this leaching process did not require addition of H_2O_2 as an oxidation agent and thus the formation of hazardous head space gas mixtures (containing H_2 and Cl_2 gas) was avoided. During vacuum filtration, the leach residues were washed with 6 M HCl at room temperature. Both leachate and washing liquids were collected.

Overall, ~ 1.3 kg of material was leached by performing 18 MW-leaching runs. Three batches of material with different grain sizes and total masses were processed, hence three leachates (L1, L2, L3) and washing waters (W1, W2, W3) samples were obtained (Table III).

4.2 Separation: Non-Conventional Liquid-Liquid Extraction

The leachate containing L1, L2 and L3 (Table III), as prepared by VITO, was processed using the solvent extraction flowsheet developed at KU Leuven (Figure 5). Due to the low pgm concentration of the leaching residue washings, these solutions were not processed. A continuous solvent extraction demonstration using multi-stage mixer-settlers was undertaken to process the leachate (Figure 14).

First, Pd(II) and Pt(IV) were quantitatively extracted in two countercurrent stages with [A336] [I] in *p*-cymene at O/A = 1/3, leaving Rh(III) in the raffinate. The impurities (mainly aluminium, barium, cerium, iron and tin) in the loaded organic phase were removed with NaCl solution. Then

selective stripping of palladium was achieved by equilibrating the scrubbed organic phase with aqueous ammonia in NaCl solution in four-stage mixer-settlers at O/A = 3/1. Followed by the recovery of platinum from the palladium-free loaded organic phase was performed using acidic thiourea solution [CS(NH₂)₂/HCl] in four countercurrent stages (O/A = 2/1). After being washed with diluted HCl, the IL requires regeneration by contact with KI to replace the chloride for an iodide anion reforming [A336] [I].

The work at KU Leuven demonstrated that continuous solvent extraction is feasible for not only the preparation of [A336][I] but also the selective recovery of individual pgms, with recoveries of 81 ± 3% Pd(II), 62 ± 2% Pt(IV) and 54 ± 5% Rh(III), from the feedstock leachate. The mass loss was mainly as a result of the samples taken

Table III Average Properties of the Recovered Leachates and Washing Waters During Leaching

Solution	pH	Oxidation-reduction potential, mV vs. Ag/AgCl (2sf)	pgm recovery, %		
			Palladium	Platinum	Rhodium
L1 ^a	-0.9	940	86.4 ± 0.1	91.1 ± 0.1	66.7 ± 0.2
L2 ^a	-0.8	930	82.1 ± 0.2	89.7 ± 3.1	59.7 ± 2.8
L3 ^a	-1.0	940	82.3 ± 2.1	90.5 ± 1.9	67.6 ± 6.0
W1 ^a	-0.7	850	4.752 ± 0.001	4.88 ± 0.02	3.8 ± 0.3
W2 ^a	-0.8	830	4.72 ± 0.03	5.11 ± 0.02	3.6 ± 0.3
W3 ^a	-0.9	840	3.22 ± 0.05	3.6 ± 0.1	2.7 ± 0.3
Average total recovery ^a (with washings)			87.9 ± 2.7	95.0 ± 1.2	68.0 ± 4.1
Average total recovery (without washings)			83.7 ± 2.0	90.5 ± 0.6	64.7 ± 3.6

^a Errors for individual leachates and washing waters are based on duplicate inductively coupled plasma (ICP) analyses. Errors of the average total recoveries are based on relative standard deviation of the individual values

