NATIONAL TECHNICAL UNIVERSITY OF ATHENS

SCHOOL OF MINING AND METALLURGICAL ENGINEERING

Recycling of Precious Metals from Automotive Catalytic Converters with Hydrometallurgical Methods

PhD Thesis

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Athens, May 2023

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Introduction

The present PhD thesis deals with the Recovery and Valorization of Platinum Group Metals from Automotive Catalytic Converters via hydrometallurgical processing.

Platinum group metals (PGMs) are widely used in various industrial areas, being part of exhaust catalytic system, electronics, photovoltaics, dental materials, pharmaceuticals, jewelry, nuclear reactors, glass, ceramics and pigments. More than 68% of PGM supply is used in catalytic converters. The processing 2kg of spent automobile catalysts to recover PGMs can prevent the mining of 150kg of their ores. Platinum group metals are rare, due to their low natural resistance, complicated extraction and refining process. Classified as critical raw materials (CRMs), PGMs have high economic importance and supply risk. To conserve the PGM resources and meet the future market demand, it is necessary to develop economical and eco-friendly processes, in order to recover noble metals from secondary resources, particularly from spent automotive catalytic converters. Assuming that secondary PGM resource equals the primary supply, multiple industrial approaches have been developed, such as pyrometallurgy, hydrometallurgy and biometallurgy. Pyrometallurgy has been widely used in factories for many decades and has been further improved. Through the pyrometallurgical process, high recovery rates of PGMs can be achieved (88% Pt, 66% Pd, 57% Rh), especially through PGM-Cu collection technology.

The demand for eco-friendlier, cost-efficient and high purity approaches led to the development of hydrometallurgical processes. Following hydrometallurgical procedures, the PGMs recovery reaches almost 95%, by using various leaching solvents and extractants. As for bio-metallurgical method, bacteria with metal-sequestering properties, like Chromobacterium violaceum, Pseudomonas fluorescens, and Bacillus megaterium, can sequester the dissolved precious metals ions of dilute complex solutions (i.e., cyanide complexes). An optimized bioleaching procedure is capable of leaching Pt, Pd, Rh at a rate of 63.1%, 38.4% and 99.3%, respectively.

Regarding the hydrometallurgical methods, considerable advantages are offered, such as suitability for various scales, use of mild temperatures, waste control and high metal purification. The hydrometallurgical process consists of two main stages, the leaching stage, where metals are leached from their ores in an aqueous media, and the separation stage, where the leached metal complexes are extracted from the pregnant solution. After separation, further refining steps lead to noble metals of high purity.

The PGMs dissolution tends to be challenging, as noble metals are highly resistant to acid solutions. More specifically, Rh forms an oxide protective layer that inhibits Rh complex dissolution. In this aspect, pretreatment stages, such as hydrogen reduction, roasting and calcination, facilitate the dissolution stage. Although pretreatment stages improve recovery rates, such processes tend to be costly and energy-intensive. Remarkably, prereduction in hydrometallurgical processing is quite similar to reduction melting stage in pyrometallurgy, where the noble salts are reduced to their metallic form at temperatures above 250°C. From an environmental viewpoint, strong acid solvents produce remarkable amounts of waste. It has been proved that liquid by-products can be eliminated in case of diluting the acid reagents using lower acid concentrations, or by minimizing total solution volume.

In this thesis, PGMs have been leached directly under mild experimental conditions, by using low acidity reagents, namely the widely tested leaching system, $HCl–H_2O_2–NaCl$ at 70°C for 2 h. The addition of oxidizing agent H_2O_2 together with the additional source of chlorine leads to promising leaching yields for PGMs, prohibiting high acidity. The novelty of the leaching system of this work attributes to high solid to liquid (S/L) ratio reached 70% (w of spent catalyst/v of solution) without any pre-concentration or further pretreatments (reduction, roasting). Moreover, a large homogenized batch of spent automotive catalysts has been gathered, characterized and leached, ensuring reproducibility. The spent catalyst has been characterized by scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy analysis (EDS) and X-ray powder diffraction (XRD). The efficiency of leaching is ensured through X-ray fluorescence analysis (XRF), where the leaching rates of PGMs are determined. As for the XRF analysis, an external calibration has been performed, regarding X-ray fluorescence analysis (XRF) and Inductively coupled plasma-optical emission spectrometry (ICP-OES). Finally, a kinetic evaluation of the leached catalyst sample has been conducted.

The Thesis provides a complete and circular valorization route for the PGM of spent automotive catalysts starting from a critical review of the literature (Chapter 1) of all proposed and state-of-the-art technologies including hydrometallurgical, pyrometallurgical and bio-metallurgical processes [Annex 1]. In Chapter 2, the collection, pre-processing and characterization of bulk spent catalytic monoliths is described. Special emphasis has been given in the calibration of the analytic instrumentation since PGM concentrations are in the area of part-per-million (w/w) and their market cost very high (up to 500,000 Euros per Kg of Rh – prices of July 2022) [Annex 2]. The proposed hydrometallurgical leaching process is described in detail in Chapter 3 [Annex 3] optimized in a way that no chemical or thermal pre-treatment is needed whilst retain low acidity and high Solid to Liquid Ratio (very important industrial parameters). An integrated circular economy model is proposed in Chapter 4 for valorizing the recycled PGMs in the production of new catalysts without the need of purifying them [Annex 4] reducing the process steps/costs. The development of new Three-Way and Diesel-Oxidation Catalysts from recycled (impure) PGMs is described in Chapter 5, whilst their catalytic efficiency (as fresh and as aged catalysts) has been assessed by CRFiat [Annex 5 and Annex 6]. New secondary sources rich in PGMs have been investigated, such as Euro 6 Heavy Duty Emission Devices (Chapter 6 - Annex 7] and End-Of-Life Fuel Cells Devices (Chapter 7 - Annex 8], retaining the same leaching parameters and arriving to extraordinary good leaching efficiencies for secondary sources, for which no commercial technique is applied, yet. Finally, a market analysis is contacted and presented in Chapter 8 to prove the potential of the emission control market for the decades to come. The Thesis is concluded by Conclusion and Future Work Chapter (Chapter 9).

In Annexes 1-8, the full references and the first page of the 8 peer-reviewed publications contacted in the framework of this Thesis are presented. The application of the novel method to the PGM recovery coming from fuel cells and electrolyzers (hydrogen generators) electrocatalysts has been submitted to the Greek Patent Office (patent pending/245-0004386313/1.11.2021).

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I wish to express my gratitude to my children **Vassilis and Maria**, for the long hours I spent away from them trying to accomplish this goal of my life. **Maria and Vassilis** stood by me, with their smile and hug, helping me to overcome all difficulties arisen in the course of the elaboration of this dissertation.

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Unfortunately, **my parents** are not around to celebrate the defense of this Thesis. However, I am grateful to them for teaching me that, with hard work, everything is possible in life. They were not educated or wealthy, however their encouragement to aim high and try to be better every day is following me.

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Dedicated To:

Vassilis and Maria

Maria and Vassilis

and their wonderful mother

Περίληψη

Όλα τα σύγχρονα οχήματα που λειτουργούν με μηχανές εσωτερικής καύσης, διαθέτουν καταλυτικά συστήματα (τριοδικούς καταλύτες για τα οχήματα καυσίμου βενζίνης ή οξειδωτικούς καταλύτες για τα οχήματα καυσίμου πετρελαίου - diesel), με στόχο να μετατρέπουν τα τοξικά αέρια του μονοξειδίου του άνθρακα (CO), των υδρογονανθράκων (HC) και των οξειδίων του αζώτου (NOx) σε μη τοξικά, χρησιμοποιώντας πλατινοειδή μέταλλα, όπως Πλατίνα, Παλλάδιο και Ρόδιο.

Τα πλατινοειδή μέταλλα περιλαμβάνουν τα μέταλλα της Πλατίνας, του Παλλαδίου, του Ροδίου, του Ιριδίου, του Οσμίου και του Ρουθηνίου, τα οποία ανήκουν σε μια μεγαλύτερη κατηγορία υλικών, αυτή των κρίσιμων. Η κρισιμότητα αυτών των υλικών εξαρτάται από την επαρκή τους προσφορά και την κάλυψη της ζήτησης τους για την παραγωγή νέων αγαθών, αλλά και τη συνεισφορά που έχουν στην οικονομική ανάπτυξη της βιομηχανίας και του τρόπου ζωής μας.

Η μακροπρόθεσμη ζήτηση των πλατινοειδών διαφαίνεται να σημειώνει ιδιαίτερη αύξηση, λαμβάνοντας υπόψιν την βελτίωση και την ανάπτυξη νέων πράσινων τεχνολογιών, που στόχο έχουν τη συμμόρφωση με τις οδηγίες της Ευρωπαϊκής Ένωσης για αυστηρότερα όρια στις εκπομπές των καυσαερίων. Η κάλυψη αυτών των αναγκών θα μπορούσε να πραγματοποιηθεί είτε με αύξηση του ρυθμού εξόρυξης αυτών των μεταλλευμάτων είτε με την ανακύκλωση συσκευών/υλικών μετά το τέλος ζωής τους, ανακτώντας τις απαιτούμενες ποσότητες πολυτίμων μετάλλων. Καθώς η διαδικασία και οι μέθοδοι της εξόρυξης είναι πολύ κοστοβόρες και ενεργοβόρες, ενώ ταυτόχρονα παράγονται δυσανάλογα μεγάλοι όγκοι αποβλήτων σε σχέση με τη συγκέντρωση των μεταλλευμάτων, η ανακύκλωσης αποφαίνεται πιο οικονομικά συμφέρουσα και περιβαλλοντικά φιλική. Για παράδειγμα, τα μεταλλεύματα των πλατινοειδών της Νοτίου Αφρικής, η οποία είναι από τους κύριους εξαγωγείς Pt, παγκοσμίως, διαθέτουν μόλις 2-6g/t πολυτίμων μετάλλων, ενώ ένας απενεργοποιημένος καταλύτης αυτοκινήτου, περιέχει 2000g/t πολυτίμων μετάλλων, καθιστώντας τους ιδιαίτερα ελκυστική λύση για την εξαγωγή πολυτίμων μετάλλων.

Στη παρούσα εργασία παρουσιάζεται ένα ολοκληρωμένο βιομηχανικό μοντέλο κυκλικής οικονομίας σύμφωνα με το οποίο περιγράφεται η χρήση των πολυτίμων μετάλλων τα οποία έχουν ανακτηθεί από δευτερεύουσες πηγές και πρόκειται να χρησιμοποιηθούν στην παραγωγή νέων υλικών, εξίσου αποδοτικών με αυτά εξ ων ανακτήθηκαν.

Τα επιμέρους χαρακτηριστικά βήματα τα οποία συνθέτουν το κυκλικό μοντέλο περιγράφονται λεπτομερώς σε κάθε κεφάλαιο που ακολουθεί. Στα κεφάλαια που ακολουθούν αναλύονται τα βήματα της προ-επεξεργασίας των πηγών που περιέχουν τα πολύτιμα μέταλλα, θα περιγραφούν και μέθοδοι με τις οποίες γίνεται η εξαγωγή των μετάλλων (leaching) σε μορφή αλάτων του χλωρίου, η μετατροπή τους σε νιτρικά άλατα (όπου απαιτείται), η εναπόθεση τους σε νέα υποστρώματα και τέλος η δημιουργία νέων υλικών καθώς και η αξιολόγηση τους όσον αφορά στην καταλυτική τους ενεργότητα.

Παράμετροι που επηρεάζουν την απόδοση της ανάκτησης των πλατινοειδών μετάλλων, όπως το είδος διαλυτών, τα οξειδωτικά μέσα, ο χρόνος ανάδευσης και η θερμοκρασία, μελετήθηκαν συζητούνται εκτενώς. Η υδρομεταλλουργική μέθοδος που αναπτύχθηκε, χρησιμοποιήθηκε για την ανάκτηση πολυτίμων μετάλλων από απενεργοποιημένους καταλυτικούς μετατροπείς αυτοκίνητων (τόσο μικρών οχημάτων – τριοδικοί καταλύτες – όσο και βαρέων οχημάτων – οξειδωτικοί καταλύτες) και πολυμερικές ηλεκτρολυτικές μεμβράνες από κελιά καυσίμου (Fuel Cells) και συσκευές παραγωγής υδρογόνου (electrolyzers).

Τέλος, το μοντέλο της κυκλικής οικονομίας συμπληρώνεται με την παρασκευή νέων υλικών, τόσο τριοδικών όσο και οξειδωτικών καταλυτικών μετατροπέων και την αξιολόγηση της καταλυτικής τους ενεργότητας αναφορικά με τους καταλύτες πρώτης τοποθέτησης. Επιπλέον, πραγματοποιείται η ανάλυση της αγοράς για την παρασκευή καταλυτικών μετατροπέων εξ’ ολοκλήρου από ανακυκλωμένα μέταλλα.

Abstract

Every modern vehicle equipped with an internal combustion engine possess catalysts (Three-Way Catalytic Converters for petrol engines, or Diesel Oxidation Catalysts for diesel engines), in order to reduce efficiently the emission of harmful compounds like carbon oxides (CO), hydrocarbons (HC) and nitrogen oxides (NOx). Car manufacturers mainly use platinum group metals (PGMs) such as platinum, palladium and rhodium to perform these catalytic functions.

In general, the platinum group metals are comprised of six similar elements: iridium, osmium, palladium, platinum, rhodium and ruthenium. These elements are included by the European Commission in the list of critical raw materials, based on their economic importance and supply risk. The long-term demand fundamentals for PGMs are strong, with their consumption closely related to the global green energy transition and imposition of stricter emissions standards – particularly in the automotive sector. Recycling could contribute to the reduction of supply risk and increasingly cover the future PGM demands in the EU and globally. Moreover, concerning the advantages of recovering precious metals over their mining, these are mainly their limited resources, scarcity, expensive and energy-intensive mining process and the significant amount of waste generated during this process. Platinum group metal ores contain very small amounts of these metals. For example, in South Africa (the largest producer of platinum), PGM bearing ores have a low content of between 2 and 6 g/t . At the same time, it should be noted that automotive catalytic converters typically contain up to 2000 g/t PGM in the ceramic catalyst brick, the active part of the converter. Therefore, due to the high value of PGMs and the fact that autocatalysts comprise a rich source of PGMs, the attractiveness to recover those metals from end-of-life products such as spent autocatalysts, is extremely high.

In the specific thesis, an industrial driven, integrated ***circular economy*** model is proposed for the sustainable valorization of platinum group metals (***PGMs***) contained in automotive catalytic converters. The 4 main steps of the cycle are, a) pre-processing, b) leaching/recovering c) new catalyst preparation from recovered (impure) material, and d) introduction to the market of the new catalysts. The circular economy model is based on leaching/recovering of PGMs with an industrially optimized

hydrometallurgical method from spent automotive catalytic converters and the preparation of new catalyst from recovered material. State of the art methods, principles and theory on PGMs extraction are described in detail providing an insight of the advantages and difficulties of each process.

Several parameters, such as temperature, acidity and time, have been studied and examined for the hydrometallurgical method to be optimized for automotive catalysts. A novel hydrometallurgical process has been developed, resulting in recovery rates for Pt, Pd and Rh, namely, 100%, 92% and 61%, respectively. In order to highlight the importance and significance of recovering PGMs, alternative secondary sources, such as membrane electrode assemblies from spent fuel cell and electrolyzers and emission control devices derived from Euro6 heavy duty vehicles have been examined.

Recovered material has been used to produce new three-way catalysts and diesel oxidation catalysts and their catalytic activity has been validated on a synthetic gas bench. Their performance has been discussed in terms of commercial benchmarks. Finally, the essential market analysis has been conducted for the manufacturing of automotive catalytic converters (ACC) integrating 100% recycled PGMs.

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1st Chapter

1. Literature review of state-of-the-art technologies for recycling of automotive catalytic converters

1.1. Introduction

The Platinum Group Metals (PGMs), i.e., Pt, Pd, Rh, Ru, Ir and Os, are classified by the European Commission as a Critical Raw Materials (CRMs). Moreover, PGMs are used in a wide range of industrial applications for which there are often no substitutes. Platinum Group Metals (PGMs) are widely used in high-tech applications ameliorating the quality of life, due to the unique properties of high corrosion and oxidation resistance, high electrical conductivity and catalytic activity. In this context, the European Union (EU) is the world's largest consumer of PGMs in industrial applications, with a demand of 69 t/year approximately (worth more than 3b€ with current PGMs prices), with ~70% channeled currently to the production of automotive catalysts (autocatalysts, see **Figure 1.1).** However, the primary production of PGMs in the EU is insignificant, since about 64% of the global supply (364 t) comes from South Africa and Russia, countries where long-term stability is not assured due to geo-political conflicts. More precisely for the primary production of PGMs, mining ores are divided to Platinum Group Element (PGE) dominant ores (Merensky Type, Chromite Type, Placer Type, Dunite Pipe), Ni-Cu dominant ores (Class I-IV Ni-Cu Ores) and miscellaneous ores (Copper Molybdenum Ores, Ni Laterites, Black Shales, Carbonate Ores, Porphyry Copper Ores). Both PGE and Cu-Ni dominant ores are feasible ones for exploitation. On the other hand, PGM content in miscellaneous sources is very low; therefore, the recovery is not possible or has little economic advantage for the primary producers [1, 2].

Figure 1.1: Automotive catalysts

Only about 25% of the worldwide PGMs supply comes from secondary resources (catalysts, jewelry, high-grade PCBs), while mining of primary deposits, localized in geopolitically sensitive areas, presents extensive operational costs and environmental footprint. Most of the large recycling companies (e.g., Umicore, Johnson Matthey, BASF and Nippon PGM) apply pyro-/hydro-metallurgical processes for the recovery of PGMs. However, these routes still suffer from high energy consumption, high environmental footprint and adverse impacts to both human health and environment, such as those caused by Pb-collectors in the smelting process. Additionally, there is still a large untapped potential for the recycling of End-Of-Life (EoL) autocatalysts in

Europe and neighboring countries, as more than 4 million European end of life vehicles (ELVs), 40% of the total ELVs, exhibit unknown whereabouts. Most of these ELVs are abandoned or hoarded, causing a loss of approximately 8t of PGMs/year for the EU-27 countries. 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, while also dramatically reducing the environmental impact of PGMs when compared to primary sources: high energy use, large amounts of waste from mines and significant CO_2 emissions.

The common extraction process refers to pyrometallurgy combined with hydrometallurgy, where platinum group metal ores (e.g., Merensky Reef ore grades contain 3-8g/t PGMs, associated with nickel, copper, as sulfides) are mined, grinded and subjected to gravity separation and flotation. Thereafter, PGM ore concentrate (typically 200 to over 2000g/t PGM with 0.4%-2.8% Cr_2O_3) is melted at high temperatures (> 1500^oC) and PGMs are refined via hydrometallurgy [3]. According to hydrometallurgical process, PGM-contained matte is leached into an autoclave under high pressure conditions to oxidize sulfur to sulfates; then, PGMs separation and refining lead to the lowest impurities content. Process difficulties, such as PGMs ore oxidation, remobilizations and additional metal content during floatation, should be considered. It should be highlighted that during PGMs ore treatments, considerable amounts of PGMs are getting lost, affecting the global economy. In general, 27% of total PGMs loss occurs during the mining process, compared to 15% of overall processing. Besides, 13% PGMs loss refers to the concentration stage [4].

Concerning primary production feasibility, PGMs content is quite low (~10g/ton), PGM ratio varies and high energy is consumed. Moreover, even the smelters/refineries recover almost 96% of PGMs, recovery efficiency is only 85% of PGMs. Compared to primary production, secondary resources exploitation is preferable, since higher PGMs concentrations are involved, 70-100 times less energy is consumed, higher recovery yields are achieved and the environmental footprint, highly-related to mining, is improved.

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

EoL vehicles recycling is a well-established process, including EoL catalyst collection, sorting, dismasting (i.e., metallic cannister removal) and crushing of the catalyst monolith. Thereafter, the crushed monolith is grinded and milled, in order to obtain a fine powder [6]. The obtained powder, concentrated in PGMs, is subjected to recovery techniques, such as pyrometallurgy, hydrometallurgy and biometallurgy processes. Nowadays, state-of-the-art recovery approaches focus not only on higher PGMs recoveries, but also on economic and environmental perspectives following the rules of the green principles (**Table 1.1**).

There are several PGM refining facilities across Europe but almost all of them 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. 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 have been assessed for autocatalysts recycling with the focus on reducing the environmental impact of PGM recycling. The hydrometallurgical dissolution of the spent autocatalyst using aqua regia, cyanide or strong acids (HCl, HNO_3 or H_2SO_4) usually combined with an oxidizing agent which is the most commonly used dissolution process. Among these, cyanide leaching was widely implemented for its high dissolution efficiency. However, due to the severe toxicity and energy consumption, it has been replaced with less hazardous 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, the most employed by global refineries are solvent extraction and multi-stage precipitation techniques. Although solvent extraction is mostly preferred due to its high efficiency and selectivity, efforts are still made to find safer and environmentally friendly organic extractants and diluents without compromising the efficiency that has already been achieved. Moreover, modifications and improvements ought to take place throughout PGM recycling flowsheet not only to solvent extraction but also for other industrially employed processes as well.

To date, 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.

This chapter provides an overview summarizing the most promising technologies proposed in the literature. The great majority of them are at the research and innovation development phase. Discussion on the most promising technologies, operational parameters, objectives and environmental validation is also provided.

Automotive catalytic converters consume the largest amount of PGMs, estimated that above 360t of PGMs are required for the production of autocatalysts for the year 2018 [7]. Regarding the recycling of spent automotive catalytic converters, spent catalyst feed is to be received, focusing on homogeneous sampling and precise assaying, aiming at the PGMs upscaling recovery. Pyrometallurgy, hydrometallurgy and biometallurgy methods and parametrization of each method are reported, focusing on hydrometallurgical leaching trends.

1.2. Pyrometallurgy

Pyrometallurgy has been widely applied by automotive catalyst recycling industries. In general, pyrometallurgical procedure is automated, used to upscale recovery and offers promising recovery yields. Nevertheless, special equipment is required, high temperatures and energy demand are incorporated and significant waste is produced (e.g., volatile waste, slag), resulting in high capital and operational cost. A significant drawback of pyrometallurgical processes is the cost of oven continuous operation. Due to this reason, great variety of secondary resources are used as feed (automotive catalysts, electronic scrap, industrial scrap), in order not to disturb the operation. Such variety of secondary feedstock results in high concentration of impurities.

Novel pyrometallurgical techniques focus on appropriate metal collector/flux use, milder smelting conditions, and pretreatment of the feed material [8]. New trends for smelting refer to plasma smelting technology [9] and fluxes incorporation (CaO, CaF_2, cryolite) [10]. On the one hand, plasma smelting achieves high recovery yields, while generates less wastewater and gas emissions. Smelting is the most crucial step in pyro-recovery and several challenges must be overcome, such as sulfur dioxide emissions generated from sulfur-matte exploitation and chromite contaminations, which limit PGM recovery and create hazardous working conditions.

Melting to slags/alloying with metal collector and chlorination/fluorination are common methods used [10]. Moreover, electrorefining, matte leaching (pyro-, hydro-metallurgy) and cementation offer promising PGMs recovery yields. In the case of spent catalytic converters recycling, spent monolith is crushed, milled and smelted (> 2000^{o}C), while feed material is mixed with fluxes, collector metals and additives. Thereafter, PGM concentrate is separated and further refined (**Figure 1.2**). It should be noted that materials used in autocatalytic converters, such as CeO_2, ZrO_2 and Al_2O_3, exhibit high economic value as well, but slag melting process challenges their co-extraction.

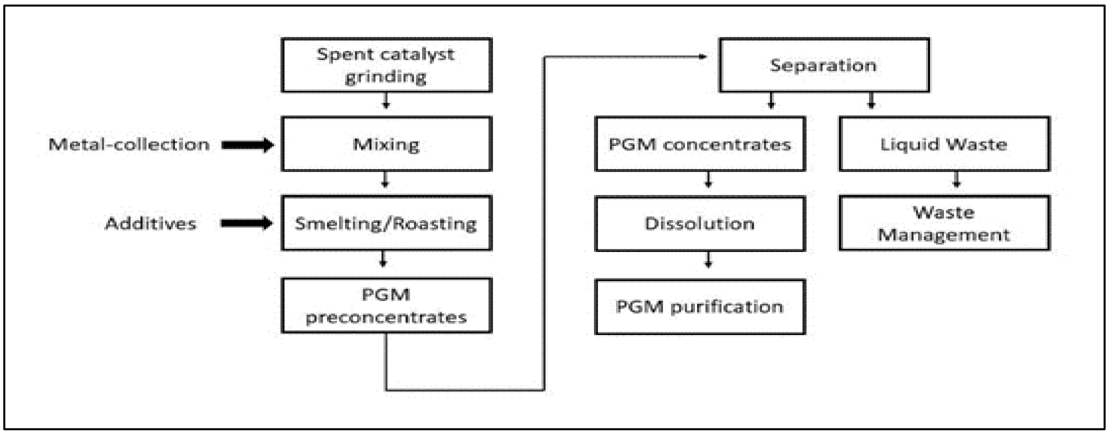

Figure 1.2: Pyrometallurgy combined with hydrometallurgy for PGMs recovery

1.2.1. Smelting in presence of a metal collector

Metal smelting collection is the most mature technique used in plants, where the crushed catalyst mixed with fluxes is melted into a crucible, which contains a collector metal (> 1600°C), such as Cu, Fe, Pb, Ni or mattes (Ni_2Se_3-CuS). After melting, the base metal is removed and PGMs are refined. Generally, matte separation is well known for metal-bearing sulfide ores in primary PGMs production, where PGMs are collected from metal base-rich matte placed into an electric furnace. Then the base metal incorporated into catalyst is extracted and PGMs content is obtained as a residue [11]. The melting point, the rheological behaviour, the solubility, the droplet size, and the environmental factor are parameters to be controlled. Moreover, it is possible for impurities to form complexes with PGMs during the melting high temperature stage.

Regarding copper-collector for the PGMs recovery, the feed material is smelted into an electric arc furnace (1450-1600°C) with fluxes (e.g., SiO_2, CaO), copper collector (e.g., CuO, $CuCO_3$) and reductants [8]. Another efficient copper-collection technology refers to crushing, milling, homogenization, pelletizing, drying, melting, and electrolytic refining, where the final anode contains 20-25% PGMs [12]. As for iron-collection method, smelting with plasma smelting technology at 1500–2000°C results in promising recovery rates, where 7% PGM pass through the iron phase. During lead collection, the spent catalyst is grounded, mixed with additives (e.g., Na_2CO_3, $KC_4H_5O_6$) and smelted (1100°C). Thereafter, lead volatilization and final purification are followed. Although the Rh recovery is around 70-80% [13], PbO emissions should be taken under consideration.

1.2.2. Chlorination-volatilization

Using pyrometallurgy to convert PGMs to chlorine species, dry chlorination should be performed on the recycled material. When this method takes place in low temperatures, then then chlorine PGMs species remain solid and H_2O or HCl is required to get these species in aqueous solutions. On the other hand, when this recovery method takes place in high temperature, then chlorine species become gases and are condensed either in a cooling stream or diluted in H_2O or HCl solvents [14]. According to Dong et. al., recovery rates of 95%Pt and 92%Rh were obtained by incorporating carbochlorination using CO/Cl_2 (4:6) system at 550°C for 1h. It should also be mentioned that during carbochlorination, hazardous CO and Cl_2, which have a negative environmental footprint, were emitted.