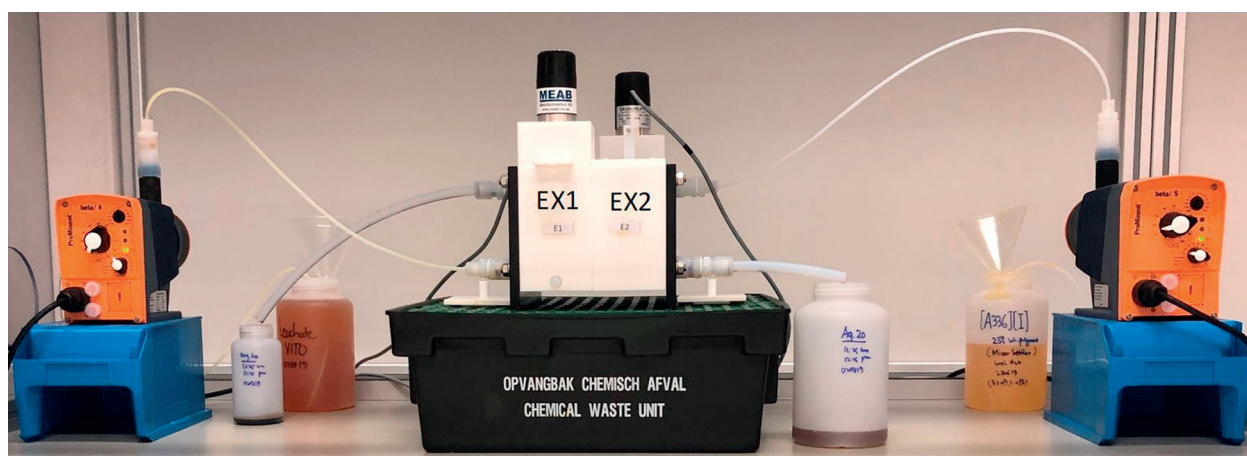


Fig. 14. Extraction of pgms from leachate of spent autocatalyst in two-stage mixer-settlers at KU Leuven. 75% v/v [A336][I] in *p*-cymene (4 ml min⁻¹); Feed (6 M HCl + H₂O₂) (12 ml min⁻¹); two stages; O/A = 1/3; retention time 15 min; 298 K

for analysis and the mixer-settlers start-up and finish steps. These losses are not representative of industrial scale operation in which mixer settlers would operate continuously.

The rhodium raffinate and platinum strip were further processed using conventional chemical transformations to convert the pgms to the nitrate form. The palladium strip was sent for further processing by the GDEx process.

4.3 Recovery: Gas-Diffusion Electrocrystallisation

GDEx attained a recovery of $\sim 70 \pm 1\%$ of palladium from the KU Leuven strip sample (Figure 15). Palladium was recovered with a purity of 91–93%, with platinum, rhodium and aluminium as the major impurities, and additional minor impurities of barium, iron, magnesium, cobalt and copper. Only two batches were processed in comparison to the eighteen leaching batches performed thanks to the up concentration in the solvent extraction process. The selectivity of the recovery can be optimised by further investigation into the effect of the different GDEx operational variables, such as the influent concentration, hydraulic retention time, applied potential or current.

The palladium sponge generated from the GDEx technology was further processed using conventional chemical transformations to convert it to palladium nitrate.

5. Autocatalyst Generation and Testing

To comply with emission regulations, within the autocatalyst the unburnt hydrocarbons are oxidised to CO_2 and H_2O , whilst the toxic gases NO_x and CO are converted to N_2 and CO_2 ; these reactions require a catalyst containing pgms coated onto a porous monolith (58).

In the final validation step of the PLATIRUS project, the industrial end-users aim to test the recovered pgms for their application as emission control autocatalysts. To achieve this, autocatalysts were generated from three sets of pgm origins: benchmark systems using market grade pgm compounds; recycled material from the cascade activity; synthetic solutions which mimic the PLATIRUS outputs in chemical form and purity profiles. This final stage of the project is underway at the time of writing and the outcomes will be disseminated at the culmination of the project.

The autocatalysts were prepared according to the patented wet impregnation method of MONOLITHOS (59) (Figure 16). Firstly, the diameter, length and weight of the cordierites (monolithic carrots or honeycombs) were measured and the amount of washcoat calculated. Before the impregnation, an acetone wash step of the cordierite was performed before drying the cordierite at 105°C and cooling to room temperature. A slurry containing the catalytic