1.3. Hydrometallurgy

Hydrometallurgy, under specific conditions, can contribute to PGMs sustainability in an eco-friendlier manner than pyrometallurgy. Compared to pyrometallurgy, hydrometallurgy offers several advantages, such as higher purification yields, scalability, milder process temperatures, minimized energy consumption, process control and promising recovery yields. However, waste management (liquid wastes, gas emissions), the duration of the process, as well as the reagents cost and the environment should be considered [15]. Concerning the stages of hydrometallurgy, during the leaching stage PGM-complexes are formed (with or without pretreatment); then, the dissolved PGM precursors are separated from the leaching media and refined via purification. Regarding thermodynamics, high stability of the metal complexes enhances the dissolution efficiency. Leaching efficiency is affected by leaching reagents concentration, specified solid-to-liquid ratio (S/L), particles size, entrapment of soluble species into less soluble/insoluble ones, pH value of leachate, leaching temperature, stirring conditions and leaching duration [16].

Regarding spent catalyst recycling, feed material is grinded and homogenized, in order to be further dissolved (**Figure 1.3**). Various leaching systems have been examined, such as aqua regia (HCl/HNO_3), cyanides (CN^-), mineral acids (H_2SO_4, HCl, HNO_3), chlorides (NH_4Cl, $CuCl_2$, $FeCl_3$), hydroxides ($NaOH$, NH_4OH) and carbonates (Na_2CO_3, $(NH4)_2CO_3$) [17]. State-of-the-art leaching systems focus on eliminating the reagents toxicity, reduce or eliminate waste generation, improve recovery yields, minimize the process duration, as well as the energy consumption (**Table 1.1**).

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

Table 1.1: State-of-the-art leaching requirements

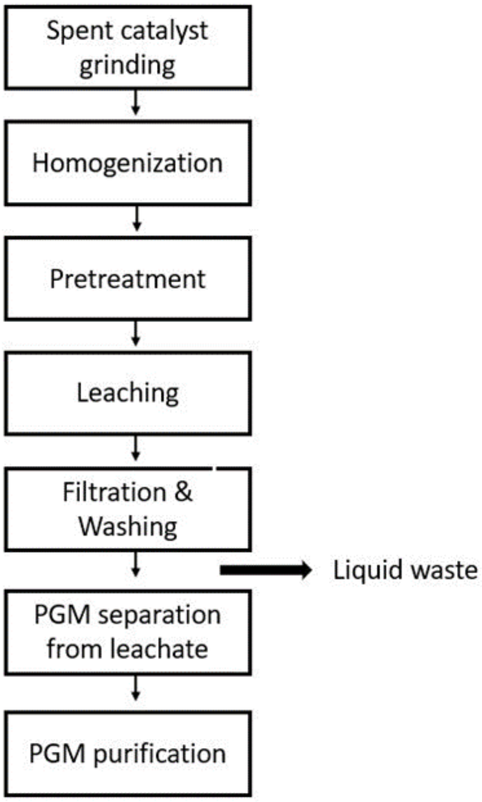

Figure 1.3: Hydrometallurgical process for PGMs recovery

Among leaching systems, the chloride-based system is mainstream and thoroughly investigated, where PGMs chloro-complexes are quite stable in chloride acid solutions (**Table 1.2**), and consequently, the noble complexes can be easily dissolved [18]. The most stable chloro-complexes refer to $PtCl_6^{2-}$, $PdCl_4^{2-}$ and $RhCl_6^{3-}$ for Pt, Pd, Rh, respectively [19]. It should be mentioned that the chloro-complexes formation highly depends on chlorinating media concentration, where hydrochloric acid and additional Cl^- sources could be used in balance.

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

Table 1.2: The PGMs (Pt, Pd, Rh) chloro-complexes

Concerning the recovery of PGMs from the pregnant leachate solution, precipitation [20] solvent extraction [21], ion exchange resins [22], cementation [23], ionic liquids [24], deep eutectic solvents (DES) (ionic liquid group) [25], switched solvent systems [26], electrowinning [27], molecular recognition technology [29] and cloud point extraction [29] have been proposed. It is vital that recovery methods require the minimum possible steps, utilize non-hazardous reagents and increase the cost savings. The most popular recovery methods refer to precipitation, solvent extraction and ion exchange, while molecular recognition technology, optimized ionic exchange resins and greener solvents (e.g., switched solvent systems, Deep Eutectic Solvents (DES), ionic liquids) are the newest and most promising methods used (**Figure 1.4**). Another promising upscaling technology refers to electrowinning, where high purity separations are achieved, as well as inexpensive equipment is used. In summary, each separation method should be tested on scale-up to ensure their industrial competitivity.

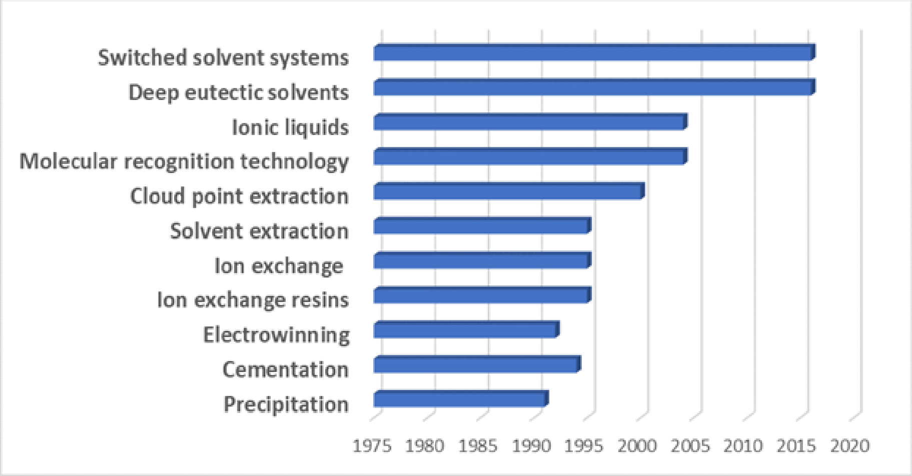

Figure 1.4: The most common extraction methods for precious metals over the years from 1975 to 2016

Beyond any doubt, refining is the most expensive and challenging stage of PGM recovery, because of the noble metals common chemistry, the cost of the reagents, and the duration of the process. The main PGM refiners include Johnson Matthey, BASF, Umicore, Anglo American, Krastsvelmet refinery and Vale Refinery. During the complex refining cycle, PGMs are precipitated as complex salts, PGM salts are recrystallized and calcinated into electric furnaces under controlling conditions, producing PGMs foams or pure powders [30]. Another refining process relates solvent extraction with ion exchange [31]. Common ion exchange resins use refers to the final refining stage and extraction of low concentration target metals, due to their expensive supply. In case of electrorefining, the anode refers to the impure metal and the cathode to the pure metal. A promising refining technique refers to the combination of solvent extraction with electrowinning (SXEW), resulting in faster and higher copper refining levels than the one achieved via solvent extraction [32]. Therefore, an investment in SX/EW technique for PGM refining could be supported.

1.3.1. Pretreatment stages

Pre-treatment techniques before leaching process improve the dissolution rate, avoiding the use of high acidity solvents. Reduction roasting, oxidative roasting, alloying and mechanochemical activation are basic pretreatment methods used. Through reduction roasting, PGMs passivation layer is removed, especially in case of Rh, stabilizing noble metallic form. As for oxidative roasting pretreatment, PGMs metallic phases (or alloys) are formed, while base metal sulfides are converted to metal oxides. Oxidation heating is also performed to remove metallic surfaces impurities, inhibiting the PGMs recovery [33]. In the case of spent automotive catalytic converters, oxidative heating tends to remove unburned hydrocarbons that deteriorate the catalyst surface being chemically attacked.

Calcination treatments involving salts (Na, Li, K) at temperatures higher than 800°C accelerate the leaching kinetics. Concerning PGMs alloying treatment, alloying with more reactive metals (Cu, Pb, Ni, Al) promotes the base metals leaching; consequently, PGMs surface is more easily exposed to chemical interactions. As for the mechanochemical activation, milling and leaching take place simultaneously, minimizing the process cost by reducing duration and steps [34].

In the case of Rh, reductive heating under H_2 conditions results in almost 80% Rh recovery yield. Otherwise, Rh kinetics are very slow, requiring stronger leaching conditions. Common reductive agents include formic acid, Al powder, $AlCl_3$, NaOH, thiourea and sodium borohydride. As for formic acid reduction pretreatment, leaching efficiency is ameliorated at lower lixiviant concentrations, minimizing the environmental impact and the cost of the reagents used [35]. Another pretreatment refers to calcination at 800°C with 10 wt.% Li_2CO_3, where leaching in HCl media results in Pt and Rh 95% and < 50% for Pd recovery yields, respectively [36]. It is also proposed that recovery of PGM-Zn alloy from spent automotive catalytic converters is achieved by reduction pretreatment with Zn-vapour, where leaching in aqua regia of hydrochloric acid is further improved [37]. Concerning mechanochemical pretreatment, the PGM-rich waste is mechanically activated in proportion to oxidizing agent and complexing agents; then, the as-activated waste is leached in chlorinating media, resulting in recovery yields of 77%, 62% and 97% for Pt, Rh, Pd, respectively [38].

Referring to cyanide leaching, stable PGMs complexes are formed but slow kinetics of this process require higher temperature and pressure. It is evident that pretreatments and leaching stimulation techniques tend to improve the leaching conditions, where aqua regia and cyanide-based systems are used. The amelioration of aqua regia leaching (HCl/HNO_3) has been investigated by several groups such as [39, 40, 41] as well.

1.3.1.1. Conventional acid leaching systems

Long-established leaching systems utilize aggressive leachates, such as high acidity aqua regia (HCl/HNO_3) and cyanide solutions media (CN^-, sodium cyanide). Referring to cyanide media leaching, PGMs deriving from spent catalysts have been recovered via autoclave leaching using solution of NaCN-NaOH system at 160°C [42]. Cyanide solution is hydrolyzed at temperatures higher than 100°C, where temperature effect is linear to hydrolysis rate. Referring to the dissolution of Pt-complex into aqua regia, the activation energy for leaching Pt is suggested to be 72.1 kJ/mol, as the reaction is controlled by surface chemical reactions [43]. Aqua regia and cyanide media systems tend to be replaced, because of hazardous waste produced during the decomposition of gaseous products (NOx, Cl_2, acid fumes), leading to unhealthier working conditions. The exposure to hazardous by-products could be limited, in case of feed material pretreatments.

The mainstream for PGMs leaching refers to HCl-H_2O_2 system (**Table 1.3**). The addition of oxidizing agents is preferential, since it leads in greener leaching. Leaching system HCl (12M)-H_2SO_4 (18M)-H_2O_2 (10% v/v) results in 95% PGMs recovery at 90°C for 6 h, after hydrogen and thermal treatments (250°C, 22 h), while the oxidizing agent H_2O_2 implies the reduction of the pollutant gases [44]. In the work of Sarıoğlan *et al.* [45], the utilization of HCl (10%)-H_2O_2 (5%) media at 90°C for 3h resulted in 98% recovery yield for Pd; thereafter, precipitation by using 7% $NaBH_4$ at reduction temperature of 100°C follows. In the work of Sun *et al.* [46], roasting treatments (700-900°C, 10°C/min) tend to improve the leaching rate of the HCl (10%)/H_2O_2 (1%) system. The well-tested HCl (2M)-H_2O_2 (1M) system has been used at 25°C for 1h, where 84% of Pd was recovered after 10min of dissolution [47].

Leaching System	Reagents and Processing	Pretreatment	Extraction	Aspects	Reference
Acid leaching	HCl(12M)-H_2SO_4(18M)-H_2O_2 at 90°C, 6 h	Thermal treatment (250°C, 22 h)	95% of PGMs	H_2O_2 implies reduction of pollutant gases	*[44]*
Hydrochloric acid	HCl(2M)-H_2O_2(1M) at 25°C, separate Pd (II) from Al (III)	No pretreatment	90% Pd	Al (III) shows a harmful effect on the solvents	*[6, 14]*
Hydrochloric acid	HCl(5M)-NaClO(3%)- H_2O_2 (1%) at 65°C, 3 h	Hydrogen reduction	Pt 88%, Pd 99%, Rh 77%	Lower acidity	*[48]*
Hydrochloric acid	HCl-H_2O_2-O_3 system at 60°C for 0.5-4h and residue aqua regia leaching	No pretreatment	48% Pt for 3g/h O_3 flow	Alternative oxidizing agent O_3	*[5]*

Table 1.3: Description per leaching system

1.3.2. State-of-the-art leaching systems

Hydrometallurgy trends refer to sustainable leaching systems, by using non-hazardous reagents (H_2O_2, NaCl, NaClO, $NaClO_3$, O_3, HNO_3), as well as by following milder leaching conditions (lower acidity, milder temperature, shorter leaching duration). The HCl-H_2O_2 leaching system has been further improved following greener principles, when balancing HCl/H_2O ratio and with the addition of oxidizing agents and chlorinating sources (NaClO, NaCl, $AlCl_3$, $CuCl_2$) (**Table 1.4**).

In the work of Harjanto *et al.* [48], HCl(5M)-NaClO(3%)-H_2O_2 (1%) upon leaching at 65°C for 3h, Pt 88%, Pd 99% and Rh 77% recovery yield was achieved, with the aid of reduction pretreatment. By the partial substitution of HCl with NaClO, lower acidity is adjusted without changing the dissolution efficiency of PGMs [48]. Referring to NaCl additional source, leaching system HCl-H_2O_2-NaCl has been used after calcination (600-1000°C) at 90°C for 2h, suggesting that HCl concentration is the most crucial factor, compared to S/L ratio and H_2O_2 concentration [49]. An alternative oxidizing agent was used, namely O_3 under hydrochloric acid environment [50], proving that under high temperature conditions 21.1% of Pt is recovered, by using 1 g/h flow of O_3, while 47.8% Pt, by using 3 g/h flow of O_3.

Concerning additional chloride sources, in the case of $AlCl_3$, three chloride ions per molecule are incorporated, and it is believed that aluminum addition reduces the substrate dissolution [53]. In the study of Angelidis [51], PGMs were leached into HCl (5%)-$AlCl_3$ (0.33M)-NaOCl (4%) at 70^{o}C for 1h, after reduction pretreatment with acid H_2SO_4 (10%) and reductive agent $N_2H_6SO_4$ (0.1M), resulting in recovery yields of 90-99% for both Rh and Pt, while alse $AlCl_3$, $Al_2(SO_4)_3$ and CeO_2 can be recovered. As for the $CuCl_2$ as an additional source, Rh-complex dissolution seems to be affected both by leaching temperature and leaching duration. Concerning $CuCl_2$ engagement, leaching is conducted at relatively low acid and high cupric ion concentrations, otherwise lower Rh yields (20-38%) were achieved [52]. As for the NaCl as a source, H_2SO_4 (60%)-NaCl (0.1M) leaching at 125^{o}C for 2h, where leaching residue was filtered and washed with bi-distilled water acidified with 5% aqua regia, leaded to promising results (95% Pt, 85% Rh, 85% Pd). It is remarkable that leaching order varies when changing the acid concentration, namely Pd>Pt>Rh using 50% H_2SO_4, but Pt>Rh>Pd for higher acid concentrations.

Leaching system	Source of Cl^- ions	Extraction	Reference
HCl(5M)NaClO(3%)H_2O_2(1%) at 65^{o}C, 3 h	NaClO	Pt 88%, Pd 99%, Rh 77%	*[48]*
HCl(5%)-$AlCl_3$(0.33M)- NaOCl(4%), at 70^{o}C, 1h	$AlCl_3$ & NaClO	90-99% Rh, Pt	*[51]*
HCl(6M)-$CuCl_2$(0.3M) at 80^{o}C, 4h	$CuCl_2$	95% Pd, 86% Rh	*[52]*
H_2SO_4 (60%)-NaCl (0.1M) at 125^{o}C, 2h	NaCl	95% Pt, 85% Rh, 85% Pd	*[39]*

Table 1.4: The PGMs (Pt, Pd, Rh) chloro-complexes

Iodide-iodine leaching media is used for gold extraction, but researchers have also managed to dissolve PGMs into iodine-based leaching media [53]. In the study of Dawson and Kelsall [53], dissolution of Pt from secondary materials into iodine leaching achieved under milder conditions, recovering > 99% of Pt content on graphite spheres. Moreover, Pt, Pd iodo-complexes were dissolved under high pH conditions, preventing the stabilization of oxide phases; thus, it is suggested that iodide/tri-iodide species could be used as oxidizing agents, where triiodide (> 1M) can effectively dissolve Pd under mild conditions.

It has been demonstrated that pre-treatment are widely used affecting acidity requirements and acting synergistically to the final purification yields. On the other hand, pre-treatments are, most of the times, costly and time consuming procedures that incorporate reduction of the catalytic powder in controlled nitrogen atmosphere and/or high temperature operations. According to Yakoumis *et al.* [54], a state-of-the-art industrial one-step leaching process is suggested. The leaching rates presented are 100%, 92% and 61% for Pt, Pd and Rh, respectively. Given the complexity of the composition, morphology and the original manufacturing process of the spent catalyst, and the aging the spent catalyst has been subjected into, there are several reasons the relatively low Rh recovery rate can be attributed into. The catalyst may sometimes adsorb organic matter and bring in other impurities, resulting in carbon accumulation on the catalyst surface. Therefore, according to the physicochemical properties of different types of catalysts, organic compound may hinder the leaching of the metals out of the carrier. Moreover, the encapsulation of platinum-group metals by catalyst carrier could be a possible reason for limited leaching out of the spent catalyst. Dissolution is one of the most important steps in separating the carrier (cordierite) from the platinum-group metals in spent catalysts, and three methods are commonly used: carrier dissolution, active component dissolution, and total dissolution. The carrier dissolution method is to dissolve the failed catalyst carrier so that the platinum-group metals are enriched in the insoluble slag, which has stable chemical properties and is difficult to be eroded by common mineral acids. The spent catalyst carrier alumina, however, is an amphoteric oxide that is both soluble in acids to produce aluminum salts that are easily soluble in acidic solutions ($pH < 4$) and in bases to produce partial aluminates that are easily soluble in alkaline solutions ($pH > 13$). Therefore, acid-soluble or alkali soluble methods are used to treat alumina carrier catalysts so that they are transferred into solution and separated from the active component to enrich platinum-group metals. The carrier dissolution method is suitable for the treatment of catalysts with γ-Al_2O_3 carrier, but if the carrier is α-Al_2O_3, the dissolution rate is not high and other methods must be used to separate α-Al_2O_3. In addition, the alkali dissolution method requires much equipment and the operation of solid-liquid separation is difficult, so it is not used much in practice. The active component dissolution method, which is the opposite of the carrier dissolution method, refers to the use of one or more oxidant hydrochloric acid solutions to dissolve the platinum group metal components in the waste catalyst, so that the $PtCl_2^{-6}$, $PdCl_2^{-}4$, $RhCl_3^{-6}$ ion form into the solution, and are then extracted from the solution. With the active component dissolution method, the reagent consumption is low, the recovery cost is low, and the recovery rate is high, but the leaching residue still contains a high level of platinum-group metals and impurities, which will cause a lot of waste if not recovered efficiently. In contrast, the total dissolution method is to dissolve both the carrier and the active component of the spent catalyst into solution in the presence of an oxidizing agent, mixed with one or two acids, and then extract the platinum-group metals from the solution. High recovery of platinum-group metals can be ensured, but the acid consumption is high, the treatment cost is high and, like the carrier dissolution method, it is only suitable for the treatment of catalysts with γ-Al_2O_3 as a carrier. Currently, the recovery of remaining Rh catalyst relies mainly on a combination of pyroprocessing, wet metal separation, and subsequent purification processes. With the growing demand for avoiding large-scale disposal and the requirement of environmental protection, in addition to developing new recovery processes, it is necessary to further optimize the existing recovery process by adding a second leaching step or reduction step prior to first stripping and improve the industrial chain of spent catalyst recovery [55]. The leaching system proposed in this study is HCl–H_2O_2–$NaCl$ media under mild conditions (70°C, 2h), while the significant high solid per liquid ratio (S/L 70%) provides very promising ground for industrial upscaling.

1.3.3. Kinetic Studies

Crucial parameters that affect the leaching kinetics refer to the reagents acidity, the S/L ratio, the leaching temperature and the leaching time. As for the mainstream system for PGMs leaching, namely H_2O_2-HCl, various studies have been carried out. As demonstrated in the work of A. M. Yousif [56], HCl-H_2O_2 leaching system depends on the HCl-H_2O_2 ratio, the leaching temperature and the contact time. The increase of the HCl-H_2O_2 ratio up to 0.8/100 v/v, results in a dissolution sharp raise of the PGM complex, while afterwards leaching yields for Pt, Pd, Rh do not further alter. The optimum HCl-H_2O_2 ratio has also been evaluated under different temperature conditions (20-80°C), revealing the optimized kinetic behaviour at 60°C. As for the parametrization of contact time (0.5-3h), the system H_2O_2 (0.8vol%)/HCl (9M) at 60°C reached equilibrium at 2h, while Rh-complex dissolved at the highest level (86%) after

2.5h of contact time [56]. The leaching system H_2O_2 (0.8vol%)/HCl (9M) at 60°C for 2.5h resulted in leaching yields 98%, 96%, 86% for Pd, Pt and Rh, respectively.

In the following study, the kinetic conditions of HCl-NaCl-H_2O_2 have been examined. The optimized leaching system HCl (3M)-NaCl (4.5M)-H_2O_2 (1% v/v) at 70 °C for 2h resulted in 100%, 92% and 61% recovery yields, for Pt, Pd and Rh, respectively. According to the kinetic graph (**Figure 1.5**), PGM chlorides formation sharply increases up to 0.5h, while leaching for 2h is the optimized duration for the Pt, Pd, Rh dissolution. After 2h of leaching, recovery yield does not further increase. Comparing Pt and Pd dissolution, a plateau is reached after 0.5h in the case of Pd, while Pt plateau appears between 1h and 2h. As for the leaching order Pt>Pd>Rh, Rh exhibits the slowest kinetics, due to its stereo tactical structure and passivation layer formed under acidic conditions.

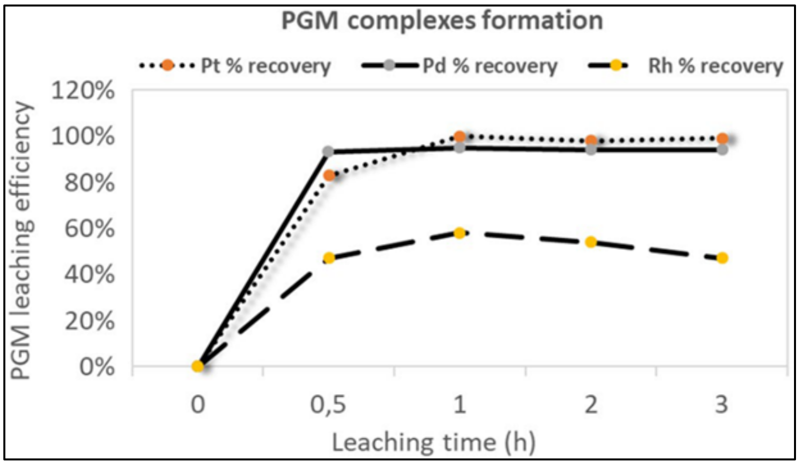

Figure 1.5: PGMs kinetic behaviour for 0.5, 1, 2 and 3h leaching time [6]

The leaching kinetics of HCl-H_2O_2-NaClO system have been evaluated by Harjanto *et al.* [48], where HCl (11.6 mol/L)–H_2O_2 (1 vol%) at 65°C for 3h has been proved to be the optimum one. A significant result refers to 0.5%vol H_2O_2 addition which leads in a sharply dissolution increase. Moreover, the addition of NaClO (3 vol%) into HCl (5 mol/L)–H_2O_2 (1 vol%) improved the dissolution of PGMs about 3-5%.

Concerning different leaching systems, NaCl-HCl-$FeCl_3$ media has been evaluated for Pd leaching, indicating that the Pd dissolution is controlled by surface chemical reactions, following a shrinking-core model. Different leaching temperatures (40°C-80°C), leaching durations (10-360min), under the stable ratio concentrations of HCl (2.0 mol/L)-NaCl (4.0 mol/L)- Fe^{3+} (0.67 mol/L) have been investigated. The leaching efficiency of Pd increased significantly at 60°C, while elevated temperatures at 80°C promoted the dissolution more. Under conditions of leaching between 30-60 min at 80°C, Pd dissolution raised sharply, reaching the optimized recovery yield (99.5%Pd) for leaching duration of 90 min [49].

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

1.3.4. Intensification Leaching techniques

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

According to the study of Spooren and Abo Atia [57], PGMs were recovered from spent automotive catalyst using a two-step microwave assisted extraction. The first step refers to microwave sulfation roasting in the presence of $NaHSO_4 \cdot H_2O$ or $KHSO_4$ and $NaClO_3$; then, a second short (30 min, 105°C) microwave acidic leaching step at a liquid to salt ratio of 10 leads to Pd 96%, Pt 85% and Rh 96%, respectively. It was also demonstrated that sulfation roasting attacks both the cordierite material and rare earth elements, which are present in the washcoat, in order to form sulfate salts.

Regarding pressure-assisted leaching, which is commonly applied for primary PGMs production, soluble minerals are dissolved under pressure conditions (> 20 atm). This technique is widely used in industry over the last 75 years, offering promising leaching results for a variety of minerals. Pressure-assisted leaching is used in the Kell process, in order for the base metals to be removed from the PGM-rich material [38], as well as in cyanide leaching systems [58]. A novel method for spent automotive catalyst recycling refers to a two-step pressure cyanide leaching [59], where catalyst feed is pretreated to remove carbon and fuel contaminants and PGMs are dissolved twice into pressure cyanide leaching media, resulting in 95–96% and 90–92% recoveries for Pt, Pd and Rh, respectively.

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

1.4. Biometallurgy

Concerning the biometallurgical contribution to PGMs recovery, techniques such as bioleaching and biosorption are applied in lab scale by this time. According to Zhuang *et al.* [60], the three major PGMs streams comprise end of life products, manufacturing residues and urban, industrial wastewater. PGMs can be recovered from metal refining residues [61] and spent catalytic converters [62] via the interaction between micro-organisms and metal-bearings. As for the wastewater resource, the precious metal content is quite low, but the waste volume generated from industrial, pharmaceutical, chemical, geothermal [63], municipality water, and electrochemical sector is enormous. Thus, the aforementioned waste streams are considered to be potential PGMs resources. Research attention is focused on the biometallurgical recycling of wastewater streams, in order to contribute to urban waste management and CRMs recovery.

Several advantages are provided via biometallurgy recovery methods, such as lower carbon footprint, utilization of greener solvents than in hydrometallurgy, less energy consumed and absence of hazardous gases. However, the non-biocompatible nature of PGMs, in combination with a variation of multiple parameters that must be controlled should be considered as challenges. Effective control of pH, leaching temperature, ionic strength, as well as the reduction of PGMs salts, play a crucial role in both PGM leaching and extraction.

In addition, PGMs appear into waste streams in a mixed complex form, requiring an extensive research on proper extraction methodologies. Generally, a scale-up investigation is critical, in order for biometallurgy to become industrially established [13].

Biometallurgical recovery of spent catalytic converters through bioleaching (leaching step) and bio-absorption (extraction step) (**Figure 1.6**) involves the PGMs interaction with biomaterial substances (e.g., bacteria), as well as PGMs absorption by various media, such as NaCN, NaOH, HCl. Bacteria such as *Chromobacterium violaceum, Pseudomonas fluorescents*, *Acidithiobacillus thiooxidans* have metal-sequestering properties, sequestering the dissolved noble metal ions from dilute complex solutions (e.g., cyanide complexes). Additionally, for biosorption, various techniques can be followed, such as absorption precipitation, solvent extraction, ionic exchange that should promote the interaction of target metal ions and charged surface microorganisms. Common bio-absorbents for Pt and Pd refer to bacteria *Desulfovibrio desulfiricans, Desulfovibrio vulganis* [14], chitosan derivatives [65] and collagen fiber membranes [22].

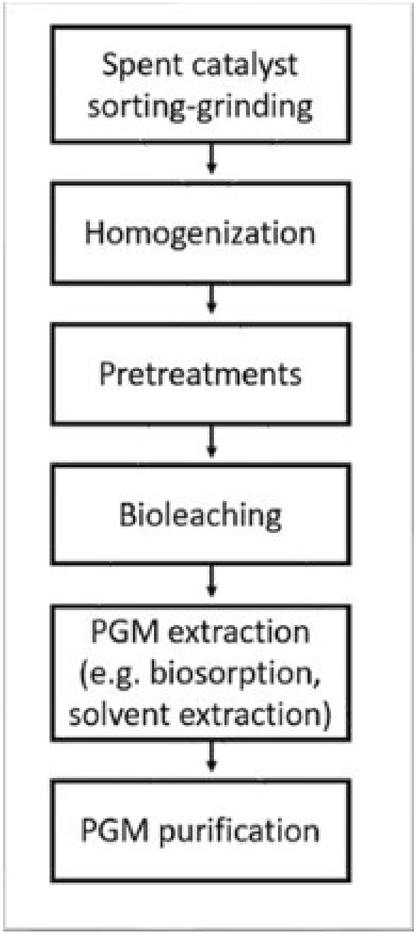

Figure 1.6: Biometallurgy steps for the PGMs recovery

According to S. Das and K. N. Goh [15], utilization of *Chromobacterium violaceum* (pBAD) under glycine concentration (11.81 g/L), ultrasound power, pH (10.73), agitation speed (150 rpm) and pulp density (2%) resulted in promising PGMs extractions, namely 63.1% of Pt, 38.4% of Pd and 99.3% of Rh. Moreover, Das *et al.* [15] mentioned that ultrasound pretreatment acts synergistically in PGM cyanide-complexes formation, by removing the base metals. The factors that affect ultrasound pretreatment are ultrasound power, sonication frequency, acid concentration and pulp density, and ultrasound duration. According to Hosseinkhani *et al.* [66], bacteria, such as *Halomonas* and *Vibrio*, can be incorporated for Pd reduction in saltwater, offering perspectives for PGMs recovery.

1.5. Methods Comparison

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

1.6. Discussion on proposed leaching systems

In regard to the green chemistry principles, state-of-the-art leaching systems are based on mild solvents, lower temperatures and direct processing. In several studies, a chlorine system seems favorable, as PGMs chloro-complexes are quite stable under acidic conditions. The beneficial methodology of PGM-complexes dissolving is improving, by balancing the acidity of chlorinating media (e.g., HCl aqua media) with the addition of chloride anion sources (e.g., NaCl, NaClO, $AlCl_3$, $CuCl_2$) [48, 51, 52] and oxidizing agents (e.g., H_2O_2, ozone, NaClO) [5, 54]. By utilizing milder solvents, less waste is produced than in high chloride acidity (e.g., HCl 12M, aqua regia), preventing further waste management procedures.

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

1.7. Feed material identification

Spent automotive catalysts are the PGM-richest secondary feedstock material. Spent catalytic monoliths, containing high PGMs concentrations, should be characterized to define bulk composition, surface morphology, impurities, as well as any contamination that deteriorates the leaching procedure [54, 67]. The mechanically processed spent monoliths that are collected in a powder form have to be analyzed by elemental analysis methods, such as X-ray fluorescence (XRF) and Inductively Coupled Plasma spectroscopy (ICP) to define the elements involved, such as base metals, cordierite elements (MgO, SiO_2, Al_2O_3) washcoat materials (CeO_2, ZrO_2, Al_2O_3, TiO_2) and poisoning elements (e.g., As, Cr_2O_3, CaO, Cd, C, S, BaO, ZnO). Moreover, Scanning Electron Microscopy (SEM) combined with Energy-dispersive X-ray spectroscopy (EDS) evaluates the catalyst size, morphology, composition and distribution on the carrier. Soot and unburned hydrocarbons deposition should be detected and removed; otherwise, catalyst surface area is not adequately active to chemical reagents.

The assaying of secondary resources is crucial for the design of the process since the material properties could lead to the decision for the appropriate leaching system. Characterization of both leach residue and leachate is crucial for the further extraction of PGMs and the co-extraction of rare earths, when the resources are spent catalysts.

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

1.8. Input material preparation

Concerning spent catalysts, the material to be leached should exhibit a homogenous granulometry, ameliorating the chemical reactions within the leaching system. As described in the work of Yakoumis *et al.* [54] spent catalysts should be sorted according to their characteristics (i.e., Diesel Oxidation Catalysts, Three-Way-Catalysts and Selective Catalytic Reduction devices) in separate batches and processed individually to achieve higher recovery yields. The sorted batches are de-canned, in order for all metallic parts and canisters to be removed, facilitating the leaching/smelting of spent catalytic monoliths process. Thereafter, the broken catalytic monoliths are crushed, milled and sieved, obtaining a fine granulometry (< 2mm). By reducing material grain dimensions, the specific surface area is increased, playing a crucial role in the reactivity of the feed material [68]. Regarding the impurities, the catalyst powder is thermally treated, in order for humidity and contaminations to be removed and surface interaction with the leachate media to be eliminated. Via proper sampling and assaying of the feed, the determination of leaching efficiency and any material loss, which significantly affect the refining stage, is enabled.

1.9. Economic & environmental perspectives

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

Concerning the leaching route, which is the most important step process in hydrometallurgy, mild leaching systems prevent liquid waste; otherwise, extensive waste management raises the total cost. Furthermore, non-toxic reagents utilization benefits both the environment and the working conditions. Compared to common cyanide and aqua regia systems, mild chloride solvents do not emit poisonous gasses or by-products. Direct leaching refers to another adding value technique, where the mechanical processed PGMs resource is fed into the leaching media without any pre-concentration or thermal reduction [54]. The simplicity of direct leaching methods offers cost effectivity in upscaling recycling processes, as pretreatments are energy-intensive and require special equipment.

Regarding the state-of-the-art recovery techniques, toxic, flammable and expensive solvents tend to be replaced with biological reagents (biometallurgy), inorganic reagents (precipitation methods), ionic liquids, switchable solvent systems, and surfactant micelles (cloud-point extraction). Moreover, large equipment and long-term steps are required for ion exchange processes, while mass transfer rates achieved are considerably limited. Ionic liquids are expensive solvents with complex molecular structure used only for lab-scale recoveries. Deep eutectic solvents (DES) refer to a new class of ionic liquids, exhibiting limited environmental impact, less expensive and easily produced in large scale batches [69]. As for the extraction of metals, by following electrochemical methods, DES are proper electrolytes for electrowinning/electrodeposition extraction techniques. Molecular recognition technology (MRT) seems to be the latest big trend in noble metals recovery, due to its time- and cost-effectiveness, green technology, high purification achieved, high selectivity and scalability [70].

1.10. Industrial Aspect

Secondary PGMs sources recycling should be designed to achieve sustainability and high recovery yields, in order to be technoeconomically feasible. In terms of cost effectivity, pyro-based recovery consumes high amount of energy, while metal purity is on average level. In the case of catalytic converters, washcoat materials, such as alumina, are hardly recovered, due to the high temperature smelting stage, as support materials are driven to the slag phase. Although pyrometallurgical process dominates in industrial application, it is a common trend that hydrometallurgy gains the foothold over the years. Hydrometallurgical extraction is favorable, due to lower temperature conditions required, lower energy consumption, higher purity achieved, potential of co-extractions, and better process control. However, the aforementioned factors do not guarantee the adaptation of hydrometallurgy in industrial scale, since further requirements should be fulfilled and studied. In terms of industrialization, hydrometallurgical processes should focus on higher solid to liquid (S/L) ratio dissolution, under milder leaching conditions. Moreover, by using additional chloride salts and oxidizing agents, the media acidity can be considerably reduced.

It is vital that new business models are established for noble metals recovery, in order to decouple Europe from PGM imports [71]. An effective circular economy model for PGM sustainability requires the continuous engagement of PGM producer companies, service providers, consumers and recycling companies [72]. The major mining companies refer to IMPALA, ANGLO PLATINUM, NORTHAM PLATINUM

LIMITED, NORNICKEL, while PGMs refiners include BASF, UMICORE, JOHNSON MATTHEY [73]. Suppliers of primary and secondary PGM resources, manufacturers of automotive catalytic converters, integrators of exhaust systems, recycling companies, even automotive companies should collaborate for PGMs recovery, following green chemistry principles and cost-effective solutions. A 'green circular label' adopted by all industrial operators, recovery process optimizations, Operational and Capital Cost estimations and continuous PGMs feed supply are critical factors for closing PGMs loop. Furthermore, the implementation of an innovative hydrometallurgical technology will further assist in raising public awareness for PGM recycling.

1.11. Conclusions

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

1. State-of-the-art leaching systems refer to chlorinating media, where milder acidity is achieved by adding chlorinating media and oxidizing agents. Mild leaching temperatures contribute to the protection of the environment as well.
2. The optimized leaching systems should dissolve an even greater amount of noble metals (high S/L ratio) into less leachate volume, generating less liquid waste. Moreover, by increasing the S/L ratio, smaller plant installations may be required. Although liquid waste from leachate volume is minimized, washing stage must be controlled; otherwise, the considerable wastewater produced will increase process expenses. Real time analysis is required to prevent pollution and reduce process cost.

3. Co-extraction of rare earths, in the case of recycling of spent automotive catalyst, could add higher value to the industrial process. Agile production design is being further developed; thus, many opportunities of easier, parallel waste steams management will be provided within the next few years.
4. Direct leaching seems beneficial, minimizing energy consumption. Undoubtedly, feed material composition, as well as contaminations should be defined and validated, in order to choose the most appropriate leaching and extraction method. Post-treatments, such as PGM salt re-dissolution and purification, may be required.
5. Future research should be focused on high S/L ratio leaching, co-extraction techniques, multiple waste streams management and replacing of pretreatments by post-treatments.

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2nd Chapter

2. Mechanical Pre-Treatment and Elemental Analysis of Spent Automotive Catalysts

2.1. Introduction

The secondary PGM containing material of interest to the specific Thesis is Commercial (full-scale) Spent Automotive Catalysts. Prior to the metallurgical treatment (Pyro/Hydro/Bio-), a mechanical pre-processing step should be followed, since the spent catalysts should be sorted according to their types (i.e., Diesel Oxidation Catalysts, Three-Way-Catalysts and Selective Catalytic Reduction devices) in separate batches and processed individually to achieve higher recovery yields. The sorted batches are de-canned, in order for all metallic parts and canisters to be removed, facilitating the leaching/smelting process of spent catalytic monoliths. Thereafter, the broken catalytic monoliths are crushed, milled and sieved, obtaining a fine granulometry (< 2mm). By reducing material grain dimensions, the specific surface area is increased, playing a crucial role in the reactivity of the feed material. The spent catalyst powder is thermally treated, in order for humidity and contaminations to be removed and surface interaction with the leachate media to be eliminated. Via proper sampling and assaying of the feed, the determination of leaching efficiency and any material loss, which significantly affect the refining stage, are enabled.

In this chapter, the pre-processing step of the metallurgical treatment is addressed. Namely, the steps of spent catalyst collection, mechanical pre-processing, elemental analysis and sample preparation are presented followed by the X-Ray fluorescence (XRF) instrument calibration. Technical and experimental details are discussed to achieve the appropriate sampling preparation and characterization.

2.2. Collection of the converters from the scrap yards or car service workshops

Appropriate classification is the foundation for ensuring that the collection, transportation, storage and treatment of spent autocatalysts are carried out in a manner that provide protection for the environment and human health and in compliance with legal requirements (**Figure 2.1**).

Figure 2.1: Collection of spent automobile catalysts

Spent automotive catalysts can be provided by car workshops specializing in exhaust aftertreatment, car-manufacturer's official repairing workshops, dismantling plants, car service station, wholesalers and retailers.

2.2.1. Sorting and dismantling of the converters

The precious-metal-bearing carrier material and the non-precious-metal-bearing steel casing are separated (De-canning of ceramic converters/Shredding of metallic converters). Inlet and outlet exhaust extension tubes are cut (**Figure 2.2**) and main bodies of the catalysts proceed to the sorting step.

Figure 2.2: Inlet and outlet exhaust tubes are removed from the main body of the catalysts during the shredding procedure

Once spent catalyst have been collected, they are firstly sorted in subcategories according to certain criteria they are based on (**Figure 2.3**):

- The engine type (combustion engine or hybrid car)
- The fuel that the car uses (diesel, gasoline, LPG)
- Type of the spent catalyst (diesel oxidation catalyst, three-way-catalyst, catalyzed Diesel Particulate Filter, selective catalytic reduction device)
- Type of the monolith (ceramic or metallic), and
- If the converter is the genuine part or a replacement part (Original Equipment Standard or Aftermarket).

Figure 2.3: Sorting of the collected spent/deactivated catalyst according to certain criteria

After the sorting, the converters are de-canned, i.e., the metallic canister and the wool (fibre mat) are removed from the ceramic catalyst using a mechanical process which is usually called guillotine or modified alligator shear (**Figure 2.4a**). Most damage occurs during the dismantling process. The steel casings are removed by an automatic cutting machine, either in one piece (**Figure 2.4b$_1$**) or in powder/brick form (**Figure 2.4b$_2$,c**). This may also damage the catalyst inside, while further losses may occur through handling and transit. Optimized method should enable the decanning of ceramic substrate in one piece.

Figure 2.4: (a) Automatic cutting machine for the ceramic catalyst decanning, removal of metallic case preserving the shape of the cordierite (b2) empty case of ceramic catalyst and (c) crashed ceramic honeycomb.

The ceramic monoliths are driven to a pre-crusher in order to reduce their dimensions and to a mill in order to extract a fine homogeneous powder which contains the PGMs. Different minerals behave differently during pulverization – most (brittle) minerals will easily break down to small particles while for some, only their shape will change if proper sample preparation methods are not used. Since, the recovery of PGMs requires sophisticated large-scaled metallurgical processes, the most common approach is to extract samples from each consignment in order to determine the PGMs content of each lot, in every stage of the procedure. The former process has been established in order to verify representative sampling from large batches and accurate results of the processed material.

2.2.2. Preparation of uniform batches

To accurately determine the amount of precious metal present in the monoliths, suitable samples for laboratory analysis are prepared. The goal of the experimental procedure is to obtain a sample that is considered as representative of the overall material, as homogenous as possible of the recoverable metals within the lot. Moreover, a constant process steps ought to be firmly followed so as for the measurements to be reproducible and comparable.

More specifically, a batch, consisting of approximately 1,400 spent catalysts, was originally de-canned. The total mass of the batch of the ceramic honeycombs was roughly 1,047kg, which on average is 0.737kg per honeycomb with particle size 10cm.

The specific batch was introduced to the ball mill (**Figure 2.5a**) in order to obtain particle size - 2mm.

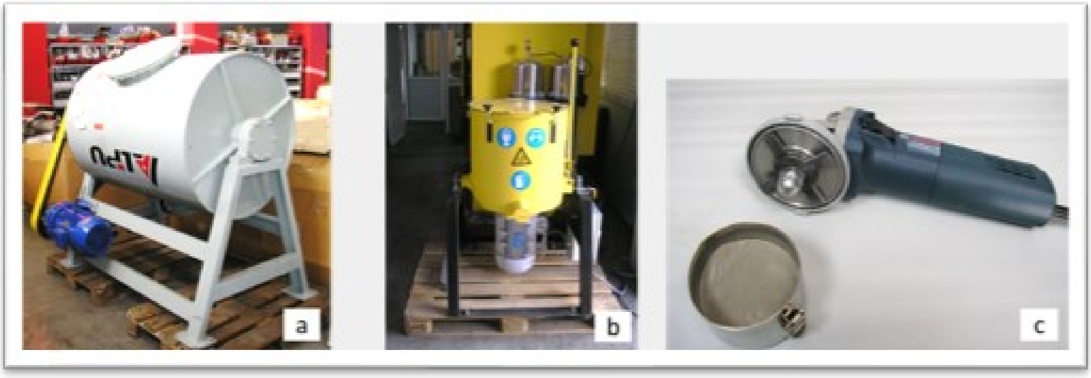

Figure 2.5: (a) Ball mill, (b) chain mill and (c) analytical mill used for the downsizing of the ceramic monolith particles before the analysis

90% of the milled powder was removed for storage and the rest 10% (100kg) was grounded again, in order to obtain a particle size of less than 1mm. 90% of the milled powder was removed and sent for storage and 10% (10kg) proceeded in the analytical mill (**Figure 2.5c**) to be grounded to 160µm.

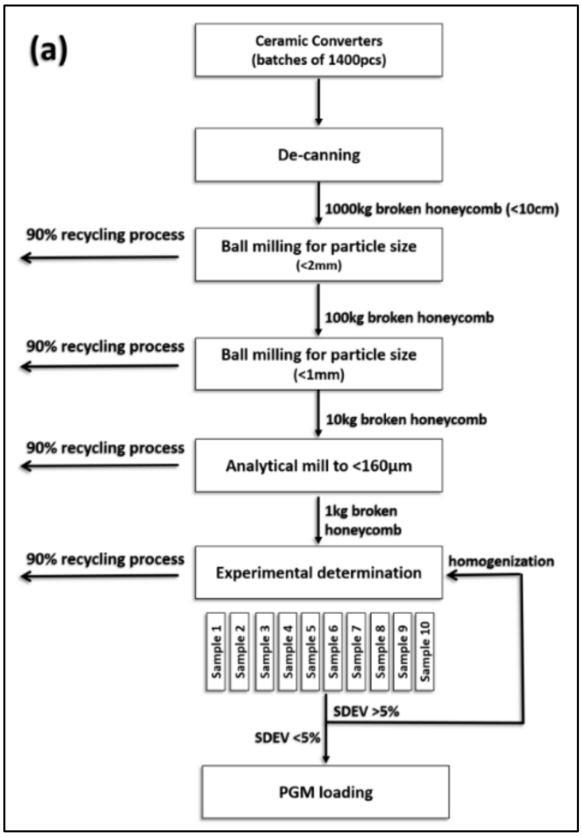

Figure 2.6: Sampling and homogenization process for ceramic catalysts

Finally, 90% of the powder was sent for storage and the rest 1kg was used for elemental analysis according to **Figure 2.6**. Ceramic honeycomb final step powder was collected so as to prepare one set of 10 samples, each of 10g. Each sample was used for elemental XRF analysis. If the standard deviation of the identified values of the set was greater than 5%, then the samples were mixed again and proceeded with the homogenization. On the other hand, if standard deviation was lower than 5%, the experimental values were reliable, revealing that the batch was homogeneous.

The size of the particles was determined between the mill crushing steps using a series of stainless steel sieves with appropriate mesh openings (**Figure 2.7**).

Figure 2.7: Sieving of the obtained sample to determine granulometry

The content of spent catalysts in Pt, Pd and Rh was determined with X-Ray fluorescence spectroscopy (XRF) on solid samples. Since small variations in analytical determinations impact critically on financial performance, XRF analysis was used for the determination of noble metals due to the instrumentation high accuracy in trace metals. The XRF analyzer provides a high level of performance when measuring metals such as Pt, Pd, Rh in fresh catalytic converters loading and in recovered metals from spent catalysts. While benefiting from the convenience of fast analysis, it also provides high confidence by achieving results that assure high level of accuracy, repeatability and precision of almost 1%. The accuracy of the method was verified by the ICP-MS technique.

The content of the other metals existing in the ceramic monolith and the washcoat were determined with a combination of the Atomic Adsorption Spectroscopy (AAS) and the Inductive Couple Plasma Mass Spectrometry (ICP-MS), using liquid samples produced after fusion of solid samples with LiB_4O_7 & KNO_3. Before XRF analysis and fusion procedure, the solid samples were dried overnight at 110°C for the adsorbed water to be removed.

2.3. X-ray fluorescence *(*XRF*)* analysis

The X-ray fluorescence analysis is used for elemental and chemical analysis for spent and fresh catalysts. XRF analysis is held to determine the concentrations of Platinum Group Metals (PGMs), namely Pt, Pd and Rh, for spent catalysts and ultimately to calculate the recovery rate (%) in leaching experiments.

2.3.1. Sampling preparation

In order for the spent catalyst to be accurately measured, appropriate amount of milled powder is collected from the large volume batch as described in **Figure 2.6**. A powder sampler is immersed in the tank (**Figure 2.8$_1$**) and powder is collected from different depths (**Figure 2.8$_2$**). Finally, powder is distributed in the plane area (**Figure 2.8$_3$**) and divided in 4 parts (**Figure 2.8$_4$**).

Figure 2.8: Sampling preparation

Appropriate amount of 10g is weighted for each of the four samples (measured in precision scale: **Figure 2.9**$_1$) and dried, in a laboratory oven, at 120°C for 2 hours (**Figure 2.9**$_2$) so as for the adsorbed humidity to be removed, since water content may affect the performance of the instrument and measurements might be distorted. Then, the sample, which is taken from the Binder vacuum drying oven, is prepared for the XRF analysis. The measured sample gets the fine powder form through pulverization, using an agate mortar. The material should be moistened with mild circular motions. (**Figure 2.10**).

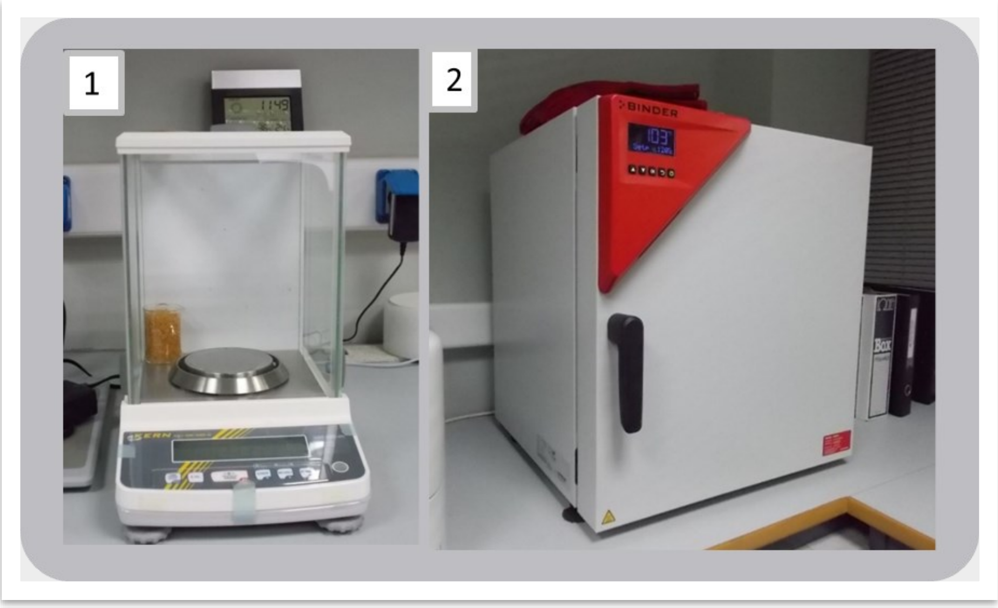

Figure 2.9: Sample weighting and drying

The prepared powder is taken from the mortar and placed into a double open-ended cup (cell), above an aluminum foil. With respect to the cell, its pieces are assembled, a prolene thin-film membrane is applied at the bottom of cell and a seal tape is sealed on the cell lid. The powder is pressed gently into the cell – otherwise the thin-film might be teared – and a slight curvature is created at the bottom of the cell. A well stacked cell with curved bottom line results in a homogenized grain distribution, which affects synergistically the measurement by increasing the surface area and allowing the incident beams to analyze grains of different angles (**Figure 2.10**).

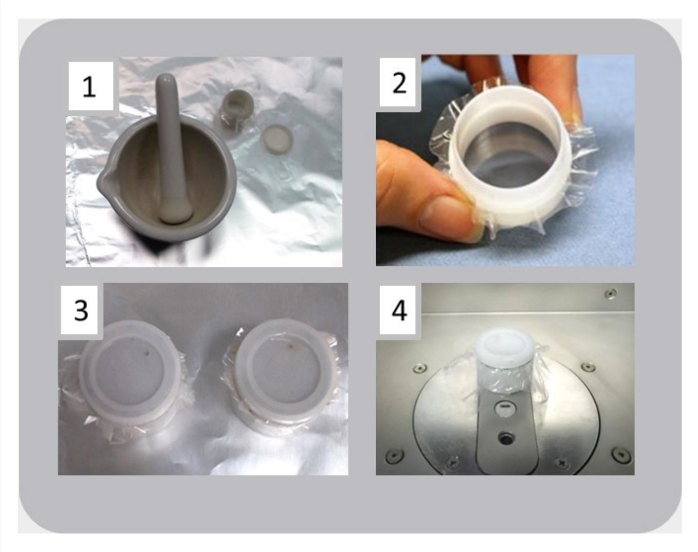

Figure 2.10: Preparation of the sample for XRF analysis. Agate mortar for homogenization (1), cup preparation (2), powder encapsulation in the cup (3) and XRF measurement

The prepared fine powder is placed into a double open-ended cup (cell) and is subjected to X-ray Fluorescence analysis (XRF). It is crucial that the cell is well stacked with a curved bottom line. In this way, a homogenized grain distribution is achieved, which affects synergistically the measurement by increasing the surface area and allowing the incident beams to analyze grains of different angles. Furthermore, cell must be completely fulfilled, so that high reliability of measurements is ensured according to the penetration depth of the X-ray beam.

Finally, the appropriate settings and the correct calibration mode are set. The XRF analysis begins and all data are recorded in the XRF instrument software. Once the XRF analysis process has finished, the concentration values are recorded in the correspondent Microsoft Excel File and the average concentrations for each PGM metal are calculated.

2.3.2. Calibration Mode for analytical XRF results

In general, the accuracy of the X-ray Fluorescence analysis (XRF) is determined by the appropriate calibration mode for the sample measured. The calibration accuracy depends on the sample morphology, which should coincide with that of the standard sample. PGMs emit at specific wavelengths, thus proper calibration mode for automotive catalyst samples is required. For this reason, the appropriate software (Olympus OSSA, version 3.8.540.0) is adopted.

However, the determination of the PGMs recovery yields requires calibration of higher accuracy, detecting both high (before leaching) and low (after leaching) concentration ranges, because even a small variation may affect the leaching procedure. In this respect, external calibration using two different elemental analysis techniques is conducted. The X-ray Fluorescence analysis [XRF (Vanta Olympus 2017, Waltham, MA, USA)] measurements are compared with the ones derived from certified Inductively coupled plasma - optical emission spectrometry (ICP-OES Thermo Scientific X-Series II Spectrometer). As for the samples before recovery, high PGMs concentrations are demonstrated, while the samples after recovery show low PGMs concentrations ranges.