Fig. 15. Electrochemical reactor, pump and recirculation vessels at VITO

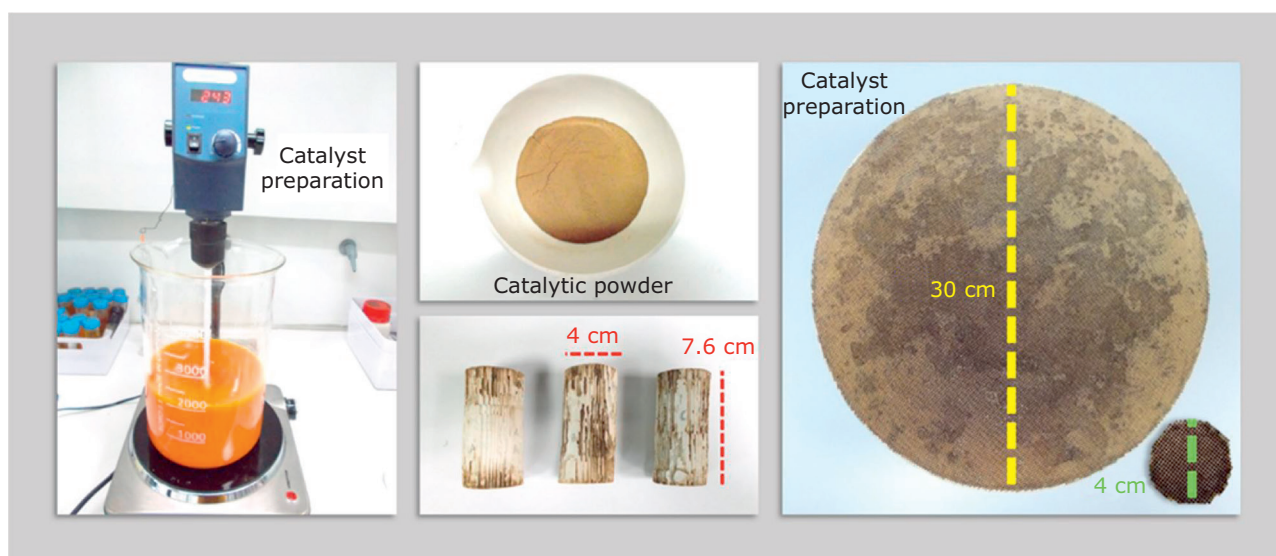


Fig. 16. Catalyst preparation steps. Catalyst nanoparticles are prepared *via* hydrothermal process. Ceramic matrices are used for the catalyst to be impregnated on their surface

Table IV Summary of Autocatalysts Produced in the PLATIRUS Project

Type of feed material	User	Number	Type ^a	pgm loading, g ft ⁻³
Recycled	CRF	2	TWC: test scale	60
Recycled	CRF	2	DOC: test scale	110
Synthetic	CRF	2	DOC: test scale	110
Synthetic	FORD	1	DOC: full scale	30
Benchmark	CRF	2	TWC: test scale	60
Benchmark	CRF	2	DOC: test scale	110
Benchmark	FORD	1	DOC: full scale	30

^aTest scale catalysts have a diameter of 1.5" (3.8 cm) compared to the full-scale catalysts at 12.0" (30.5 cm)

powder and the binder (Al_2O_3 , 10% of the catalytic powder), dissolved in deionised water (volume five times the solid mass) was prepared and the pH adjusted to 7.0 ± 0.1 (at room temperature). The cordierites were impregnated with the slurry and then dried at 105°C while being rotated. Once dried, the cordierites were calcined at 350°C for 1 h. The procedure was repeated until the desired weight increase was achieved and after the final impregnation the cordierites were calcined at 500°C for 1 h. Finally, the catalysts were placed under an air stream and their final weight was measured. The loading was calculated according to the weight increase compared with the original weight of the cordierite used.

Different types of autocatalysts were produced using different pgm loading as well as types of cordierites (900 cells per square inch (cps) hexagonal, 400 cps and 300 cps) (Table IV).

FORD and CRF will age and test their allocated autocatalysts (Table IV) to evaluate their performance as both fresh and aged catalysts for steady state and transient operation. The evaluation will be dependent on the organisation and type of autocatalyst but conventionally includes conversion efficiency of the pollutant gasses *vs.* temperature: (a) NO and NO_2 oxidation; (b) hydrocarbon and CO oxidation; (c) exotherm generation.