2.3.3. Calibration for the XRF instrument for Pt, Pd and Rh

To conduct external calibration, samples of varying PGMs concentrations are examined. Namely, 13 automotive catalyst samples were subjected to certified ICP-OES spectrometry (**Table 2.1**). Thereafter, these 13 samples, having known concentrations via ICP-OES, were also subjected to XRF analysis, after the granulometry was controlled. Individual calibration curves for each element (Pt, Pd, Rh) were drawn, according to the linear least-square approach, using XRF analysis concentration curves for the x-axis data and ICP-OES values for the y-axis data. The measured concentration values of Pt, Pd and Rh for each of the 13 samples are demonstrated in **Table 2.1**. Therefore, the actual values are determined by the slope a of the lines of each element which are presented in **Table 2.2** and refer to samples before leaching (high concentration ranges). The comparison is accurate, when intercept β is set as zero, so that the linear function passes from the axis origin. Calibration curves are demonstrated in **Figures 2.11-2.13** for Pt, Pd and Rh, respectively.

Samples	Pt (ppm) ICP-OES	Pt (ppm) XRF	Pd (ppm) ICP-OES	Pd (ppm) XRF	Rh (ppm) ICP-OES	Rh (ppm) XRF
1	634	635,5	1553	1543,3	289	288,0
2	743	708,8	1884	1902,2	308	310,0
3	821	846,0	1360	1383,8	302	312,1
4	693	743,7	1572	1578,3	290	294,8
5	830	829,1	1505	1548,3	312	314,7
6	885	876,1	1302	1267,7	293	305,3
7	656	670,9	1611	1653,5	286	291,1
8	660	680,9	1702	1753,7	295	294,4
9	625	614,4	1780	1822,1	312	312,7
10	673	649,3	1784	1884,2	306	318,3
11	601	618,2	1423	1374,0	248	249,3
12	2751	2759	2722	2728,7	239	237,0
13	912	919,6	1588	1599,6	317	321,6

Table 2.1: PGM concentrations, calculated by ICP-OES and XRF

Element	Slope α	Intercept β
Pt	**0,9951**	**0**
Pd	**0,9889**	**0**
Rh	**0,9886**	**0**

Table 2.2: Coefficient slope for Pt, Pd, Rh for high concentrations, obtained from the calibration curves for Pt, Pd and Rh from ICP and XRF measurements

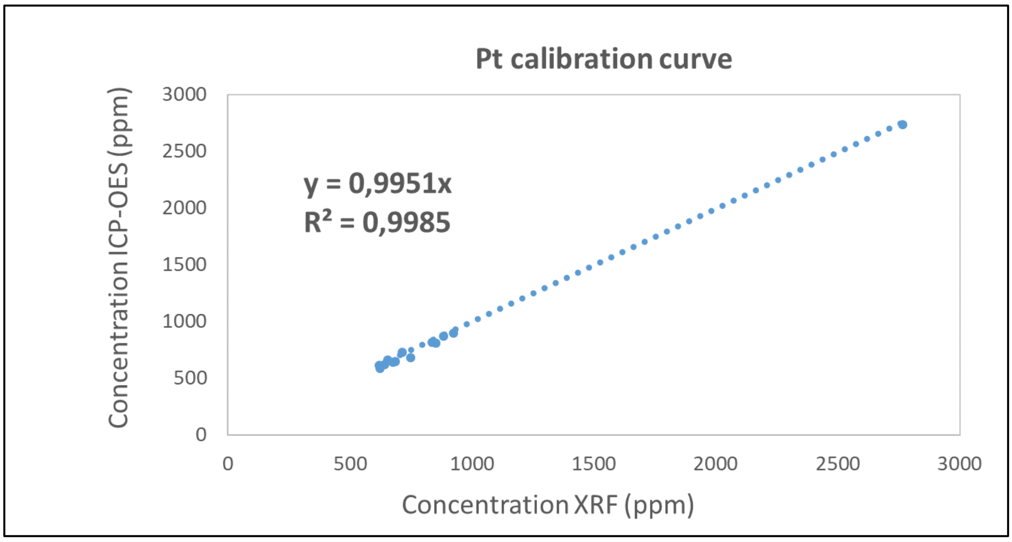

Figure 2.11: Calibration curve for Pt in the loading range 614-2760ppm

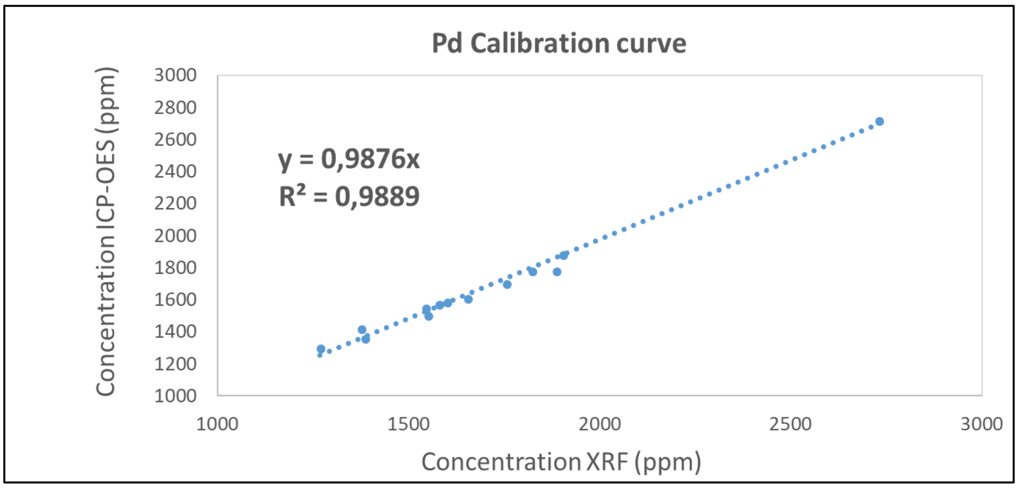

Figure 2.12: Calibration curve for Pd in the loading range 1270-2730ppm

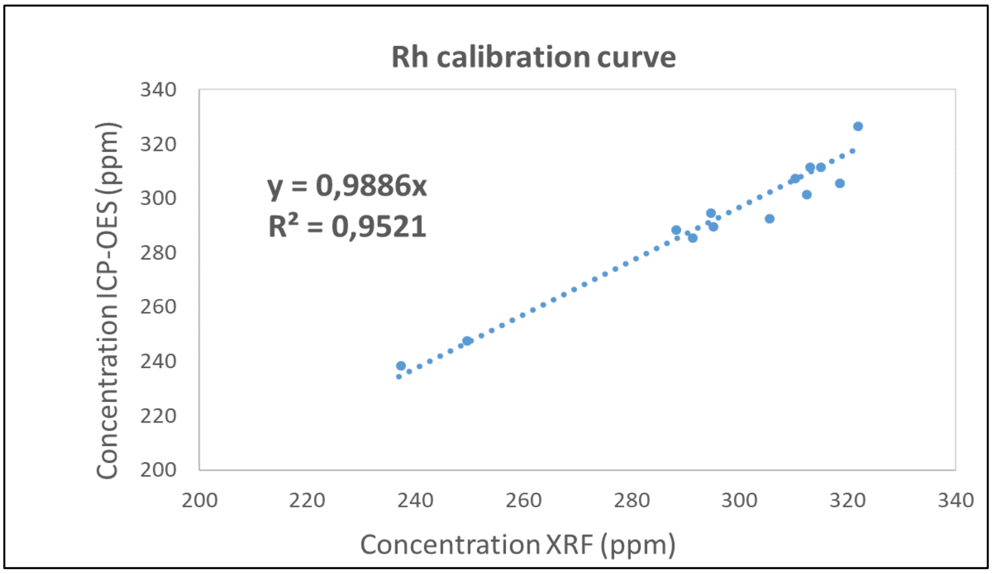

Figure 2.13: Calibration curve for Rh in the loading range 237-322ppm

In order to increase the sensitivity of the method and the accuracy of the measurements, calibration was conducted for the low concentrations of PGMs, on leaching residue samples. New pair of values were obtained for the calibration curve. For this calibration region, a ceramic catalyst with specific concentration of Pt 912ppm, Pd 1588ppm Rh 327ppm, was diluted with cordierite powder, so as to obtain diluted samples with low concentrations. The granulometry of both powders, samples and cordierite should be the same, achieving a homogenized dilution. The concentration of the PGMs on the diluted samples was calculated according to dilution steps and the initial concentration. The diluted samples are measured via XRF analysis in manufacturing calibration modes, in order to determine the detection limits of the elements. The first calibration mode is the one established by OLYMPUS (the manufacturing company of the instrument) and is appropriate for the measuring samples of relatively high concentration (before leaching), named 'HIGH VALUES'. Subsequently, the same diluted samples are measured using no calibration mode, named 'LOW VALUES'. The calculated concentrations of Pt, Pd and Rh are listed in the 1st column of each (**Table 2.3-2.5**). The determined concentration measured with the OLYMPUS internal calibration mode ('HIGH VALUES) is presented in 2nd column of each Table (**Table 2.3-2.5**), for Pt, Pd and Rh, respectively. Finally, the concentrations determined with the use of no calibration mode are presented in the 3rd column of each Table (**Table 2.3-2.5**).

Pt concentration (ppm)	Pt concentration (ppm) High values	Pt concentration (ppm) Low values
28.7098	0	60.5
57.4378	83.1	80.9
143.585	166.55	155.3
287.152	291.7	279
430.738	456.000	423.00
574.305	582.700	525.20

Table 2.3: XRF analysis of Pt for different calibration modes

Pd concentration (ppm)	Pd concentration (ppm) High values	Pd concentration (ppm) Low values
46.91	0	60.3
93.83	0	119.6
234.57	0	276.2
469.14	248.8	518.625
703.71	630.600	839.00
938.28	842.900	1009.30

Table 2.4: XRF analysis of Pd for different calibration modes

Rh concentration (ppm)	Rh concentration (ppm) High values	Rh concentration (ppm) Low values
10.294	68.8	1.9
20.594	86.4	27.5
21.4829	108.61	59
102.959	145.45	109,5
154.442	194.700	176.20
205.918	221.400	207.10

Table 2.5: XRF analysis of Rh for different calibration modes

Two different calibration curves were prepared and compared for each noble metal (Pt, Pd, Rh). The former curves were designed with x-data received from the 1st columns, while y-data from the 2nd columns. The optimum calibration curve for each element was considered the one with the coefficient of determination R^2 close to 1 (R^2~1).

According to the concentration values, the appropriate calibration mode for low PGM concentrations (**Figure 2.14-2.16**) proved the 'LOW VALUES' (**Table 2.6**), since there was the lowest deviation from the calculated values, indicating that for low concentration ranges, the 'HIGH VALUES' was unsuitable. The corresponding slopes for low concentrations (Pt < 600ppm, Pd < 1000ppm, Rh < 250ppm) are listed in **Table 2.6**.

PGMs	Slope α
Pt	0.9645
Pd	0.9502
Rh	0.94

Table 2.6: Coefficient slope for Pt, Pd, Rh for low concentrations

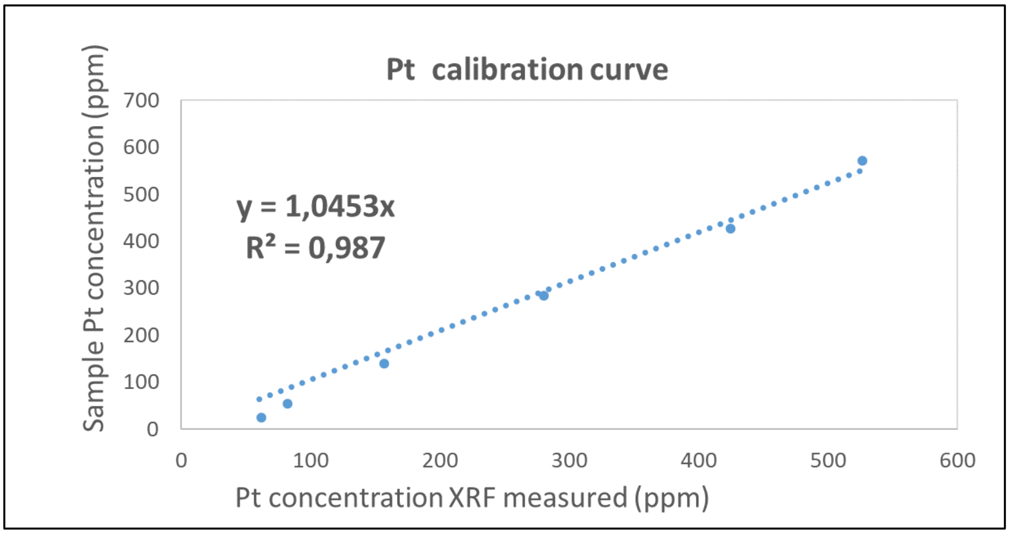

Figure 2.14: Calibration curve for Pt low concentrations, < 600ppm

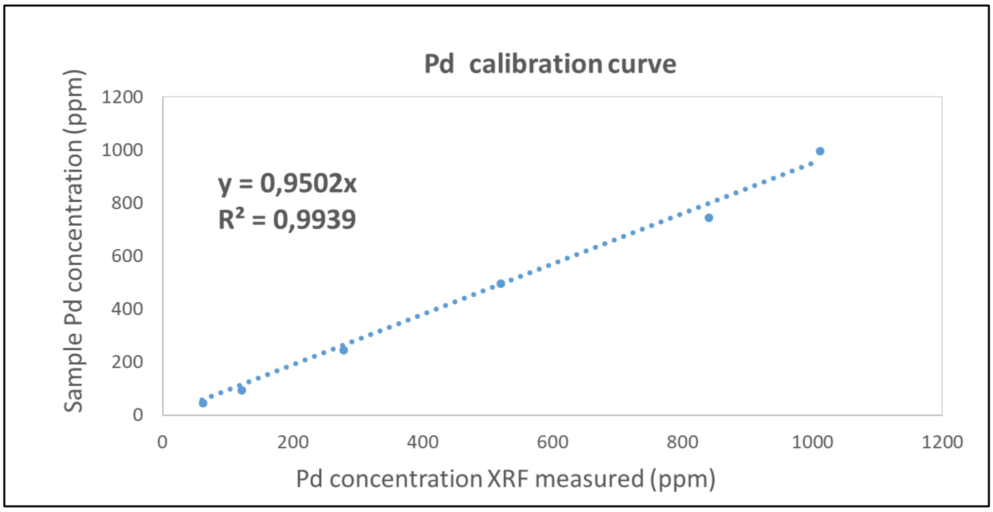

Figure 2.15: Calibration curve for Pd low concentrations, < 1000ppm

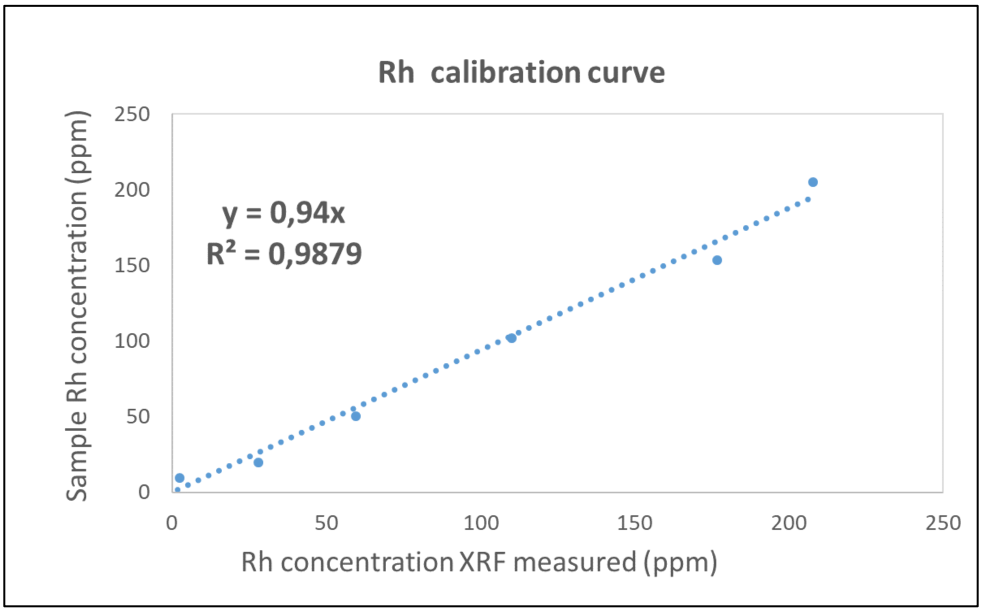

Figure 2.16: Calibration curve for Rh low concentrations, < 250ppm

2.3.4. PGMs content in spent catalytic converters

For the most accurate and reliable determination of the noble metal concentration on ceramic honeycombs and metallic foils, we chose to investigate a large number of auto-catalysts in order to reach the highest possible homogenization and representative values. More than 40,000 ceramic catalytic converters and more than 4,000 metallic catalysts were collected and treated for the elemental analysis.

The precious metal loading in each batch of ceramic and metallic catalysts was determined by X-Ray Fluorescence spectroscopy and the results are described in **Table 2.7** for the ceramic honeycombs and in **Table 2.8** for the metallic foils. Commercial data of an actual recycled quantity of more than 40,000 catalytic converters demonstrate that the mean concentration of PGMs in spent ceramic catalytic converters is 2,596 ppm or 0.26% w/w for the case of ceramic catalysts (**Table 2.7**). The mean concentration is 200% higher for the case of metallic catalytic foil, i.e., 7,872 ppm or 0.79% (**Table 2.8).**

A/A	Weight of Ceramic Honeycomb (kg)	Number of Ceramic converters	Weight of ceramic monoliths (kg)	Pt (ppm)	Pd (ppm)	Rh (ppm)	Total PGMs (ppm)
1	0.758	1,600	1,212.27	724	1,633	302	**2,659**
2	0.740	1,597	1,181.75	731	1,521	255	**2,507**
3	0.739	1,526	1,127.28	760	1,620	305	**2,685**
4	0.737	1,374	1,012.12	673	1,734	315	**2,722**
5	0.734	1,377	1,010.76	710	1,471	295	**2,476**
6	0.739	1,516	1,120.41	734	1,522	285	**2,541**
7	0.729	1,383	1,008.89	705	1,606	283	**2,594**
8	0.720	1,369	985.09	749	1,573	308	**2,630**
9	0.700	1,476	1,032.44	630	1,760	299	**2,689**
10	0.706	1,496	1,056.03	661	1,701	343	**2,705**
11	0.736	1,360	1,001.32	720	1,533	301	**2,554**
12	0.780	1,270	990.52	811	1,426	294	**2,531**
13	0.756	1,335	1,008.90	802	1,541	284	**2,627**
14	0.791	1,280	1,012.54	830	1,505	312	**2,647**
15	0.770	1,304	1,005.00	821	1,360	302	**2,483**
16	0.788	1,336	1,053.54	885	1,302	293	**2,480**
17	0.775	1,287	997.07	819	1,373	287	**2,479**
18	0.748	1,329	994.29	660	1,702	295	**2,657**
19	0.729	1,369	997.33	693	1,572	290	**2,555**
20	0.756	1,368	1,034.25	656	1,611	286	**2,553**
21	0.725	1,382	1,001.54	625	1,780	312	**2,717**
22	0.748	1,358	1,015.73	705	1,531	276	**2,512**
23	0.745	1,351	1,007.44	801	1,511	285	**2,597**
24	0.696	1,611	1,120.87	711	1,818	298	**2,827**
25	0.714	1,405	1,003.94	743	1,884	308	**2,935**
26	0.687	1,459	1,001.85	673	1,784	306	**2,763**
27	0.727	1,386	1,007.01	625	1,532	264	**2,421**
28	0.696	1,959	1,362.74	634	1,553	289	**2,476**
29	0.718	1,401	1,005.94	601	1,423	248	**2,272**
AVERAGE		**0.737**	**720.414**		**1,582.138**	**293.793**	**2,596**

Table 2.7: PGMs concentration of twenty nine typical consignments of spent ceramic catalytic converters recycled from the Greek market

The analysis of the results has proven that a typical consignment of spent ceramic automotive catalytic converters contains 2,596 ppm of Platinum Group Metals (Platinum, Palladium and Rhodium) in the ceramic substrate (or 1.913g PGMs per catalytic converter, average weight of ceramic converter = 0.737 kg). The mass ratio of the three precious metals is: 2.7/6.2/1.1 Pt/Pd/Rh.

	Weight of metallic foil (kg)	**Metallic**	**Weight of metallic foil (kg)**	**Pt (ppm)**	**Pd (ppm)**	**Rh (ppm)**	**Total PGMs (ppm)**
1	0.206	484	99.61	1,619	5,877	757	**8,253**
2	0.233	482	112.234	1,130	6,442	692	**8,264**
3	0.214	445	95.344	1,766	5,411	619	**7,796**
4	0.210	423	88.621	1,503	6,334	748	**8,585**
5	0.208	412	85.685	1,608	4,935	625	**7,168**
6	0.242	447	107.966	1,851	4,718	480	**7,049**
7	0.209	438	91.338	1,555	6,306	654	**8,515**
8	0.223	439	98.098	1,242	5,112	577	**6,931**
9	0.184	529	97.59	1,069	6,587	626	**8,282**
AVERAGE	**0.214**			**1,482.55**	**5,747**	**642**	7,872

Table 2.8: PGMs concentration of nine typical consignments of spent metallic catalytic foils recycled from the Greek market

Quantitative analysis of nine batches of metallic foils showed that the average PGM loading was 7,872 ppm on the foil (or 1.68 gr PGM per catalyst, with average foil weight 0,214 kg). The mass ratio of the noble metals is 1.02/3.9/0.5 Pt/Pd/Rh and the average PGM loading is 1,482 ppm for Pt, 5,747 ppm for Pd and 642 ppm for Rh.

Analytical measurements of PGMs and the other elements of spent catalytic converters were performed on one single batch and the results are presented in **Table 2.9**. The total amount of noble metals is 0.2375% w/w or 2,375 ppm. Therefore, the laboratory analysis confirms the aforementioned XRF commercial catalysts measurements. Furthermore, the poisoning of the washcoat of the ceramic honeycomb is clearly listed in **Table 2.9**.

The studied ceramic-based catalyst contains up to 40% SiO2, up to 10% MgO and up to 5% Ce, Zr and Ti and other mixtures introduced from gasoline and oil additives during operation. The identified values are in accordance with spent catalysts studied in the literature. Several oxides such as Na_2O and P_2O_5 and Fe_2O_3 were also determined on the structure of the spent catalyst as poisoning substances in particular high concentration.

Oxide/ Metal	w/w	(ppm)
Ceramic Monolith-cordierite		
MgO	8.51%	**85,100**
Al_2O_3	37.15%	**371,500**
SiO_2	35.33%	**353,300**
Poisoning (Lubricants - Fuels)		
Na_2O	3.07%	**30,700**
P_2O_5	1.81%	**18,100**
CaO	1.16%	**11,600**
Cr_2O_3	0.80%	**8,000**
Fe_2O_3	2.44%	**24,400**
ZnO	0.33%	**3,300**
BaO	0.77%	**7,700**
S	0.44%	**4,400**
C	0.43%	**4,300**
Catalyst Support (Washcoat)		
TiO_2	0.29%	**25,900**
ZrO_2	4.55%	**45,500**
La_2O_3	0.29%	**2,900**
CeO_2	3.51%	**35,100**
Catalyst (Noble Metals)		
Pd	0.1364%	**1,364**
Pt	0.0754%	**754**
Rh	0.0257%	**257**
PGMs sum 0.2375%		

Table 2.9: Laboratory chemical analysis of typical spent catalytic converters ceramic honeycomb

In both substrate cases, the PGMs concentration in spent automotive catalytic converters is significantly higher than the PGMs content in primary ores (on average 10-20 ppm). The high intrinsic metal values make recycling attractive from an economic point of view and, due to the much higher concentration compared to mined ores, it also helps to reduce the environmental burden of metal supply significantly, especially in terms of climate impact.

2.4. Conclusions

The recycling of platinum group metals from spent automotive catalysts is becoming increasingly important. Thus, the procedures related to the evaluation of the spent catalyst and the recycled metals loading ought to be designed in detail. This study has determined that particular steps should be constantly followed in the sampling procedure in order to obtain representative, reproducible and high quality analytical data for spent catalysts loading.

In this work, more than 40,000 spent ceramic catalytic converters have been collected and pre-processed in order to extract homogeneous samples of ceramic honeycomb. The average content of ceramic honeycomb has been found to 2,596 ppm or 1.913 gr of PGMs per catalyst. Moreover, more than 4,000 spent metallic catalysts have been collected and pre-processed in order to extract honeycomb metallic foil. The average PGM content of metallic honeycomb has been found to be 7,874 ppm (or 1.68 gr of PGM per spent metallic converter). The PGM loading in ceramic honeycomb was also verified with laboratory analysis based on a combination of XRF, AAS and ICP-MS methods, where less than 1% deviation was noticed for the combined technique sompared to XRF. In conclusion, XRF analysis provides an accurate and quick tool to determine PGM loading reducing cost, since the use of expensive lab wet chemistry reagents is avoided. Further, the analyses are quick and straightforward without the need of being conducted by highly educated and experienced analytical professionals.

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3rd Chapter

3. Hydrometallurgical Recovery of PGMs from Automotive Catalytic Converters

3.1. Introduction

For this chapter, milled spent automotive catalytic converters have been leached, incorporating industrial driven selected reagents and conditions. Thus, no thermal and/or chemical pre-treatment has been used prior to leaching, while the industrial promising $HCl–H_2O_2$ has been extensively studied. Different sources of chlorinating media have been studied in order to reduce solution acidity, with the best performing system to include 4.5M NaCl which reduces HCl concentration to 3M. Solid-to-Liquid Ratio (S/L) and reaction kinetics have been also studied, aiming for an optimized large-scale driven system. Extremely high solid to liquid (S/L) ratio (70%), without any pre-concentration or further pretreatments (reduction, roasting), has been achieved.

A large homogenized batch of spent automotive catalysts has been used (collected, characterized and leached), ensuring reproducibility and wide optimization studies. The spent catalyst sample has been characterized by scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy analysis (EDS) and X-ray powder diffraction (XRD). The efficiency of leaching was validated by X-ray fluorescence analysis (XRF), where the leaching rates of PGMs were determined. As for the XRF analysis, an external calibration has been performed, regarding X-ray fluorescence analysis (XRF) and Inductively coupled plasma-optical emission spectrometry (ICP-OES). Finally, a kinetic evaluation of the leached catalyst sample has been conducted.

3.2. Experimental Procedure

3.2.1. Preparation of Homogenized Catalytic Converter Batch

Initially, a plethora of spent catalyst samples from a homogenized batch was processed and characterized. The prepared homogenized batch derived from 25 commercial spent catalytic converters (**Table 3.1**), producing a 20 kg batch of spent automotive catalyst powder. The method has been described in detail in the 2nd Chapter of the Specific Thesis. The final sample produced, about 20 kg of fine homogeneous powder from spent automotive catalytic converters, enabled us to conduct multiple leaching experiments optimizing all parameters involved (reagents concentration, different sources of Cl^-, reaction kinetics and important industrial parameters like S/L ratio). The quantity of the sample is crucial for PGM research, since most of the published works involve limited experimental tests, due to the extremely high cost of spent automotive catalysts samples (almost 1,000 Euros per 100 g of sample).

Audi A3	Citroen Saxo	Toyota Carina
Fiat Tipo	Fiat Stilo	Volvo
Ford Fiesta	Ford Focus	Suzuki Swift
Ford Focus_2	Ford Mondeo	Toyota Corolla
Daihatsu Feroza	VW Golf	Rover 416
Opel Astra	Honda Civic	Suzuki Vitara_2
Kia Sorento	Mazda 323	Seat Cordoba
Nissan Almera	Nissan Xtrail	Renault Megane
Peugeot 106		

Table 3.1: 25 commercial spent catalytic converters from which catalytic converters were collected

Furthermore, the use of a single homogenized batch is necessary, so that all dissolution/separation/recovery experiments conducted to refer to a common sample of homogeneous monolithic ceramic powder. The steps of spent catalyst mechanical pretreatment are represented in **Figure 3.1**. The samples have been analyzed before and after leaching, determining their PGM concentrations. The external calibration of the XRF instrument described in Chapter 2 has been used to precisely determine the PGM concentration ranges, namely low concentrations (after leaching process) and higher concentrations (before leaching process).

3.3. Leaching Procedure for the PGMs Recovery

A predetermined quantity of catalyst powder is received after milling processing, without further thermal or chemical pre-treatment (one-step hydrometallurgical leaching process). The leaching reagents used refer to HCl (37%) Cl_2 vapours stop being generated while NaCl (99.5%) was used as an additional Cl^- species, and finally deionized H_2O was added in order to reach the final solution total volume under magnetic stirring conditions. The leaching takes place at 70°C for 2 h (or 3 h for kinetic experiments). It should be noticed that adding reagents in a different order other than

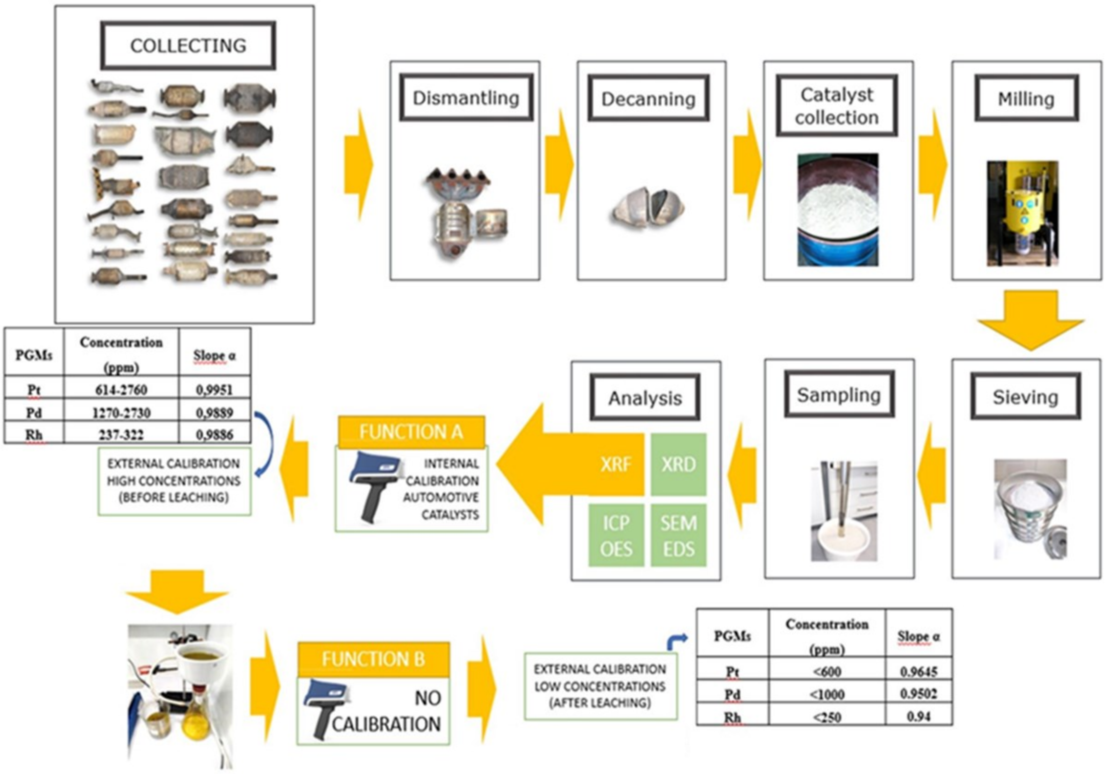
HCl, H_2O_2, NaCl, H_2O, results in a high exothermal reaction. The S/L ratio is finally adjusted by the addition of deionized water.

Selected concentrations of HCl, NaCl, as well as S/L ratio have been evaluated. Once leaching process has been completed, the solution is filtrated under vacuum, applying the Buchner method, and several washes follow. Finally, the solid phase is dried overnight at 120°C, pulverized and subjected to X-ray fluorescence spectroscopy (XRF), in order to determine the after leaching PGMs concentrations. All the experiments have been repeated twice, with the view to confirm reproducibility of process and experimental conditions. X-ray fluorescence spectroscopy (XRF) measurements were recorded twice as well, in order to prevent significant variations.

3.4. Characterization Methods

3.4.1. Morphological Characterization of the Batch Catalyst Powder

The representative sample from the 20 kg batch has been collected and subjected to basic characterization techniques, in order for the morphology and elemental analysis to be defined. These properties refer to the sample before the leaching process. Scanning electron microscopy analysis (SEM) combined with energy-dispersive X-ray spectroscopy analysis (EDS) provides additional understanding of the surface material composition. The quantitative elemental determination, as well as semi-quantitative analysis are conducted in different sample areas under × 200 magnification conditions. X-ray powder diffraction analysis (XRD) is used for the mineralogical characterization of the sample. The crystallography of the PGMs, namely crystal lattice, crystallite size and shape, could be further examined in case of higher PGM loading.



PGMs	Concentration (ppm)	Slope α
Pt	614-2760	0,9951
Pd	1270-2730	0,9889
Rh	237-322	0,9886

PGMs	Concentration (ppm)	Slope α
Pt	<600	0.9645
Pd	<1000	0.9502
Rh	<250	0.94

Figure 3.1: Characterization process

3.4.2. X-ray Fluorescence Analysis (XRF)

The PGM content was determined with X-ray fluorescence spectroscopy. The XRF spectrometer (VANTA Olympus 2017, Waltham, MA, USA) was calibrated by the manufacturer to measure precisely Pt, Pd and Rh in spent catalysts of average PGM concentrations of 1000 ppm, 1700 ppm and 300 ppm (PGM reference sample by BAM Berlin), respectively. Further to the manufacturer's calibration, a series of measurements took place, by using commercial samples of different PGM concentrations. By following this process, the accuracy of metal determination was validated by the specific method and calibration curves. Moreover, several research groups, like Prof. Binennmans' Group in KU Leuven [1] and Jeroen Spooren Group in VITO [2] have already used spent automotive catalysts samples that have been characterized with the specific method. In order to define the recovery yields of PGMs, two X-ray fluorescence measurements have been conducted, corresponding to the sample before and the sample after leaching. Prior to any XRF measurement, the dried catalyst sample was milled into an analytical mill downsizing its particle size, then grounded, in order to obtain specific granulometry (< 350 μm) or pulverized, using an agate mortar. Under standard deviation lower than 5%, the concentration of the noble metals was defined from the mean concentration value of 10 scans (90 sec/scan), taking into consideration the proper calibration mode. The recovery rate percentage of PGMs is calculated as: leaching rate (%) = $[(C_i–C_f)/C_i] \times 100$, where C_i refers to the initial PGMs concentrations (before leaching), while C_f refers to the final PGMs concentrations (after leaching). In this chapter, the differentiation of the mass of the solid residue before and after the leaching has not been taken into account for two reasons: (a) for comparison purposes, since all the literature data report leaching efficiency calculated as the difference between the obtained concentration versus the calculated one and (b) the residue mass remaining in the filter upon filtration step is negligible, thus is not considered significant to be taken into consideration in mass balance calculations.

3.4.3. Kinetics of the PGM Complex Formation

The kinetic response of the leached sample has been evaluated for different leaching time. The PGM concentrations (ppm) are defined as a function of leaching time (0.5 h, 1 h, 2 h, 3 h), in order for the most efficient leaching duration to be verified. According to the reduction potential of PGMs in $HCl–H_2O_2–NaCl$ systems ($E° = -0.744$ V for Pt, $E° = -0.620$ V for Pd, $E° = -0.450$ V for Rh), it is suggested that, compared to Rh complex, Pd and Pt chloro- complexes are better dissolved into the chloride media. It is expected that Rh should exhibit lower kinetics, due to its passivation layer and stereotactical structure.

3.5. Results

3.5.1. Morphological Characterization of the Catalyst Sample

According to the energy dispersive X-ray spectroscopy analysis (EDS), the spent catalyst sample contains amounts of Al (38–46%), Si (9–33%), Ce (11–27%), Zr (6–27%), Mg, (5–9%) Ca (~ 1%), Na (~ 1%) (**Figure 3.2**). This finding is expected, as the sample derived from spent automotive catalyst, where cordierite monolith contains Mg, Al, Si, O, with the formula of $(Mg,Fe)_2Al_3(Si_5AlO_{18})$ to $(Fe,Mg)_2Al_3(Si_5AlO_{18})$. Furthermore, the cordierite has been impregnated with alumina, or silica or ceria washcoat.

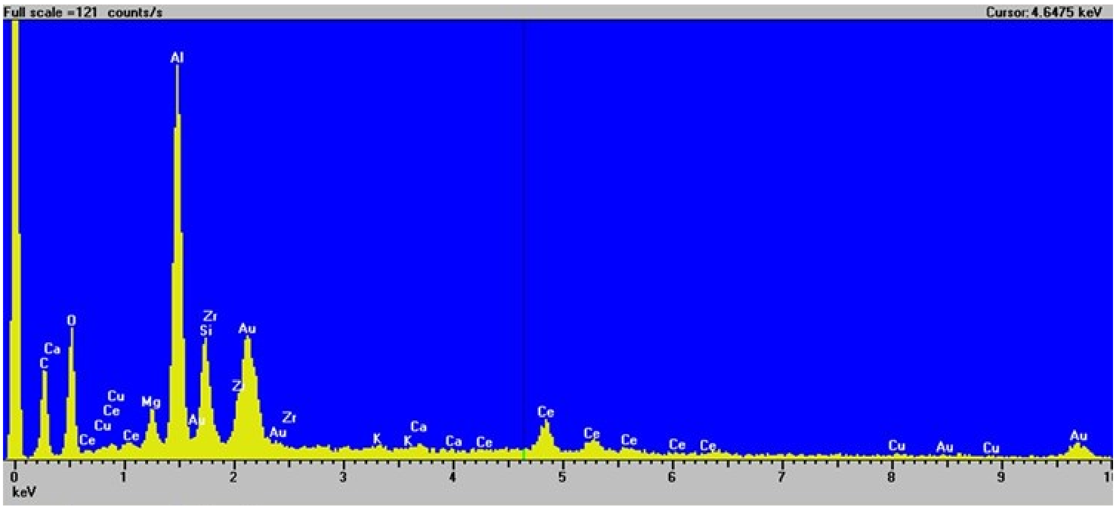


Figure 3.2: Energy Dispersive X-Ray Spectroscopy analysis (EDS) of spent catalyst sample

The surface morphology of spent catalyst in powder form was validated by SEM images. The structure analysis has been performed using Image J program. According to the histogram drawn by OriginLab (**Figure 3.3**), a slightly heterogenous particle size distribution might be observed. Via micrograph evaluation, the catalyst sample reveals mean particle size 20 μm, maximum size 27 μm and the minimum 7 μm. The formation of a fine, homogeneous powder is expected, as sieving and milling have been conducted (< 250 μm). It is suggested that both homogeneity and fine powder formation promote the leaching efficiency, due to the increased surface area.

Furthermore, small PGMs prills with have nano-dimensions (× 10,000 magnification) might be distinguished (**Figure 3.3**).

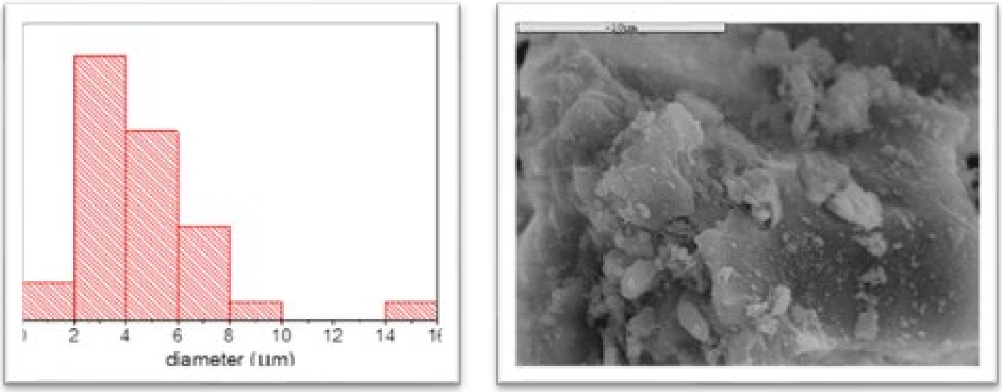


Figure 3.3: Histogram of particle size distribution/ Small PGMs prills on ceramic grain (x10000)

According to the XRD pattern (**Figure 3.4**), the main peaks correspond to indialite (syn-$Mg_2Al_4Si_5O_{18}$), cordierite ($Mg_2Al_4Si_5O_{18}$) and cerianite (Ce, syn-CeO_2). Moreover, crystal phase of potassium magnesium aluminum silicate ($KMg_2AlSi_4O_{12}$) has been detected. The XRD results for the spent catalyst are in line with EDS analysis. In both characterization techniques, PGMs content is not observed, due to their low loading on the catalyst monolith. Regarding the phase characterization, more than two crystal phases have been identified in the structure of the powder, according to the reflections and their relative intensities. Since the detection limit of the method is > 5%, crystal phases that might be formed from PGM chlorides, cannot be detected.

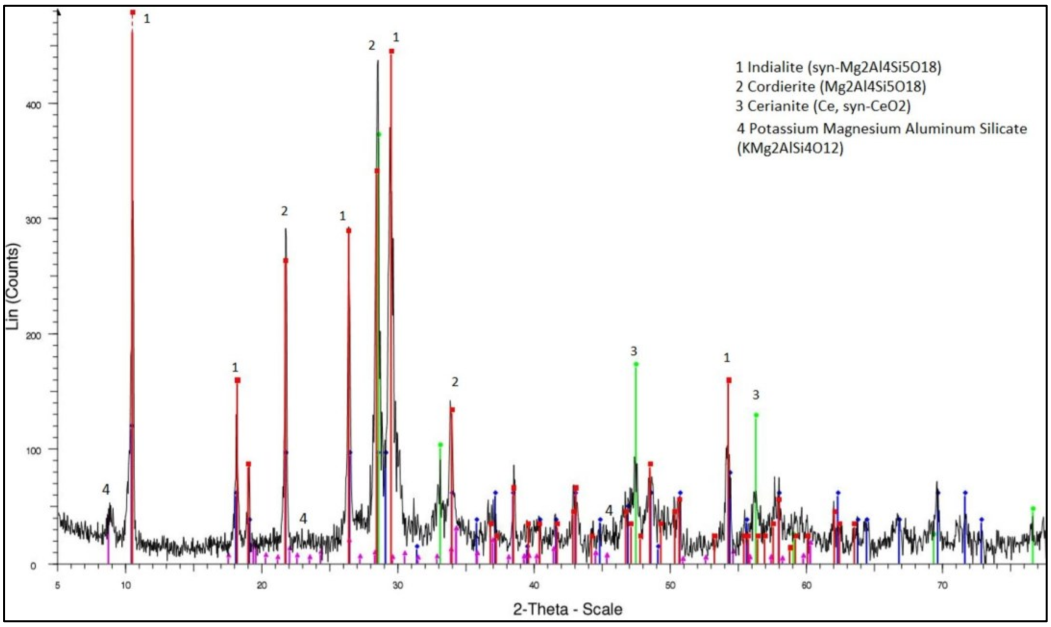


Figure 3.4: X-ray powder Diffraction pattern for spent catalyst batch samples

3.5.2. Leaching Parameters

In this one-step leaching method, noble metal oxidation and dissolution take place and PGM chloro-complexes are formed. Leaching process takes place by adding HCl acid in spent catalyst in powder form, under stirring. Subsequently, oxidizing agent H_2O_2 is added with caution since Cl_2 gas is formed, while NaCl is added as long as Cl_2 gas production has been completed. Finally, water is added as solvent in certain amount to reduce the solution temperature that has been increased due to exothermic oxidation of the metals reaction and to obtain certain volume to reach the S/L. In HCl media, the most stable species formed are $PtCl_6^{2-}$ $PdCl_4^{2-}$, $RhCl_6^{3-}$. Hydrogen peroxide (H_2O_2) is a strong oxidizing agent with standard electrode potential of + 1.77 V. The addition of H_2O_2 in leaching media proved to act synergistically in recovery rate, as well as assists in the use of milder acid concentrations. Concerning the findings of Harjanto *et al.* [3], the addition of H_2O_2 in 1 vol% concentration increases the PGM dissolution, while further increase in the H_2O_2 concentration resulted in no significant increase in recovery yield. The solubility of Platinum, Palladium and Rhodium species could also be studied with Pourbaix diagrams, in order to identify the areas of the highest solubility of PGMs chloro-complex species [4]. Based on these facts, Pourbaix diagrams would offer the potential for lower energy consumptions, decreased processing time, while increased recovery rates would be achieved. The optimized H_2O_2 addition is 1 vol%, though even in this low percentage, the corrosive nature of H_2O_2 should be considered in case of further extraction. Partial replacement of HCl with NaCl salt resulted in effective PGMs dissolution, without substrate dissolution. The use of NaCl proved to facilitate the formation of stable chloro-complexes, acting as additional source of chlorides. Furthermore, NaCl salt assists in less acid vapours, formed by partial HCl evaporation, as less acidity is obtained. Numerous leaching experiments conducted at 70°C for 2 h optimizing all crucial parameters of the process. As for the parametrization, chloride source, HCl acidity, NaCl-HCl balance, S/L ratio, and H_2O_2 concentration have been studied. Experimental conditions and recovery yields are presented in the parametrization tables.

3.5.3. *Leaching Temperature*

In order to preserve a low energy consumption, all leaching tests took place at 70 °C according to the findings of Harjanto *et al.* [3]. Low leaching temperature minimizes energy consumption, leading to a cost-effective and environmentally friendly process.

3.5.4. *Leaching Solution Acidity (HCl Molarity)*

As illustrated in **Table 3.2**, two different HCl-concentrated leaching systems have been examined (70 °C, 2 h). As it is clearly observed, leaching acidity plays a crucial role in leaching efficiency, especially in case of Rh recovery. The experiment that took place under 6 M HCl conditions, enhanced Rh recovery, which reached almost 60%. However, minimizing HCl concentrations in order to follow greener leaching processes is of high need.

S/L	HCl	H_2O_2	NaCl	Pt%	Pd%	Rh%
10	6.0M	1% v/v	3 M	100	95	60
10	4.5M	1% v/v	3 M	100	94	54

Table 3.2: PGM leaching efficiencies obtained when using different HCl concentrations

3.5.5. *Balance of C_{NaCl}/C_{HCl}*

As demonstrated in **Table 3.3**, various balances of NaCl and HCl molarities have been examined. In leaching solutions, HCl provides the appropriate acidity for the leaching to take place, where additional chlorinating media introduced by different sources, mainly chlorides salts, provide the required Cl^- concentration for the chloro-complexes to be formed. By utilizing the additional source of NaCl, balanced with the HCl concentration, milder leaching conditions are required, compared to leachates without any additional chloride source. According to the data of **Table 3.3**, the acidity of the solution plays a crucial role in the leaching process, thus the solution with 6 M HCl and 3 M NaCl added exhibits the highest recovery percentages for Rhodium.

S/L	HCl	H_2O_2	NaCl	Pt%	Pd%	Rh%
10	6.0M	1% v/v	3.0 M	100	95	**60**
10	4.5M	1% v/v	3.0 M	100	94	**54**
10	4.5M	1% v/v	4.5 M	100	94	**46**
10	3.0M	1% v/v	6.0 M	100	93	**50**

Table 3.3: PGM leaching efficiencies obtained when using different NaCl-HCl concentrations (70°C, 2 h)

3.5.6. H_2O_2 Concentration

The oxidizing agent H_2O_2 is proved to ameliorate the leaching effectiveness, at a rate of > 0.5 vol%. Two experiments have been conducted to validate the oxidizing agent effect. Molarity of HCl and NaCl remained constant at 6 M and 3 M, respectively, where solid to liquid ratio (S/L) was 10%. Evaluation on higher concentration of v/v% H_2O_2 has also been conducted (**Table 3.4**), ensuring that more than 1% v/v H_2O_2 adversely affects the recovery [3, 5, 6].

S/L	HCl	H_2O_2	NaCl	Pt	Pd	Rh
10	6M	1% v/v	3M	100	94	60
10	6M	2% v/v	3M	87	93	47

Table 3.4: PGM leaching efficiencies obtained when using different H_2O_2 concentrations

3.5.7. Effect of Other Cl^- Sources

The effect of the anions of chloride salts other than NaCl, namely $AlCl_3$ and $CuCl_2$, has been studied and demonstrated in **Table 3.5**. In the case of $AlCl_3$, three times more chloride ions were provided to the leachate compared to NaCl, with respect to the same molarity in the leaching solution. However, the addition of $AlCl_3$, substituting NaCl, following the same reagent sequence as described above in section 3.3, into leaching media caused highly aggressive exothermal reaction, where the temperature was hardly controlled, even with the use of water bath.

In the case of $CuCl_2$ salt, which introduces into the solution twice the number of Cl ions but less compared to $AlCl_3$, lower recovery values for Rh have been observed, compared to $AlCl_3$ salt. Moreover, the leachate of $CuCl_2$ (4.5 M), HCl (4.5 M), 1% v/v H_2O_2 solution resulted in unstable dispersion, forming crust on the solution surface and aggregation. The cause for this destabilization might refer to the $CuCl_2$ quantity, which could not fully react with the liquid solution (S/L ratio factor). The additional source of NaCl is preferable, giving promising recovery results, thus it has been further investigated.

S/L	HCl	H_2O_2	NaCl	$CuCl_2$	$AlCl_3$	Pt	Pd	Rh
10%	6M	1 % v/v	-	-	3M	100%	94%	63%
10%	6M	1 % v/v	-	3M	-	100%	94%	53%
10%	6M	1 % v/v	3M	-	-	100%	94%	60%

Table 3.5: PGM leaching efficiencies obtained when using different chloride source leaching

3.5.8. S/L Ratio

The S/L ratio is a crucial factor for the industrial design of leaching processes, since the higher the S/L ratio the less solvents are used, offering both economic and environmental advantages, in case of proper waste management. Evaluations on S/L ratio took place, in order to reduce the generated waste from the leaching process. By processing higher amount of catalyst powder under milder conditions, namely high S/L ratio, hydrometallurgy gains a foothold in PGMs recovery. The optimum S/L ratio achieved is 70% (namely 70 g of solid catalyst leached at 100 ml of total solution), providing promising recovery yields for industrial scale. As it is clearly observed from metals recovery rate (**Table 3.6**), when S/L > 70% the solid cannot react properly with the leaching solvent [7, 8] (**Table 3.6**). Most probably, the Cl^- species of the solvent, including those added by chloride salts, are not enough to form chloro-complex species with the metals, thus the solubility is decreased, since the solvent is saturated in leached metals. Subsequently, reduced recovery rates are observed for Rh and Pt, probably due to variations in Redox potential.

S/L	HCl	H_2O_2	NaCl	Pt	Pd	Rh
10%	4.5M	1% v/v	3M	100	94	53.8
50%	4.5M	1% v/v	3M	100	94	57
70%	4.5M	1% v/v	3M	100	93	50
80%	4.5M	1% v/v	3M	56	93	26.4

Table 3.6: PGM leaching efficiencies obtained when using different S/L ratio

3.5.9. Process Optimization

According to **Table 3.6** the highest S/L ratio achieved is 70%, resulting in promising leaching yields for Pt (100%), Pd (93%) and Rh (50%). According to **Table 3.7**, leaching optimization for Rh can be monitored by altering NaCl and HCl concentrations. By increasing the molarity of NaCl, higher Rh leaching yield is obtained, namely from 50 to 56%. Another optimization has been achieved by decreasing the molarity of HCl, leading in milder leaching acidity and higher Rh dissolution. According to the experimental parametrization, it is observed that, leaching solution of HCl (3 M), S/L: 70%, NaCl (4.5 M), oxidizing agent 1% v/v H_2O_2 at 70°C for 2 h gives promising recovery yields, following green chemistry rules. Reagents should be added in a specific order, namely catalyst powder, HCl, 1% v/v H_2O_2, NaCl and deionized water. Concerning the sample preparation before the leaching process, fine grinding affects the total recovery rate by increasing the leaching efficiency. Compared to previous studies, the low concentration of HCl achieved minimizes the production of Cl_2 gas and fumes, confirming a safer leaching procedure. The liquid wastes depend strongly on the S/L ratio and washing stage, as well. Although S/L of 70% contains an elevated catalyst content and lower amount of reagents, additional washing is required to remove chlorine anions from the leaching residue. Thus, chloride sources need to be minimized adequately for the leaching percentage.

S/L	HCl	H_2O_2	NaCl	Pt	Pd	Rh
70%	4.5M	1% v/v	3.0M	100	93	50
70%	4.5M	1% v/v	4.5M	100	93	56
70%	3.0M	1% v/v	4.5M	100	92	61

Table 3.7: Leaching system optimization

3.6. Kinetic Approach

A kinetic investigation of the optimized leaching system, namely 3 M HCl-4.5 MNaCl-1% v/v H_2O_2 at 70°C, is presented (**Figure 3.5**). According to **Figure 3.5**, 1h leaching duration is appropriate for the PGMs dissolution, as concentrations do not further increase (3-h leaching period). According to kinetics in **Figure 3.4**, all the precious metals present in the spent catalyst are dissolved rapidly within 1,5h, while dissolution rate decreases until a plateau is reached after one hour for all of them. Recovery rate for both Pt and Pd are higher than the corresponding rate of Rh, at the same timescale. Further investigation should take place, about the Rh relation to the catalyst matrix system, in order for the Rh kinetic chloroformation to be fully understood. Comparing leaching among PGMs, the dissolution follows the order Pd, Pt, Rh starting from the highest one. It is proved that Rh has the slowest kinetics (**Figure 3.5**), probably due to the stereo tactical structure and passivation layer that might have been formed under acid conditions. Structural observation with microscopy methods would reveal an insight on the structure and the properties, as well.

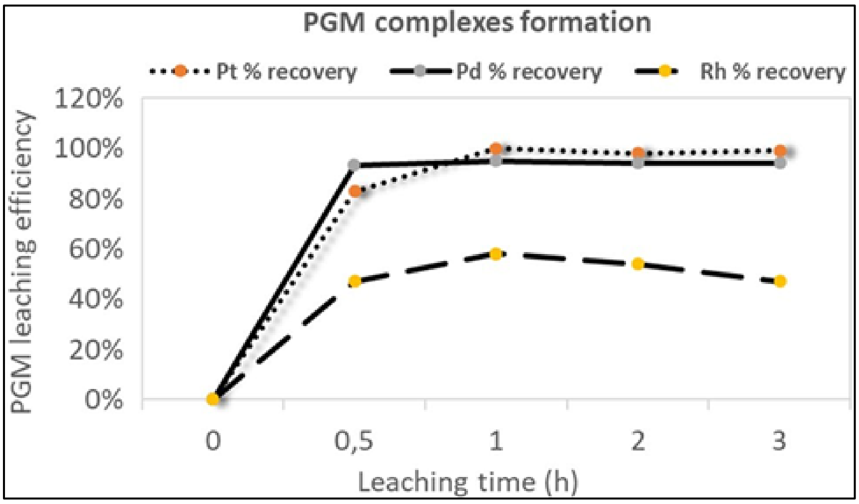


Figure 3.5: PGMs kinetic behaviour for 0,5h to 3h leaching time

Additionally, according to **Figure 3.5**, Rh recovery yield exhibits the highest rate in one hour leaching time, while is further decreased in two or even three hours of continuous leaching. This could probably be attributed to the formation of certain Rh-Cl species that might be formed, or even aggregates which might be deposited in CeZr substrate, where they were dissolved from. The saturation of the solvent in Pt and Pd species, which has reached a plateau of maximum dissolution in the HCl-based solution, might hinder the Rh from being dissolved in the solvent, or even formed species to aggregate, and due to chemical potential restriction they are not permitted to be dissolved.