6. Next Steps for Selected Technologies

Within the remaining time of the PLATIRUS project to support the flowsheet TRL increase, the following steps will be realised:

- **Optimisation** of the selected technologies for the alternative project feeds: waste electronic and

electrical equipment, metallic foil autocatalysts and tailings from copper and nickel mining

- **Leaching:** VITO will be upscaling to, and testing the leaching process in, an automated and fully monitored litre-scale MW leaching system (10 times scale increase) (**Figure 17**). This will allow VITO to utilise advanced process control, further optimise operational reaction conditions and understand the potential formation of toxic and explosive gases in the reactor headspace
- **Separation:** The loading capacity and the regeneration of the ionic liquids will undergo detailed investigation and waste minimisation will be studied
- **Recovery:** Using other gases to oxygen has shown positive results for pgm recovery and further investigation is required to confirm the exact mechanism to enable optimisation. The GDEx reactor will be further upscaled and the configuration optimised such that the volume processed per day could increase by up to 3000 times with results validated on synthetic solutions
- **Advanced environmental and economic assessment** of the validated technologies in the industrial environment will be conducted through a life cycle assessment (LCA) and life cycle cost (LCC) with the aim to support further technology exploitation and scale-up during and after the PLATIRUS project.



Fig. 17. VITO's litre-scale pressure-sealed MW leaching system with anticorrosion hybrid configuration (synthWAVE/ultraWAVE, Milestone Srl, Italy) in nitrogen-flushed confinement

After the completion of the project, the following aspects should be among those addressed for the PLATIRUS flowsheet and its technologies to progress to higher TRLs and present an offering ready for detailed evaluation by industry:

- Optimisation of H_2O_2 delivery in the leaching process to minimise decomposition before metal oxidation
- Minimisation of impurity leaching to reduce impact on the flowsheet operation and final product purity
- Identification of a platinum stripping agent for the solvent extraction process that has lower toxicity and is compatible with an electrochemical recovery process
- Confirmation of the recyclability of the liquid-liquid extraction organic across its operational lifetime
- Study of GDEx electrode maintenance and degradation to understand the operational life span and optimise the cleaning and regeneration process. Modelling from an electrochemical engineering perspective is required for larger scale-up
- Optimisation of particle size formation of the GDEx nanoparticles considering the downstream filtration process and end product form required
- Colocation and operation of the technologies in closed loop at similar scale to enable the flowsheet to increase to higher TRLs and identify destinations of recycle streams and spent reagents
- Optimisation of the auxiliary processes such as filtration, to ensure that the feed to product process is optimised as these auxiliary processes can have a significant impact on the overall pgm recovery and waste minimisation.

7. Conclusions

The PLATIRUS project has successfully achieved its objective to research, evaluate and upscale novel pgm recycling technologies. The PLATIRUS partners have applied a variety of techniques to recover pgms from secondary source material. Following assessment of the technologies against the project KPIs, the three selected technologies were able to operate in cascade to process a batch of milled spent autocatalysts. The technology readiness levels (TRLs) of the selected processes have increased throughout the duration of the PLATIRUS

Table V Technology Readiness Levels (TRL) of the Selected PLATIRUS Technologies as Described by the EU (60)

Technology	PLATIRUS project start	Post R&I phase	Post autocatalyst processing	PLATIRUS project end
MW assisted leaching	3	4	4	5
Liquid-liquid extraction	3	4	5	5
GDEx	3	4	5	5
PLATIRUS flowsheet	1	2/3	3	4

*TRL1: Basic principles observed; TRL2: Technology concept formulated; TRL3: Experimental proof of concept; TRL4: Technology validated in laboratory; TRL5: Technology validated in industrially relevant environment

project, with the technologies at the start of the project not having been tested in cascade with real life feeds (Table V).

The recycled pgms have been used to produce autocatalyst that will be validated by end users to close the recycling loop. The recycled pgm product purity (92–99%) achieved *via* the PLATIRUS flowsheet is of note. If the technologies were operated at a more industrially relevant scale and the auxiliary processes were optimised, more representative pgm recoveries are estimated by process modelling at ~60–86% for the pgms to sponge. The technologies are ready for demonstration at the next scale and evaluation for industrially relevant feedstocks to further validate their potential.

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