3.7. Conclusions

In this chapter, an optimized single-step leaching process for PGMs has been proposed, following the well-tested HCl–H_2O_2–NaCl system. Comparing with previous studies on the same system, pretreatments, such as reduction or pre- concentration, have been avoided in this novel approach. The leaching yields obtained are 100%, 92% and 61% for Pt, Pd and Rh, respectively, using low acidity reagents, namely 3 M HCl, 4.5 M NaCl, 1% v/v H_2O_2, under mild temperature conditions (70°C). Furthermore, the highest S/L ratio achieved (S/L = 0.7) leads to high catalyst mass dissolution, thus significant PGMs dissolution by direct leaching. The high S/L ratio of the proposed process offers significant advantages in industrial design, as smaller plant installation may be required. Undoubtedly, improvements in liquid waste management should be proposed to minimize waste treatment expenses. Both mild acidity and leaching temperature of the proposed leaching system led to the presumption that an environmentally friendly approach has been implemented. Further leachate analysis must be performed to evaluate the sustainability of the process.

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4th Chapter

4. Circular Economy model for the Production of Car Catalysts from Recycled Platinum Group Metals

4.1. Introduction

The attention for the circular economy increases rapidly not only in Europe as well as worldwide. It is a potential way for a society to increase prosperity and decrease dependency on primary materials and energy resources. The European Commission (EC) presented a “circular economy package” and action plan for revising legislation on waste on December 2, 2015 (1). A platform to support the financing of circular economy has also been launched. The platform brings together financial market stakeholders by increasing the awareness of the business logic of circular economy. However, the circular economy model had been embraced earlier by several businesses targeting growth and profitability increase. Nowadays there is a debate on the advantages the circular economy model can have on different stakeholders and its implications on employment, growth, and the environment. A critical parameter in circular economy is the lifetime of a product [1-4].

Longer lifetime leads to the generation of new economic activities, it triggers innovation in existing business models and also, increases the gross domestic product (GDP) and offers various societal and environmental benefits, since the waste generation should be minimized as an essential contribution for a sustainable, low carbon and resource efficient economy (2). An effective reduction in resources consumption and waste is possible via the circular economy model. However, an efficient engagement is required between the four main pillars of the economy; the procurers, the service providers, the consumers and the recyclers.

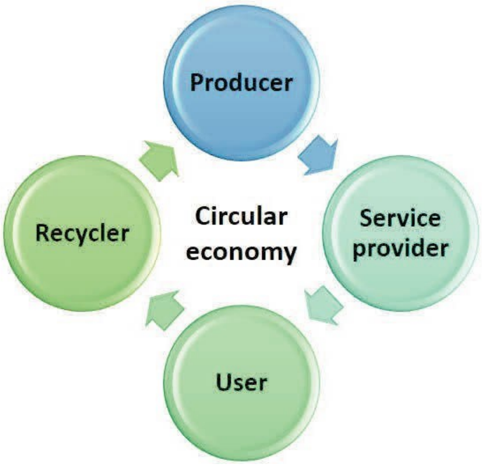

Figure 4.1: The circular economy concept

A simplified schematic representation of the circular economy concept is shown in **Figure 4.1**. The concept embraces the importance of the economy needing to work effectively at all scales; for large and small businesses, for organizations and individuals, globally and locally.

In an effort to secure long access to materials used in advanced technologies EC introduced the Raw Materials Initiative in 2008, highlighting a list of materials defined critical because their "risks of supply shortage and their impacts on the economy are higher than those of most of the other raw materials (European Parliament, 2016). The risks associated with concentration of production are in many cases compounded by limited potential for substitution and low recycling rates. Since 2017, the EC list of Critical Raw Materials enumerates 24 materials and 3 groups of elements: HREEs (heavy rare earth elements), LREEs (light rare earth elements) and PGMs (platinum group metals) that are widely used in automotive emissions control catalysts.

4.2. Autocatalysts circular economy - closing the loop

The developing of products for the circular economy of automotive catalysts offers another point of view on the way to reap the rewards of going circular by eliminating waste, recycling and creating value. A typical batch of spent ceramic-based TWCs contains almost 2600 ppm or 0.26 wt.% of PGMs per unit, while it reaches 7900 ppm or 0.79 wt.% when metallic support is used.

The above PGM concentration is almost 250 times higher than in typical ores and establishes TWCs as an excellent secondary source of PGMs. This is the driving force for collecting, sorting and recycling spent TWCs in order to recover and utilize secondary PGMs in the production of TWCs.

Over this pathway and accounting for the mentioned above ~60% TWC recycling rate in the EU, the addition of primary source PGMs cannot be avoided but only diminished. Thus, the partial substitution of PGMs by transition metals (like Copper) constitutes a potential low-cost solution to support the proper operation of the circular economy model, shown in **Figure 4.2**. Spent TWCs are collected from vehicle workshops and scrap yards. The majority (90%) are ceramic-supported, while only 10% are metal-supported [5, 6]. Upon collected, they are sorted manually according to the technical characteristics of the vehicle they were derived from, like fuel, engine size, year of manufacturing, genuine or aftermarket, etc., in an effort to categorize them by PGM content.

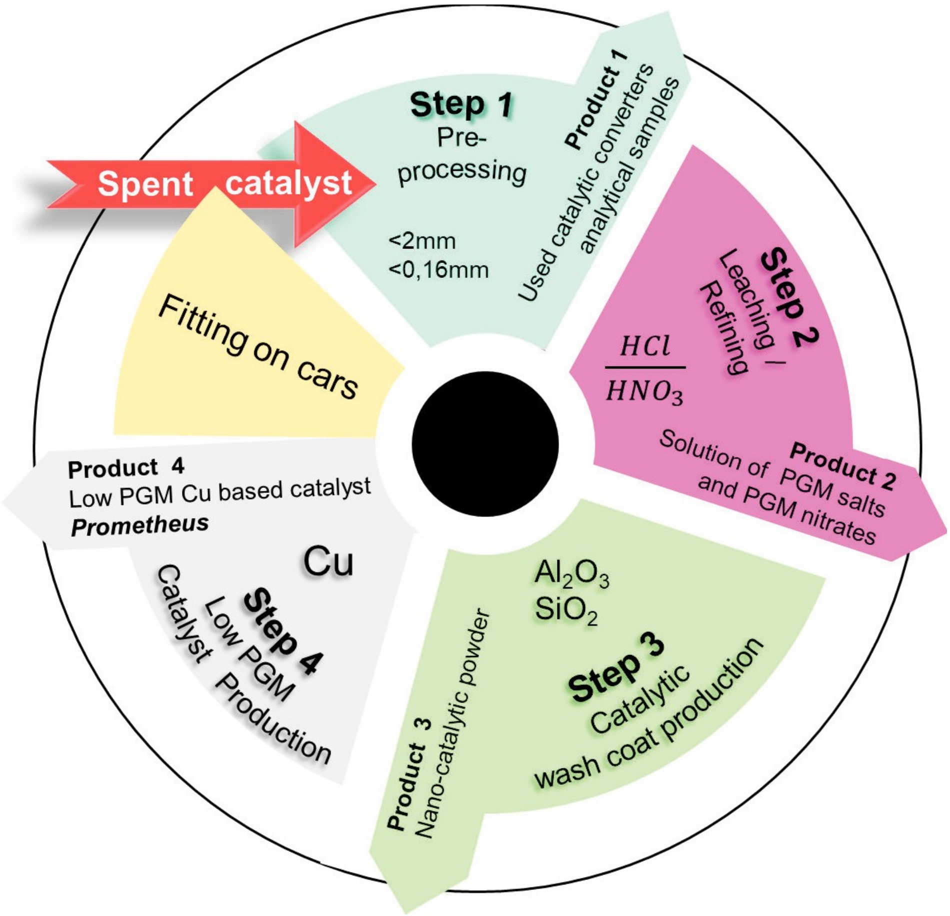

Figure 4.2: Suggested circular economy model for the production of novel low-PGM TWCs using spent autocatalysts as secondary sources of PGM and Cu.

4.2.1. Step 1: Preprocessing of spent TWCs

Preprocessing step includes decanning of the ceramic converters using an alligator type shear and shredding of the metallic ones. During decanning, the inlet and outlet exhaust tubes are cut and also, the outer metallic canister and wool coat are removed. The ceramic converters are initially crashed in a chain mill to downsize to ~2 mm particles, and afterwards in an analytical mill to prepare a homogeneous fine (< 0.16 mm) powder, as shown in **Figure 4.3**.

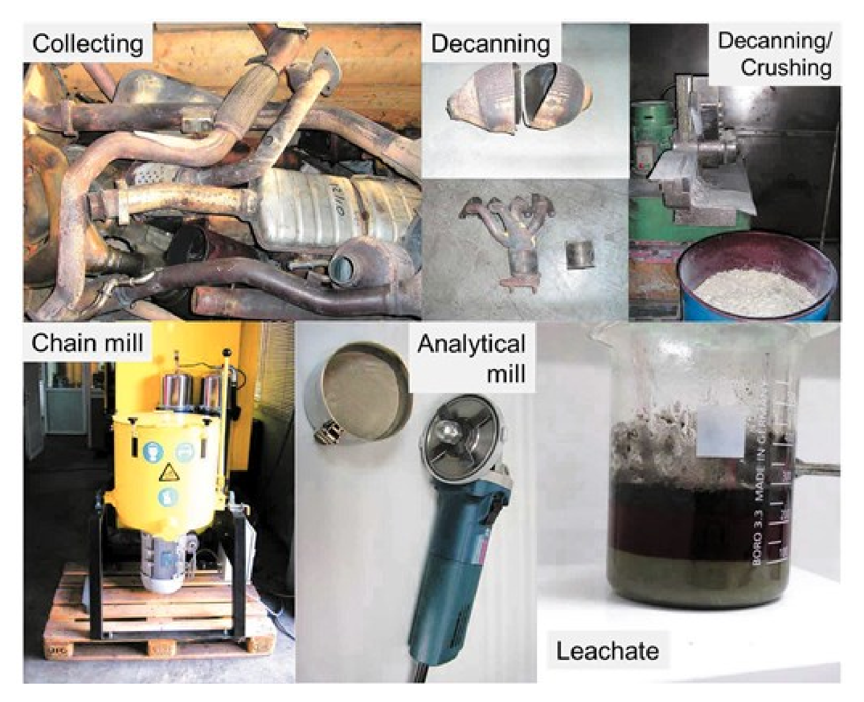

Figure 4.3: Collecting, sorting crashing and leaching steps for PGM recovery by spent catalysts

The above fine powder mixture contains the PGMs, the washcoat and the ceramic support. Pulverization time is optimized according to the initial concentration homogeneity rate of the metals in the spent autocatalysts and also, based on the required final concentration homogeneity of the metals, into the fine powder mixture. Chemical leaching and refining methods are used in this step to dissolve the PGM particles that are contained into the fine powder produced in Step 1, avoiding the energy-intensive pyrometallurgical method. Various low temperature hydrometallurgical techniques have been reported in the literature for the extraction of PGMs using either organic solvents or ionic liquids or aqueous acidic solutions. Reported in the literature recovery yields lie near those of the industrial pyrometallurgical process that reach ~98% for Pt and Pd and ~87.5% for Rh [7]. Apart from the energy consumption that imposes extremely big scale metal recovery units, the low cost of solvents and the waste management simplicity led to the selection of an aqueous acid-based hydrometallurgical process. Moreover, concentrated HCl and/or HNO_3 acids have been selected over H_2SO_4 or H_3PO_4, due to the higher solubility product constant in the examined temperature range and also, the compatibility between the resulting metal salts and the catalyst and/or catalyst synthesis procedure that follows in Step 4. It is worth noting that significant quantities of sulfur (S) and/or phosphorous (P) can result in catalyst poisoning and thus, additional intermediate treatment steps maybe required. Similar aqueous leaching solutions under extremely acidic conditions have been reported for PGMs extraction by ceramic supports [7- 12].

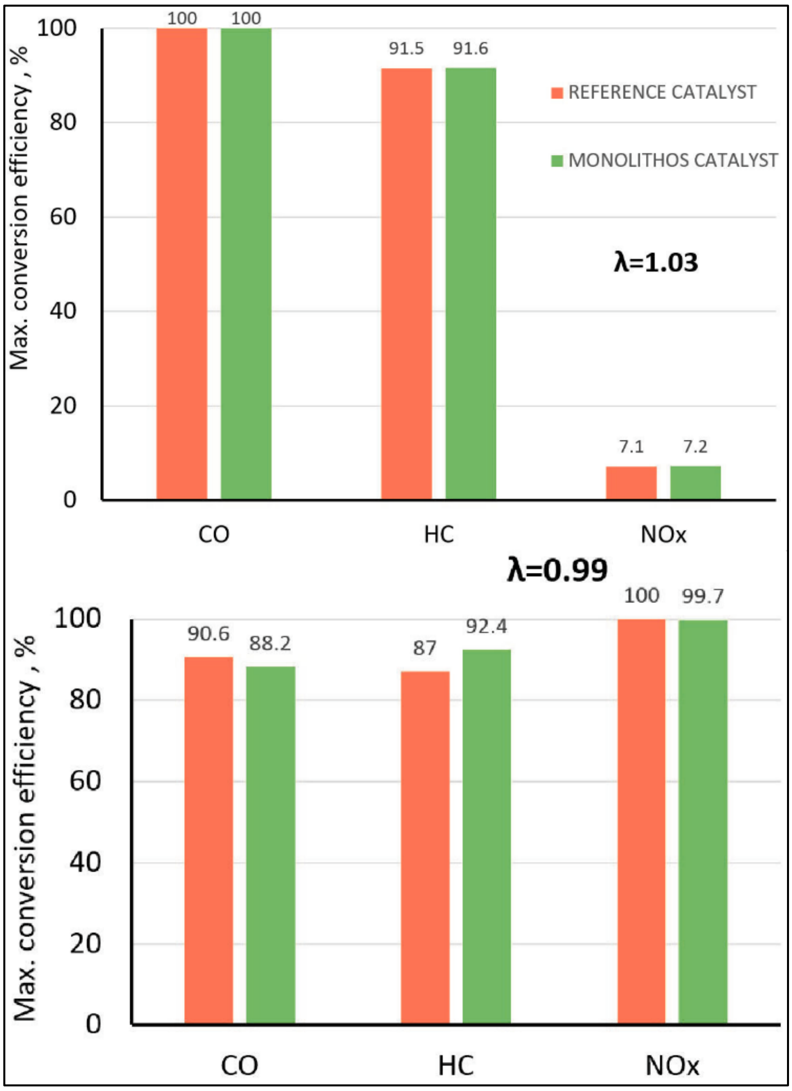

Figure 4.4: Steady state catalytic activity comparison between a commercial PGM-based monolithic catalyst and catalyst prepared with reduced amount of PGMs.

The performance under both oxidizing (λ = 1.03) and reducing conditions (λ = 0.99) has been investigated. As shown in **Figure 4.4**, the developed catalyst activity is very similar to that of the commercial, while it contains Cu and only 35 wt% of the PGMs that the compared catalyst has. The above PGM content in trimetallic low PGM catalyst (EP3569309) in combination with the mentioned recycling rate of spent TWCs and the achieved PGM recovery yield allow for the sustainability of the described in model economy cycle. Moreover, long term stability testing onboard a real passenger vehicle tailpipe has shown minor deactivation of the catalyst (EP3569309), promoting its strong potential for large scale production and practical application on road.

4.2.2. Step 2: Leaching and refining of PGMs

During leaching and refining step, spent catalyst powder of analytical fineness is introduced into the leaching solution, under optimized conditions of contact time, stirring rate, temperature and oxidizing agents. The resulting homogeneous solution of Pt, Pd and Rh salts is obtained with filtration, while the ceramic substrate and washcoat are removed as sediment.

Refining or purification of the leachate solution can be performed either via hydrometallurgical, pyrometallurgical or volatilization processes. Recovery yields can be recorded with analytical methods and standardized protocols such as X-Ray fluorescence and ICP-MS with accuracy of ±1-2%. Deficient sampling and sampling preparation can have high financial impact; thus, homogeneity of the bulk should be monitored continuously throughout the process.

It is worth noting that undesired contaminants originating mainly by the fuel, like lead (Pb), vanadium (V), sulfur (S), soot (C), fuel and lubrication oil, can have an impact in the recovery yield of the process. Thus, additional treatment may be required in batches where contaminants above a threshold value are detected.

4.2.3. PGMs nitrates to chlorides conversion

In order to prepare nitrate solutions for the production of the catalyst washcoat, the leachate hydrochloric acid based solutions had to be transformed into nitrate solutions. Nitrate Pt, Pd and Rh salts are considered as the most stable and most suitable salts as precursors to prepare automotive catalysts. Nanocatalyst formation is facilitate in nitrate environment, while no residue from nitrate salts remains after the catalyst formation, since they are efficiently removed with a calcination step in NOx species. [13, 14] The process followed for three solutions consisting of Pt, Pd and Rh is described in detail below.

4.2.3.1. Platinum Recovery and Nitrate Conversion

The process developed consists of three main stages that aim to extract the Pt contained in a solution and obtain a solution of Pt (IV) nitrate as the final product. The flowsheet in **Figure 4.5** shows the platinum nitrate manufacturing process in a schematic way. A total of 3 steps have been developed to obtain a platinum nitrate with a purity higher than 99%.

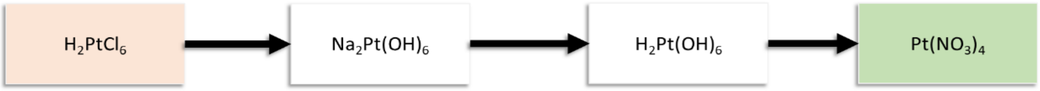

Figure 4.5: Flowsheet of the steps followed for the conversion of Pt chloride species into nitrates.

After the extraction of Pt in chlorinating media leachate solution, the next step of the proposed process consists of dissolving H_2PtCl_6 in water further to precipitate Pt as sodium hexahydroxoplatinate [$Na_2Pt(OH)_6$] by 40% w/w NaOH addition. The optimization process was carried out with a standard of H_2PtCl_6 at 90°C temperature. As the NaCl obtained was a by-product of the reaction, it should be removed from the precipitate. Chemical analysis of Pt and Na content in the precipitate obtained was conducted according to the $Na_2Pt(OH)_6$ stoichiometry and the spectrum obtained by XRD analysis (**Figure 4.6**) was consistent with that of $Na_2Pt(OH)_6$. Once the process was optimized, 83% of Pt contained in the standard was recovered in the precipitate while 11% Pt remained in the solution and 6% Pt was lost in the washing steps.

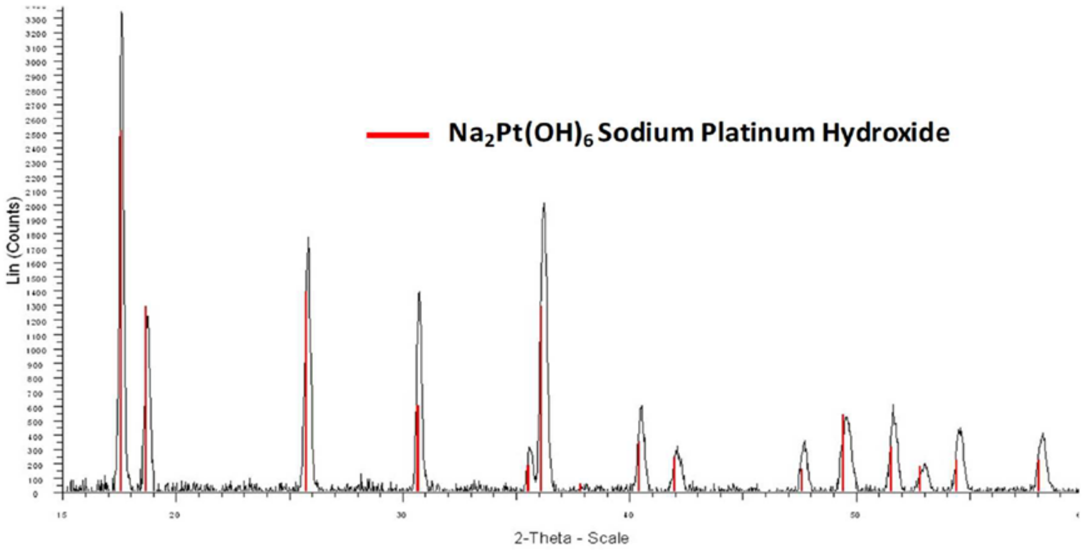

Figure 4.6: XRD spectrum of the precipitate obtained after the treatment of H_2PtCl_6 with NaOH

In the next step, the $Na_2Pt(OH)_6$ contained in the solution is precipitated as hexahydroxyplatinic acid $[0H_2Pt(OH)_6]$ using 0.5 M HNO_3 as a reagent. First, the optimization was carried out with a $Na_2Pt(OH)_6$ standard. The tests were conducted at room temperature and parameters such as final pH, reaction time, number of washing and washing agent to $Na_2Pt(OH)_6$ ratio were researched. Washing reagent was 0.001 M HNO_3. Analysis of the samples showed that 99% of the Pt precipitates when the final pH is adjusted between 2 and 3. In addition, the Pt concentration obtained (58-64%) and the XRD analysis of the precipitate are consistent with the expected compound. **Figure 4.7** shows the XRD spectrum of the precipitate obtained.

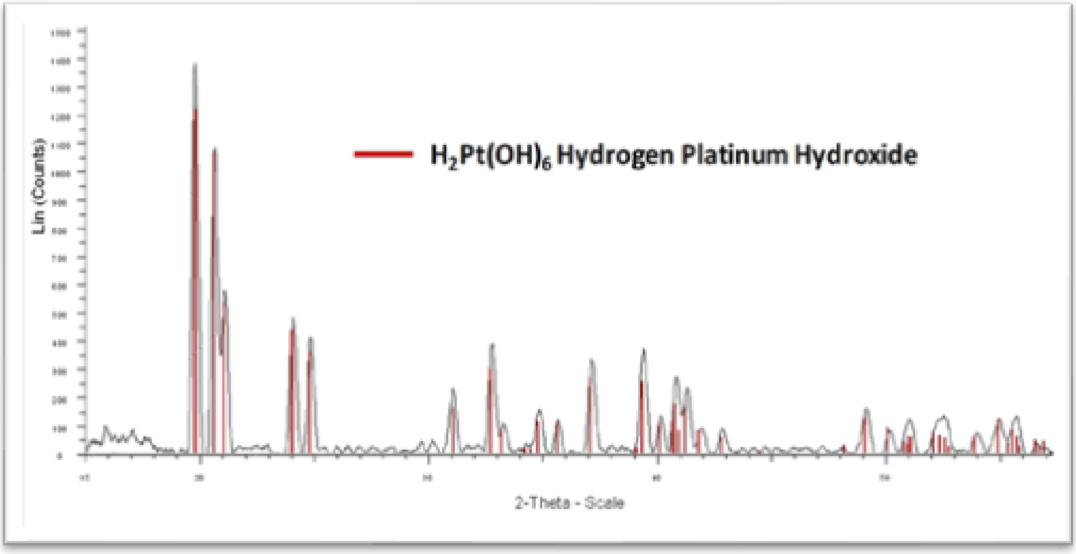

Figure 4.7: XRD spectrum of the precipitate obtained after the treatment of $Na_2Pt(OH)_6$ with HNO_3

Once the $H_2Pt(OH)_6$ was obtained, the last step was only to dissolve the precipitate in 65% w/w HNO_3. Then, the samples of $H_2Pt(OH)_6$ obtained from leachate batch were dissolved in 65% nitrate in order to obtain a $Pt(NO_3)_4$ solution with around 15 gPt/l. Nitrate solution was analysed to determine the Pt and the impurities concentrations. For this purpose, a Total Reflection X-ray Fluorescence (TXRF) analyser was used to determine the impurities present in the solution and an ICP-MS analyser to quantify the concentration of Pt and impurities. The concentration of each element detected is shown in **Table 4.1**.

ELEMENT	CONCENTRATION mg/l
Pt	14972
Na	73.20
Zn	8.72
Al	4.78
Ba	4.31
Fe	2.36
Ni	1.6
Pb	1.4
Rh	1.28
Pd	0.92
Cu	0.62
Ce	0.58
P	0.57
Mg	0.35
Ca	0.25
Ti	0.15
Zr	0.08
Sr	0.06
L	0.03
Hf	< 0.01

Table 4.1: Analysis of the $Pt(NO_3)_4$ obtained from Pt-stripping of solution

4.2.3.2. Palladium Nitrate Conversion

After hydrochloric based leaching process, the Pd containing solution was subjected to GDEx process [15] with NaCl as supporting electrolyte and CO_2 as feeding gas (**Figure 4.8**) aiming at conversion of Pd into nitrate form species.

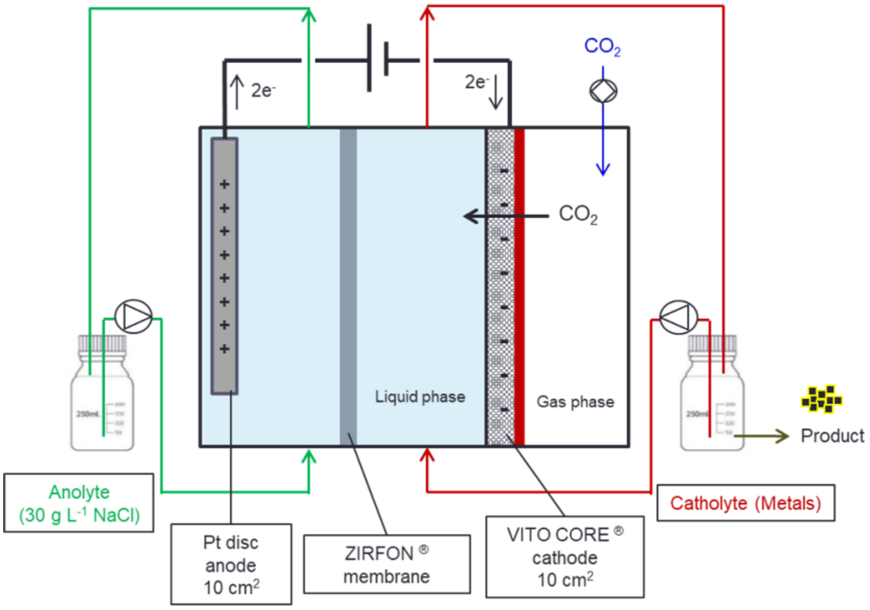

Figure 4.8: Schematic representation of the GDEx reactor using CO_2 as the feeding gas and exemplified for a model stream with NaCl as supporting electrolyte

The input material was the Pd strip sample from the leaching processing. The GDEx process was conducted using a synthetic anolyte of NaCl 0.5 M. The process was controlled via a potentiostat, by polarizing the cathode at a constant potential. The pH was simultaneously monitored in an automated way, and it was often used as an indicator of the progression of the process. Otherwise, the charge consumed was used as indicator. The anolyte and catholyte were recirculated through their corresponding reservoirs until the process is completed, i.e., until the maximum amount of metals was removed from solution in the conditions established by preliminary experiments. Once the metal precipitated, the whole liquid was collected in the external catholyte reservoir and left to sediment. The supernatant was separated from the sediment by decantation. The sediment was further washed until its conductivity was comparable to pure demineralized water and then centrifuged to obtain a pellet.

The palladium sponge generated from the latter GDEx process was dissolved in nitric acid under the following conditions L/S = 40, T: 90°C, t: 60 min, concentrated HNO_3. Palladium nitrate solutions in 4.64 g/L concentration have been reached.

4.2.3.3. Rhodium Recovery and Nitrate Conversion

The split anion extraction of PGMs from leachate of spent auto catalyst was performed in 2 counter-current stages using the ionic liquid 75% v/v [A336] [I] in p-cymene. The flowrate of the aqueous phase and organic phase was set at 12 mL min^{-1} and 4 mL min^{-1}, respectively. The phase ratio O/A = 1/3 was adjusted in all the settlers.

The Rh raffinate from the solvent extraction was treated with potassium iodide to precipitate RhI_3 prior to dissolution in nitric acid to form Rh nitrate. The precipitation of the RhI_3 took considerable time due to the small amount of material (~60mg). The purity of Rh obtained was 98.6%. The Rh nitrate solutions were used for the solution preparation for catalyst production.

4.2.4. Step 3: Catalytic washcoat production

Various nano-sized ceramic powders can be used in order to offer specific desirable features to the catalysts, like γ-Al_2O_3 for high surface area, SiO_2 for thermal and mechanical stability, CeO_2 for oxygen storage capacity, etc. The effect of the support on the catalytic activity and selectivity is major parameter in catalyst design and fabrication that is described in step 4. As a support for noble metals (mainly Pd), simple oxide mixed oxides (e.g., ZrO_2) or supported nanoparticles, ceria enhances the catalytic properties in combustion processes. Activation of oxygen on ceria gives rise to at least two species, superoxide (O^{2-}) and peroxide (O^{2-}) ions, both known to be involved in the total oxidation of hydrocarbons. Moreover, the modification of ceria with various cations is known to affect oxygen mobility, which plays an important role in the catalytic combustion of methane and improves stability towards sintering and the oxidation activity of the resulting catalysts. This modification leads to changes in redox properties and the creation of oxygen vacancies, both of which improve the oxygen exchange capacity between the gas phase and the catalyst and its oxygen storage capacity. In this sense, considerable attention has been given to incorporating different valence cations into the ceria lattice. The oxygen atoms/vacancies attached to reducible elements are mobile and contribute to the oxygen storage/release capacity of the mixed oxides and, hence, to their oxidation activity [16]. It is well established that many supports of heterogeneous catalysts, besides altering physical properties of the catalytic system, such as providing high dispersion and surface area for the catalyst, have also a chemical role in catalysis and are not inert as initially thought. Even when the active phase has the same dispersion or average crystallite size, the support can have a dramatic effect on the catalytic activity or selectivity due to the phenomenon of metal–support interactions. For example, cerium dioxide or ceria (CeO_2) is considered a very useful material as it can be used in various applications such as polishing material or solid oxide fuel cell electrolyte. Additionally, it is not toxic, a fact that makes it suitable in heterogeneous catalysis. Owing to the high oxygen storage capacity and the ability to stabilize the dispersed metal cation species, ceria has attracted researchers' attention finding many applications in environmental catalysis [17]. It is well known that size, shape, surface state and crystallinity are crucial factors for the catalytic performance of nanomaterials. Due to their tendency for aggregation during the catalytic process, their catalytic activity and stability are declined [18]. Therefore, different approaches, have been investigated, such as pH control or variation in solvent combinations, to control these properties in order to implement the most efficient catalytic synthetic materials. It has been reported that when noble metals are dispersed on "reducible" oxides, such as CeO_2 and TiO_2, the apparent activation energy of the reaction taking place at the gas phase does not depend on the nature of the metallic phase, but only on the nature of the support [19, 20]. Deep understanding of metal-support interactions is still a challenge in heterogeneous catalysis. However, the following two approaches are dominating: charge transfer between the metal particles and the support, and migration of oxide species from the support onto the catalyst particle surface.

4.2.5. Step 4: Low PGM catalysts production

The produced aqueous solution that contains the recovered PGM mixture, in the chloride and/or nitrate salts form, will be eventually used in the synthesis of novel catalysts with low PGM content using the selected washcoat material. It is worth noting that the PGM ratio in the solution depends on the recovery yield of each metal, and it has to be adjusted accordingly in case of significant variations. Targeting low-PGM content for promoting the decoupling of technology from critical raw materials and low-cost products, PGMs are partially substituted by Cu. Moreover, long term stability testing onboard a real passenger vehicle tailpipe revealed minor deactivation of the low PGM trimetallic catalyst (EP3569309), promoting its strong potential for implementation and large scale production.

4.3. Conclusions

European industry decoupling by primary critical raw materials is a major challenge where the efficient resources management throughout lifecycle and the recycling procedures as secondary sources will play a critical role.

In this chapter, a circular economy model was discussed in terms of automotive emission control sector. According to the model, PGM recovered from passenger vehicle catalytic converters via hydrometallurgical processes, can be used as secondary raw material source for the preparation of novel autocatalysts. The latter are designed low in PGM and rich in Cu in order to support the sustainability of the described circular economy model that accounts for the actual recycling rate of spent autocatalysts and the achieved PGM recovery yields.

The significant advantage of the proposed circular economy model for automotive emission control devices is that every one for the four steps presented in **Figure 4.2** can be implemented separately from the others, fitted in existing industrial operations for production new catalytic converters and/or leaching spent material.

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5th Chapter

5. Development and Catalytic Efficiency of Automotive Catalysts using Recycled Platinum Metals recovered from Spent Automotive Catalysts

5.1. Introduction

Every modern vehicle equipped with an internal combustion engine possesses a catalyst (three way catalytic converters for petrol engines, or Diesel Oxidation Catalysts for diesel engines), in order to reduce efficiently the emission of harmful compounds like carbon oxides (CO), hydrocarbons (HC) and nitrogen oxides (NOx). Car manufacturers mainly use platinum group metals (PGMs) such as platinum, palladium and rhodium to perform these catalytic functions.

In general, the platinum group metals are comprised of six similar elements: iridium, osmium, palladium, platinum, rhodium and ruthenium. These elements are included by the European Commission in the list of critical raw materials, based on their economic importance and supply risk [1]. The long-term demand fundamentals for PGMs are strong, with their consumption closely related to the global green energy transition and imposition of stricter emissions standards-particularly in the automotive sector. Recycling could contribute in the reduction of supply risk and increasingly cover the future PGM demands in the EU and globally [2]. Moreover, concerning the advantages of recovering precious metals over their mining, these are mainly their limited resources, scarcity, expensive and energy-intensive mining process and the significant amount of waste generated during this process. Platinum group metal ores contain very small amounts of those metals. For example, in South Africa (the largest producer of platinum), PGM bearing ores have a low content of between 2 and 6 g/t [3]. At the same time, it should be noted that automotive catalytic converters typically contain up to 2000 g/t PGM in the ceramic catalyst brick, the active part of the converter [4]. Therefore, due to the high value of PGMs and the fact that autocatalysts comprise a rich source of PGMs, the attractiveness to recover those metals from end-of-life products such as spent autocatalysts, is extremely high.

Besides, the very restrictive legal regulations regarding the obligation to obtain specific recovery rates for end-of-life (ELV) vehicles and the mandatory removal of catalysts have improved the situation of the European Union in the area of PGM recovery [5].

Currently, there are several PGM refining facilities across Europe. However, the recovery of automotive catalysts is conventionally carried out with pyrometallurgical processes, including smelting, as the precursor to hydrometallurgical chemical separation and purification processes. These processes, may be effective at upgrading the PGM content, however, they are highly energy consumptive methods due to their operation at high temperatures [6, 7].

In this respect, over the last decades, various technologies have been investigated for autocatalysts recycling in order to reduce the environmental impact of PGM recycling, compared to the pyrometallurgical processes [6, 8, 9, 10]. PLATInum group metals Recovery Using Secondary raw materials (PLATIRUS) is a European Union (EU), Horizon 2020 project whose aim is to bring 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, thus, addressing the platinum group metal supply security within Europe. A relevant paper, which can be regarded as a PLATIRUS project overview, has been published recently [11], summarizing the most promising technologies explored during the project. The authors have concluded that the PLATIRUS project has successfully achieved its objective to research, evaluate and upscale novel and greener PGM recycling technologies.

This chapter deals with the lab scale experiments, validation of the potential of new autocatalysts (produced from recycled through the PLATIRUS project flowsheet PGM solutions) for their application in emission control. Specifically, the aim of the present study is the testing of recovered PGMs for their application in autocatalysts for hazardous gases abatement. In this respect, different types of autocatalysts were produced, with different PGM loadings as well as types of cordierites (900 cells per square inch (cpsi) hexagonal and 400 cpsi). The performance of the produced catalysts was evaluated by CRF (Center Research Fiat/currenly Stellantis Group), as both fresh and aged catalysts, for steady state as well as transient operation. To the best of our knowledge, this is the first study performed on the evaluation of the performance of autocatalysts produced from recycled PGMs solutions containing impurities (without further refinement steps), thus closing the PGMs recycling loop. Several characterization techniques have been incorporated (XRF, Optical Microscopy, BET-N2 physisorption) for the determination of the physicochemical characteristics of the synthesized catalysts and their catalytic performance has been evaluated by measuring their conversion efficiency for the pollutant gases vs. temperature: NO and NO_2 oxidation, hydrocarbon and CO oxidation and exotherm generation.

5.2. Materials and Methods

In this chapter, a series of small scale (carrots) autocatalysts from fresh PGMs (benchmark catalysts for comparison reasons) and PGMs recycled through existing routes) have been produced. The types of catalysts are Three-Way-Catalytic Converters (TWCs) and Oxidation Catalysts for Diesel Engines applications (DOC) and the methods followed for their production are described below.

5.2.1. PGM precursors

In the case of the benchmark catalysts, commercially available aqueous solutions of palladium (II) nitrate (Heraeus, solution assay 17.94 wt%), and rhodium (III) nitrate (Hereaus, solution assay 9.27 wt%) were used, while platinum (II) nitrate was used in powder form. On the other hand, for the production of the catalysts with recycled metals, the nitrate metal solutions came from the recovery of PGMs from secondary source materials.

The nitrate metal precursors that were used for the preparation of the catalysts were received from PLATIRUS *(www.platirus.eu)* project partners and came from the recovery of PGMs from secondary source materials. The processes used for the recovery of PGMs have been described in detail in a recent publication [11. In brief, the process started with a ~1.3 kg feedstock that consisted of a mixture of diesel oxidation catalyst (DOC) and three-way catalyst (TWC) [12]. The resulting powder contained 2066 ± 24 ppm palladium, 2574 ± 15 ppm platinum and 179 ± 5 ppm rhodium. Three different technologies (Microwave -MW- assisted leaching, non-conventional liquid-liquid extraction and Gas-diffusion electrocrystallization-GDEx), were selected and used in the context of PLATIRUS flowsheet for the process of the feedstock, finally producing 1.2 g palladium, 0.8 g platinum and 0.1 g rhodium in nitrate form with a purity of 92-99 % (**Figure 5.1**).

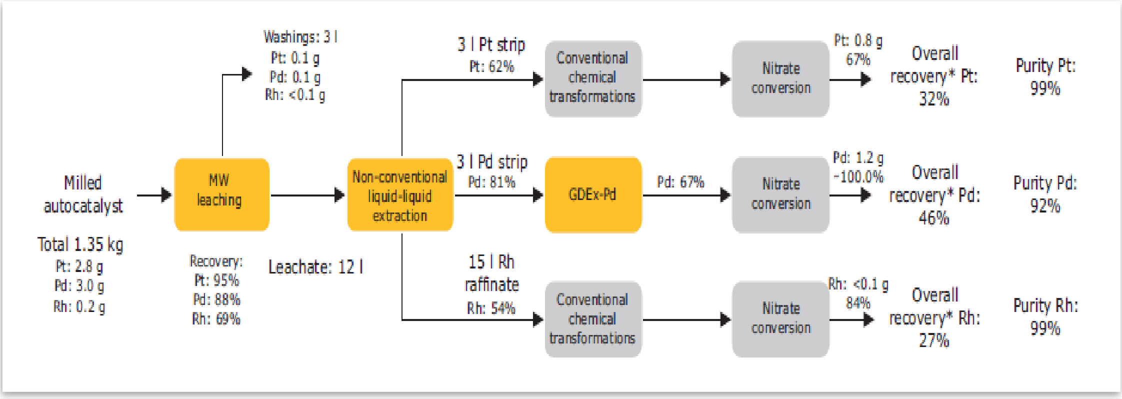

Figure 5.1: Overview of the mass balance for autocatalyst processing
(*Recoveries include losses for analysis) (Obtained from [11])

The metal nitrate solutions that were provided by PLATIRUS project partners are summarized in **Table 5.1**.

Recovered Solution	Concentration	Volume (mL)	Supplier
Palladium (II) nitrate [$Pd(NO_3)_2$]	4.64 g Pd/L	21.1	Johnson Matthey
Rhodium (III) nitrate [$Rh(NO_3)_3$]	6.00 g Rh/L	10	KU Leuven
Platinum (II) nitrate [$Pt(NO_3)_2$]	14.97 g Pt/L	22	Tecnalia
		25.1 (diluted 1:6)	Johnson Matthey

Table 5.1: Detailed description of the recovered metal solutions delivered to MONOLITHOS by the partners of PLATIRUS project

The ICP analysis of the received Pt Sample was performed by Johnson Matthey and results concerning the impurities detected are presented in **Table 5.2**.

Element	Concentration (mg/L)	Element	Concentration (mg/L)	Element	Concentration (mg/L)
Pt	14972	Pb	1.40	Ca	0.25
Na	73.2	Rh	1.28	Ti	0.15
Zn	8.72	Pd	0.92	Zr	0.08
Al	4.78	Cu	0.62	Sr	0.06
Ba	4.31	Ce	0.58	La	0.03
Fe	2.36	P	0.57	Hf	< 0.01
Ni	1.60	Mg	0.35		

Table 5.2: ICP analysis of Pt Sample and the impurities detected (as delivered by Johnson Matthey - JM)

5.2.2. Catalyst Synthesis

The coating employed for the preparation of the catalysts was 5% Pd/Rh on CeO_2/ZrO_2 (75%, 25%) for the Three Way Catalysts (TWC) and 5% Pt/Pd on CeO_2/ZrO_2 (75%, 25%) for the Diesel Oxidation Catalysts (DOC). The metal ratio is respectively Pd/Rh 55:5 and Pt/Pd 3:1.

The metal precursors used for the catalyst synthesis were described in section 5.2. All the other chemicals used for the preparation of the catalysts in the present study were commercial. The chemical reagents used were: $Ce_{0.68}Zr_{0.32}O_2$ mixed inorganic oxide (CZ, Wanfeng Technology, Shaoxing, China), ammonium hydroxide solution (Merck, 25 wt.%) for pH adjustment and γ-Al_2O_3 formed by boehmite (Disperal P2, Sasol), as binder for the impregnation of cordierites.

The catalytic powder was produced following the patented protocol (EP3569309) [13, 14]. According to the synthetic protocol, for the production of the benchmark catalysts, the commercially available metal precursors (Pt and Pd nitrates or Pd and Rh nitrates for DOC and TWC catalysts, respectively), were dissolved in water. In the case of catalysts synthesized by recovered materials, the received metal nitrate solutions (

Table 5.1) were mixed. Then, the mixed inorganic oxide (CeO_2-ZrO_2) support was added under stirring at room temperature. The pH was continuously adjusted to acidic (≤ 4.0). The solvent (H_2O) was then removed, by heating the mixture to 80-85°C under continuous stirring. The resulting catalytic powders were dried at 105°C and then calcinated at 500°C for 1h.

Using the produced catalytic powders, the monolithic catalysts were then prepared by the wet impregnation method, as described in the following section.

5.2.3. Preparation of monolithic carrots

A state-of-the-art 900 cells per square inch (cpsi) thin-walled ceramic (cordierite) substrate with hexagonal cell shape (provided by CRF) has been used for the preparation of the TWC catalysts. The cordierite had 2.5 inches length and 4.17 inches diameter. Three (3) carrots were extracted from each cordierite using a cylindrical drill with the desirable dimensions. The dimensions of the extracted carrots are 1.5 inches diameter and 2.5 inches length.

For DOC catalysts, a state-of-the-art 400 cpsi thin-walled ceramic (cordierite) substrate has been used. The cordierite had 3.0 inches length and 4.6 inches diameter. Two (2) carrots were extracted from this cordierite using the same procedure described previously. The dimensions of the carrots are 1.5 inches diameter and 2 or 2.3 inches length.

For the deposition of the previously synthesized catalyst on the walls of the aforementioned ceramic monolithic carrots, the slurry method was followed, as described below [11, 14]. The catalytic powders prepared was sieved at <125μm, obtaining a fine granulometry, in order to improve the specific surface area required for further processing. Catalytic powder was impregnated on a ceramic cordierite-based monolithic carrots ($(Mg, Fe)_2Al_4Si_5O_{18}$) in order to simulate the conditions of the catalyst performance while installed on vehicle. The impregnation steps are described in **Figure 5.2b**.

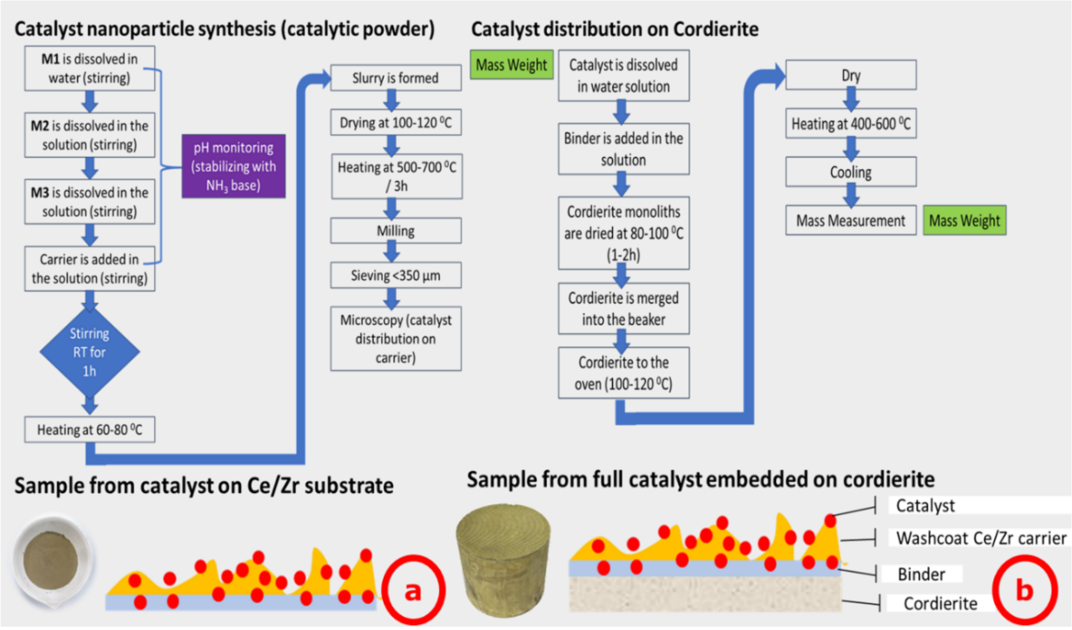

Figure 5.2: Catalyst synthesis in powder form (a) and cordierite impregnation procedure (b)

Prior to the impregnation, the characteristics of the monolithic carrots extracted from the cordierite were determined (dimensions, volume, density-g/ft^3) and dried at 90°C (1 ft= 30.48cm). An aqueous slurry containing the appropriate amount of catalytic powder and γ-Al_2O_3 formed by boehmite (Disperal P2, Sasol) as binder was prepared under stirring while the pH value was adjusted at pH 7 units with 25% aq. NH_4OH buffer solution. The monolith was impregnated in the slurry repeatedly and dried at

90^{o}C in between the impregnation repetitions. The impregnated carrot was left to dry at 90^{o}C in different orientations each time, in order to avoid capillary forces phenomena in the cells of the cordierite. The impregnated monolith was finally calcinated at 500°C for 1h (heating ramp. 10°C min-1) and then blown with air, in order to remove the non-coated particles. The metal loading of the monolith was determined by the weight of the monolith before and after the impregnation. In case the final weight of coated monolithic carrot was not the desired one, the wash coating step was repeated.

The final loading of each synthesized catalyst was calculated by considering the final weight increase of the monolithic carrots. For each carrot the exact dimensions (diameter and length) and weight were measured for achieving higher precision at the step of the impregnation and the calculation of the final loading in g PGMs/ft^3.

5.2.3.1. Catalyst Manufacturing

In **Table 5.3**, the catalysts synthesized in the present chapter, including their detailed characteristics, are summarized. As it can be observed, six new Three Way Catalysts (3 Benchmark catalysts - BECTWC and 3 catalysts from recovered PGM solutions - PLTWC) and five Diesel Oxidation Catalysts (3 Benchmark catalysts – BECDOC and 2 from recovered PGMs – PLDOC) were prepared. It should be mentioned that the exact dimensions and weight of each carrot were measured before the impregnation as well as at the step of impregnation for achieving higher precision. According to the weight increase, the final loading of each catalyst in g PGMs/ft^3 was calculated and the results are also summarized in **Table 5.3**.

Sample	Quantity	Dimensions	Metal Ratio PGM loadingPt:Pd:Rh
BECTWC	3	2.5”L×1.5”D	00:55:05 60 g PGM/ft^3
BECDOC	3	3.0”L×1.5”D	03:01:00 110 g PGM/ft^3
PLTWC	3	2.5”L×1.5”D	00:55:05 60 g PGM/ft^3
PLDOC	2	2.0”L×1.5”D	03:01:00 110 g PGM/ft^3

Table 5.3: Detailed characteristics of prepared catalytic monoliths (monolithic carrots)

In **Figure 5.3**, representative pictures of cross section, and external surface of the synthesized PLDOC monolithic carrots are presented.

Figure 5.3: Representative pictures of the carrots produced (PLDOC sample)

5.2.4. Ageing of Catalysts

To simulate the thermal aging of the catalyst in laboratory, one of most common procedures is the use of accelerated oven ageing protocols in air flow with water vapour, usually called hydrothermal aging.
In the present study a tubular oven equipped with a heated gas line to flux the gases through the sample during the operation was employed, and a peristaltic pump to add the water. The oven operates with a gas mixture composed of air and water with flexible air flow rate/H_2O ratio and maximum ageing temperatures of 1200°C, over a lab-scale sample.

5.3. Physicochemical Characterization

5.3.1. Fresh catalysts

The prepared catalysts were characterized in terms of their metal loading and structural properties. The structural characteristics of the produced carrots were determined with the use of optical microscopy. In this respect, pieces of 2.5-3" length were cut from the carrot bodies in order to be examined. The samples for the structure analysis were cross-sectionally cut so that the monolith cells can be observed. A metallurgical microscope by AmScope (ME520 series) equipped with a microscope digital camera 14MP ultrafine color was used for the analysis. The sample was placed under the objective lenses in order to be moved in the vertical direction to focus and obtain a resolution suitable for measuring the thickness of the washcoat.

The metal loading of the prepared catalysts was determined with X-ray Fluorescence Analysis of catalytic powder using a Vanta Olympus (2017,Waltham, MA, USA) XRF Analyser. It should be noted that for more precise loading measurements, the XRF instrument was calibrated for each metal separately (additionally to the internal calibration of the instrument), as described elsewhere [12]. The powder was obtained after the milling and sieving (at particle sizes < 250 μm) of the pieces of the carrot body used for optical microscopy. Finally, the obtained powder was dried at 120°C for 2h prior to sample preparation and XRF analysis. For the analysis, appropriate amounts of catalyst powder (~5g) were pressed inside polyethylene cups. Each sample was then analyzed with the measurement of 10 repeated scans (1scan/90s).

The methods employed for the characterization of the synthesized catalytic monoliths were optical microscopy and X-ray Fluorescence analysis (XRF). In this respect, one of the produced carrots (or a sample of 0.3” length extracted from the carrot body in the case of PLDOC catalyst) was used as test sample, in order to determine the loading and to examine the deposition of the catalytic powder in the cell surface of the monolith. The metal loading was calculated by XRF measurements of the powder produced by the grinding (< 250 μm) of the carrots and the results of XRF analysis of the catalysts are summarized in **Table 5.4**. Concerning the total PGMs loading, the results of XRF measurements of benchmark catalysts were found to be very close to those calculated by the weight increase of the monolithic carrots during impregnation steps. On the other hand, the measured by XRF PGMs loading of the catalysts produced by recovered PGM solutions, was found to be slightly higher than the values calculated by the weight increase. The small difference observed in the loading of the synthesized monolithic carrots may be related to the procedure followed for the preparation of the carrots. As it will be presented in the materials and methods section, the carrots were extracted from the cordierite using a cylindrical drill with the desirable dimensions. This procedure was carried out with maximum care due to the fragile walls of the honeycomb and in order to obtain carrots with as much as possible homogeneous cylindrical shape. Since the carrots were extracted from the internal part of the honeycomb, they to do not have a protective external wall, like the full scale catalyst. This makes the external walls of the carrots more fragile and more sensitive in handling. Moreover, this higher external surface of the carrots compared with the full scale catalysts may also affect the quality of the impregnation procedure. Thus, the higher loading observed can be a result of a variation of the carrot diameter in different parts of the carrot body (differences of 0.1 to 0.3 mm). This results in a relatively small error on the calculation of the total carrot volume (as indicated by the higher loading, the real volume of the carrot is probably slightly lower than the volume calculated). Concerning the higher loading observed at the samples produced from recovered PGM solutions in particular, this may be a result of PGM impurities that were found in the recycled solutions (**Table 5.4**). In terms of each metal concentration, it can be observed that the measured values for palladium are higher than expected in all samples, while the measured values of Rh and Pt are found to be lower than expected for the synthesized TWC and DOC catalysts respectively. As a result, slightly higher Pd/Rh ratios for TWC catalysts and lower Pt/Pd ratios for DOC catalysts, were achieved. A possible explanation for the deviation observed in the measured values of metal ratios, could be related to the calibration performed on the XRF instrument. More specifically, the metal concentrations (expected) of the samples of the present study are slightly higher than the ranges where the XRF analyser has been calibrated.

Sample	Pt (ppm)	Pd (ppm)	Rh (ppm)	PGM Loading (g PGM/ft^3)[1]	PGM Loading (g PGM/ft^3)[2]	PGM ratio
BECTWC	-	6067 (5835)	422 (530)	60.38 – 60.44	Pd: 57.55 + Rh: 4.00 Total: 61.55 (60.00)	Pd:Rh = 14.38 (11.00)
BECDOC	6029 (6107)	2235 (2036)	-	110.74 – 112.56	Pt: 82.00 + Pd: 30.40 Total: 112.40 (110.00)	Pt:Pd = 2.70 (3.00)
PLTWC	-	6030 (5572)	367 (507)	60.11 – 61.98	Pd: 58.64 + Rh: 5.33 Total: 63.97 (60.00)	Pd:Rh = 16.43 (11.00)
PLDOC	6567 (6015)	2295 (2005)	-	109.58 – 111.02	Pt: 89.73 + Pd: 32.72 Total: 122.45 (110.00)	Pt:Pd = 2.86 (3.00)

[1] Calculated by the weight increase of the monolithic carrots during the impregnation step

[2] Measured by XRF of the sample carrot (or a sample extracted from a carrot for the case of PLDOC)

Table 5.4: XRF Analysis of sample powders (monolithic carrots) –
The theoretical values are presented in parentheses

Structural analysis of the produced catalysts has been performed with the use of optical microscopy in order to examine the deposition of the catalytic powder in the cell surface of the monolith. Thus, the sample has been cross-sectionally cut so that the monolith cells can be observed. Pieces of 0.5” length were cut from each test carrot body (or 0.3” length for the case of PLDOC catalyst) for examination with optical microscopy.

The deposition of the coating at the walls of the monolithic carrots is of good consistency and it can be clearly observed for all the synthesized catalysts, as demonstrated by the pictures presented in **Figure 5.4**. The washcoat on the surface is rough with small size crystalline particles. It should be emphasized that the pictures of **Figure 5.4** validated the impregnation method for each catalyst, through the absence of blocked cells that can contribute to back pressure phenomena.

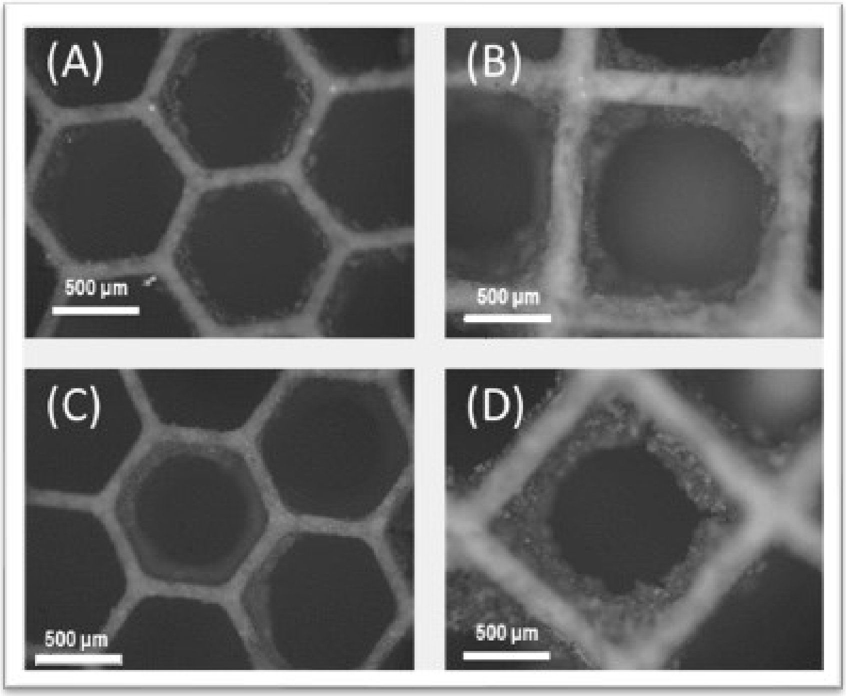

Figure 5.4: Optical microscope pictures of (A) BECTWC, (B), BECDOC, (C) PLTWC, and (D) PLDOC monolithic carrot samples (5x magnification)

5.3.2. Aged Catalysts

High temperature induces a series of physical processes that lead to sintering of washcoat components and PGM particles (Pt, Pd, Rh). The sintering is a physical process where the active surface area of the catalyst decreases through structural changes; the water vapour accelerates this reaction (hydrothermal aging).

Alumina is the most common washcoat material for catalytic devices, however there are many different types. High temperature exposure causes undesired phase transformations for alumina that change the washcoat properties: y-Alumina, having a high surface area (a strong desired property for the catalyst support), is gradually transformed to other forms of alumina with lower surface area (δ, θ, α) with an increasing rate by increasing of temperature.

In order to understand the mechanism of aging, it is necessary to determine the porosity structure of the catalysts before and after the hydrothermal aging. The best way to evaluate the porosity structure of the washcoat is a Specific Surface Area (SSA) analysis, determined by physical adsorption of nitrogen on the surface of the solid and calculating the amount of the solid of adsorbate gas corresponding to a monomolecular layer on the surface applying the Brunauer, Emmett and Teller (BET) method. The determination is usually performed in liquid nitrogen (77,53 K) and the pressure is expressed as relative pressure with respect the vapour pressure P_0.

Another interesting textural parameter for the evaluation of the aging of the catalysts is the pore diameter. The calculation method follows generally the method described by Barrett, Joyner and Halenda, hence called the BJH method, which is based on a modified Kelvin equation. Kelvin equation predicts pressure at which adsorptive will spontaneously condense in a cylindrical pore of a given size.

To measure the specific surface area (SSA), the BET equation Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry System was used. The ASAP 2020 analyser is equipped with two independent vacuum systems, one for sample preparation and one for sample analysis. The measurements are obtained from the nitrogen adsorption–desorption isotherms at -196°C. Prior to the determination of the specific surface area of the sample, a pre-treatment by heating under vacuum at high temperature (90-350°C), designed by outgassing, is done to remove gases and vapours that may have become physically adsorbed.

The nature of automotive applications demands reliable performance of catalytic converters over an extended time period with transient operating conditions. To achieve that, one of the key challenges is dealing with the chemical and thermal aging effects on the catalytic activity. Catalyst deactivation, the loss over time of catalytic activity and/or selectivity, is a problem of great concern in the practice of industrial catalytic process. Catalyst deactivation may occur by several mechanisms, nevertheless the most relevant mechanisms are sintering (also known by aging), fouling/coking and poisoning. Those mechanisms can be classified according to their nature in chemical, mechanical or thermal. Thermal ageing is the major way of catalyst deactivation. The high temperature induces a series of physical processes that lead to sintering of washcoat components and PGMs particles and the water vapour accelerates.

To evaluate the degradation of the catalytic performance, i.e., how the ageing affects the above mentioned materials, measurements of the specific surface area (SSA) (**Figure 5.5**) and pore diameters (**Figure 5.6**) of the fresh and aged samples were taken. The measurements are summarized in **Table 5.5**.

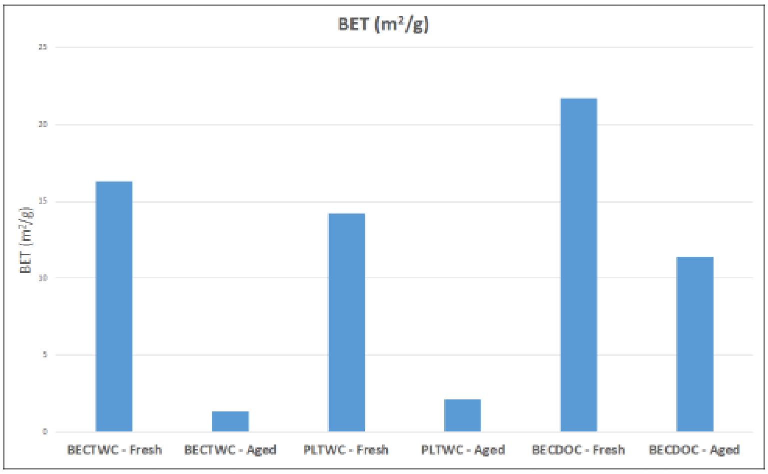

Figure 5.5: Specific Surface Area Measurements - BET Method: BECTWC, PLTWC and BECDOC

The results of the SSA measurements showed the structural changes that take place upon thermal ageing, with a decreasing of the porous structure due to sintering of support material driven to high temperature. Both benchmark (BECTWC) and PGMs recycled (PLTWC) present a huge loss of SSA over the ageing, they seem to suffer particularly from thermal deactivation. While benchmark (BECDOC) show less differences between fresh and aged samples, giving a good stability of the washcoat when exposed to high temperature.

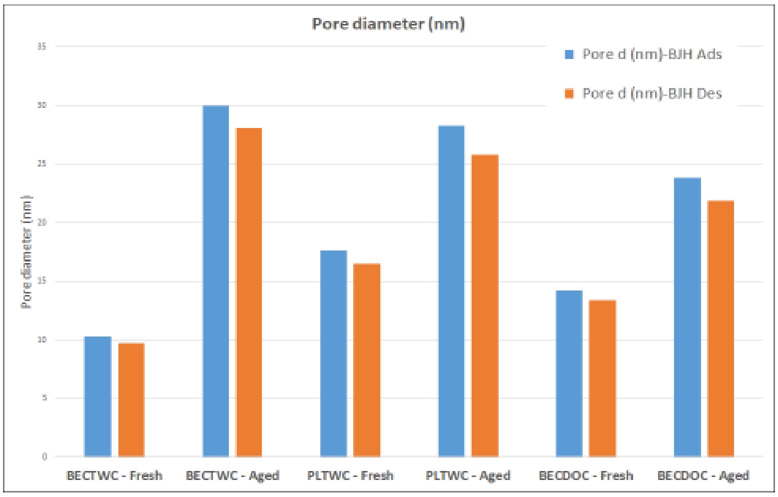

Figure 5.6: Pore Diameters - BJH Method: BECTWC, PLTWC and BECDOC

In the bar chart above the results of BJH adsorption and desorption measurements are reported, small pores loss, due to support sintering when exposed to high temperatures, denotes the TWC is more sensitive to the ageing conditions compared to the DOC.

Sample	Conditions	BET (sqm/g)	Pore d (nm)-BJH Ads	Pore d (nm)-BJH Des
BECTWC	Fresh	16.3	10.3	9.7
BECTWC	Aged	1.4	30.0	28.1
PLTWC	Fresh	14.2	17.6	16.5
PLTWC	Aged	2.12	28.3	25.8
BECDOC	Fresh	21.7	14.2	13.4
BECDOC	Aged	11.4	23.8	21.9

Table 5.5: Summary of the measurements with the BET system

5.4. Catalytic Efficiency Studies

The lab-scale samples were tested in both fresh and aged conditions to be evaluated on the key parameters:

- **Conversion efficiency**: The effectiveness of catalytic converters in reducing a given emission due to the reaction that occurs inside is typically measured as conversion efficiency of carbon monoxide CO and hydrocarbons HC into carbon dioxide CO_2, while nitrogen monoxide species NO_x are turned into nitrogen N_2.
- **Light-off temperature:** Temperature at which the conversion of a species reaches 50%. That temperature is frequently denoted **T50**. When comparing activities of different catalysts, the most active catalyst will be characterized by the lowest light-off temperature for a given reaction.
- **Oxygen Storage Capacity**: the ability of the TWC to adsorb/release oxygen during operation, storing during lean phase and releasing during rich one. The most efficient TWC catalyst will be characterized by the higher Oxygen Storage Capacity, which leads to a rate oxidation reactions increase.
- **NO_2 formation**: the ability of the DOC catalyst to produce desired amount of NO_2.

This DOC function is desirable to favor the fastest NO_x reduction reaction on the Selective Catalytic Reduction (SCR) device placed downstream and to facilitate enhanced passive PM regeneration reaction with NO_2 for example in the Diesel

Particulate Filter (DPF) or in SCR on Filter (SCRoF) devices. Most favorable amount is NO_2/NO_x~ 50.

5.4.1. Catalytic Efficiency testing

The lab-scale testing bench for catalytic systems is used for material characterization of all the after-treatment components (catalyst, substrates) (**Figure 5.7**). The synthetic mixture of gases was selected with composition that mimic the real working conditions, N_2 is used as gas carrier, being an inert gas that not participate to the catalytic reaction. All the gaseous species (CO, HC, NO_x, SO_2) passes through a mixer with a controlled flow accurately measured with a single mass flow controller in order to have the correct concentration of all the species in the final gas mixture.

The synthetic gas mixture is heated up passing through an in-line heater, while water is dosed through a peristaltic pump and injected in hot gas stream by means of a steam generator. The catalyst sample (carrot) is installed in a heated sample holder. To monitor the parameters, thermocouples are placed in the sample to control the temperature (up to 550°C) and a wide-band UEGO oxygen sensor placed before the sample holder is used to measure the oxygen amount.

The composition of the gases and the flow gas temperatures is modified according to the requirements of the tests to be carried out. The gas mixture is fluxed through the lab scale sample and is analyzed using a FT-IR Multi-gas Analyser MKS 2030 HS for the simultaneous analysis of all chemical species involved with an uncertainty of about ± 5 ppm. Fourier Transform IR is the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through. The FT-IR is connected to a PC, and it is the main data source for the analysis of tests conducted on the bench and for the determination of the composition of the streams. The concentrations of the chemical species are recorded at the inlet and at the outlet of the sample to evaluate the variation during the reactions.

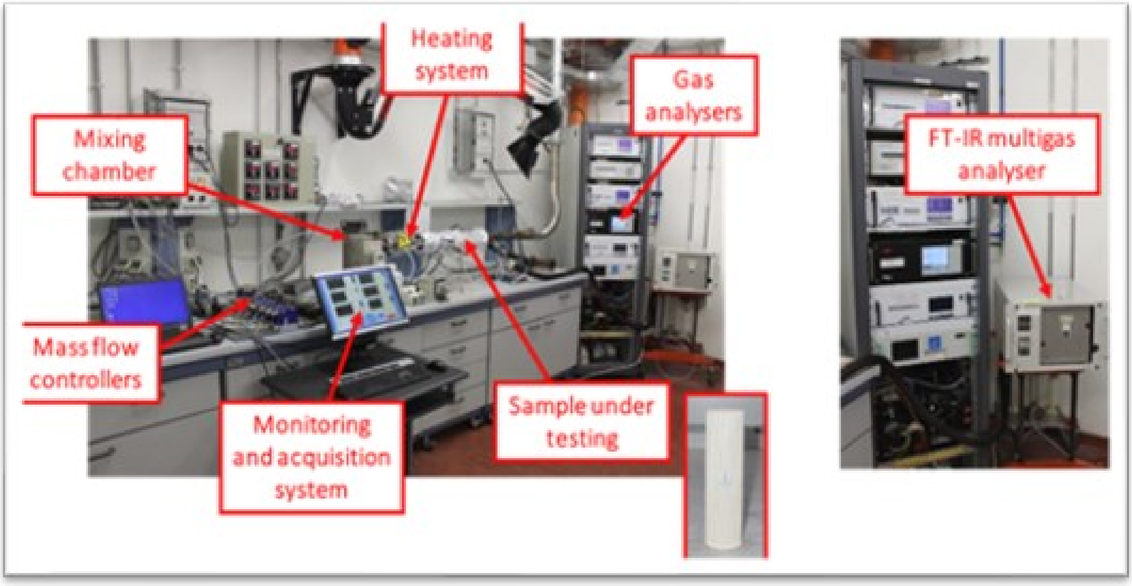

Figure 5.7: The lab-scale testing bench for catalytic systems in which prepared catalysts were measured (CRF Facilities)

Since in the real exhaust gases a large number of different hydrocarbon species can be found, these hydrocarbons may present different chemical activity inside the catalyst. HCs used in the present study is a gas mixture of short-chain hydrocarbons, ethylene-propylene-methane (volumetric ratio $C_2H_4/C_3H_6/CH_4 = 3.5/1/1$). This specification was defined after a characterization of the HCs content in the real exhaust gases downstream to the engine.

Typically, the sample dimensions are 1 to 1.5 inches diameter by 2 to 6 inches long; parts can be coated as cores or removed from full-scale monolith. Cores from larger parts, so called carrots, represent fully formulated catalysts ideally suited for laboratory reactors. Over the tests, the temperature is controlled at the inlet, the outlet and multiple positions throughout the sample. According to established and property protocols the tests were performed to measure the light-off temperatures and conversion efficiency (ramp-up curves) of the pollutant gases vs temperature.

The volumetric flow rate of the reactants entering the sample is expressed as Space Velocity (SV) and the unit is h-1: Space velocity = gas flow (l/h)/sample volume (l). The testing conditions are summarized hereafter:

1. Space Velocity (SV) = 50.000 h^{-1}
2. Heating rate: ramp up to 500°C
3. TWC tests: two levels of gases composition, varying the CO, HC and NO concentrations (expressed in ppm) in the feed gas:

- Slightly lean gas mixture, λ ≅ 1.02
- Slightly rich gas mixture, λ ≅ 0.99

4. TWC tests: Oxygen Storage procedure: only CO and O_2 in the feeding gas
5. DOC tests: three levels of gases composition, with different CO concentrations (expressed in ppm) in the feeding gas:
    - Low CO
    - Medium CO
    - High CO

5.4.2. Three Way Catalyst (TWC)

In the bar charts below (**Figure 5.8**) CO, HCs and NO_x T50 (L/O temperature) and conversion efficiencies are reported. Tests focused on the oxidation of CO and HCs need a slightly lean environment of the gas mixture, while to evaluate the reduction of NO_x, the gas mixture needs to be slightly rich ($\lambda < 1$). The most active catalyst is usually characterized by the lowest L/O temperature.

The tests were repeated three times to control the variability of the sample, and the results presented are average values. PGMs recycled material (PLTWC) was evaluated in both fresh and aged conditions.

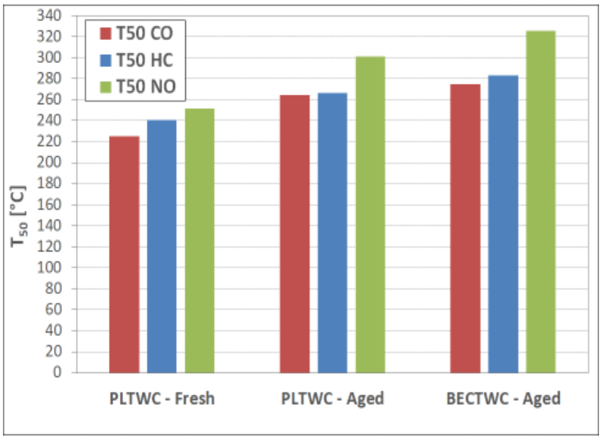

Figure 5.8: TWC light-off test: T50 (CO-HC-NO) - average values

The light-off T50 of the samples obtained from PGMs recycled (PLTWC) are in line with commercial catalysts with similar loading. TWC benchmark (BECTWC) performances are slightly worse. One possible reason for this discrepancy could be the fact that benchmark catalysts were manufactured in small scale incorporating commercial impregnation protocol suffering with high external surface of the carrot (compared with the full scale catalysts usually produced with the specific protocol). Based on the experience gained with benchmark catalysts, a customized impregnation protocol was developed for recycled, driving to better impregnation performance. In **Figure 5.9**, CO and HC conversion efficiencies are presented. The broken and solid lines show that curves rapidly increase so the conversion is rapid and effective for all the materials, mainly for PGMs recycled one (PLTWC).

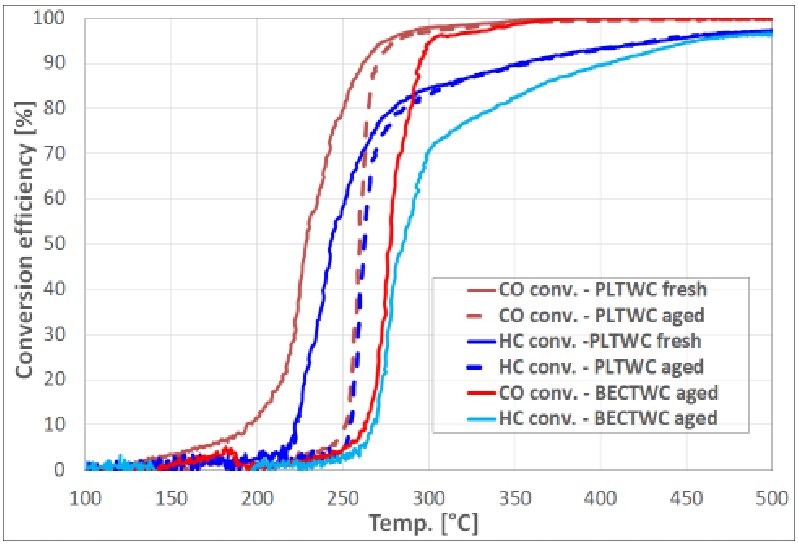

Figure 5.9: TWC light-off test: CO/HC conversion efficiencies (test in LEAN conditions)

Then, to evaluate the reduction of NO_x, the gas mixture needs to be slightly rich ($\lambda < 1$). The results of the NO_x conversion efficiency are presented in **Figure 5.10**.

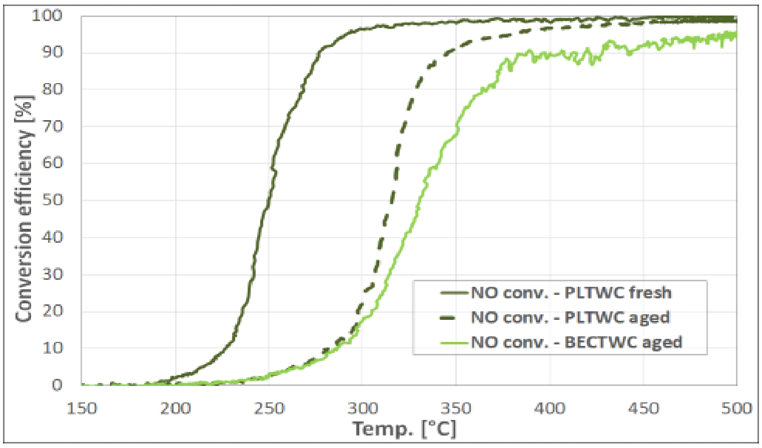

Figure 5.10: TWC light-off test: NO conversion efficiencies (test in RICH conditions)

The full conversion efficiency behavior of the samples obtained from PGMs recycled are in line with commercial catalysts with similar loading. Again, benchmark catalysts have shown slightly poorer performances, mainly for the aforementioned reason. Looking at NO → NO_2 oxidation, another possible reason for good performances of

PGMs recycled material could be drawn: the impurities present in that catalyst (such as Cerium) could lead to better performances of that material, i.e., Cerium as impurity promotes the species oxidation.

Finally, the TWC oxygen storage capacity (OSC) was tested and the results are reported in **Figure 5.11**. Typically, the most efficient catalyst is the one with the highest OSC.

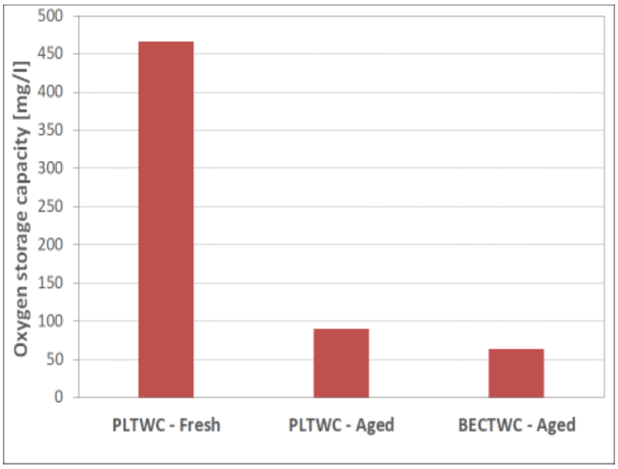

Figure 5.11: TWC light-off test: CO/HC conversion efficiencies (test in LEAN conditions)

Regarding this parameter, all samples have shown OSC values lower than typical values shown by a commercial catalyst, especially in fresh condition; this could be another sign that sample preparation probably needed further optimization, possible due to the low amount of PGM material available.

5.4.3. Diesel Oxidation Catalyst (DOC)

Hereafter the measured key parameters for the DOC are reported. The tests were repeated three times to control the variability of the sample, and the results are presented in **Figure 5.12** for CO conversion and in **Figure 5.13** for HC conversion.

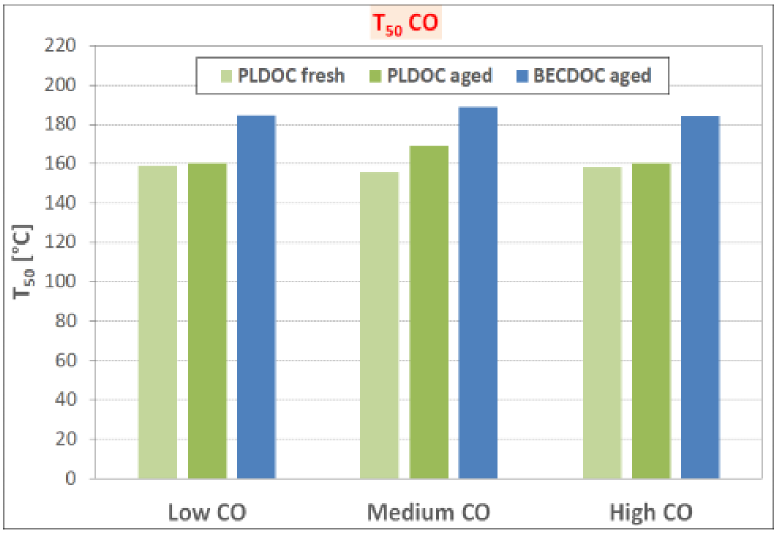

Figure 5.12: DOC light-off test: T50 (CO) - average values

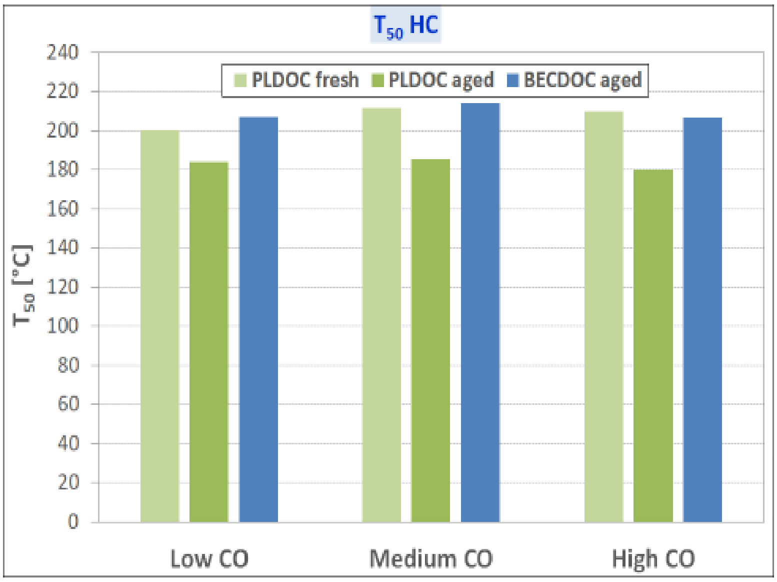

Figure 5.13: DOC light-off test: T50 (HC) - average values

Even in this case, DOC prepared from recycled PGMs have exhibited better performances. Fresh PLDOC has shown worst performances, particularly for HCs conversion and NO oxidation; this behaviour is probably related to a sample inhomogeneity, due both to the smaller size of the recycled samples in comparison with the other and also to the needs of some refining of process parameters. Benchmark catalyst (BECDOC) results are similar to expected commercial performance (though slightly less efficient).

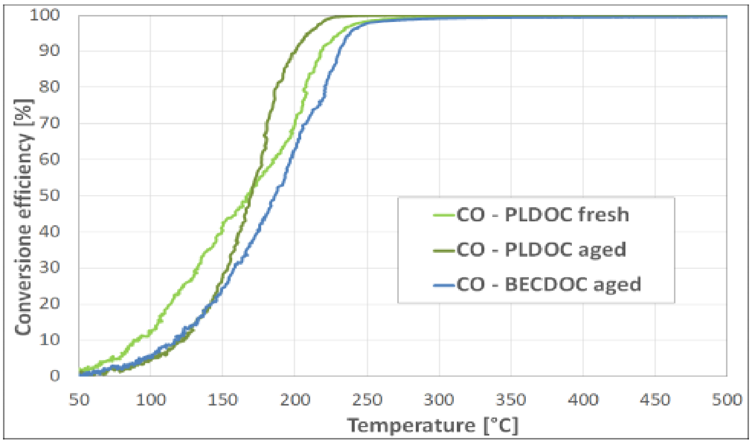

Figure 5.14: DOC light-off test: CO conversion efficiencies

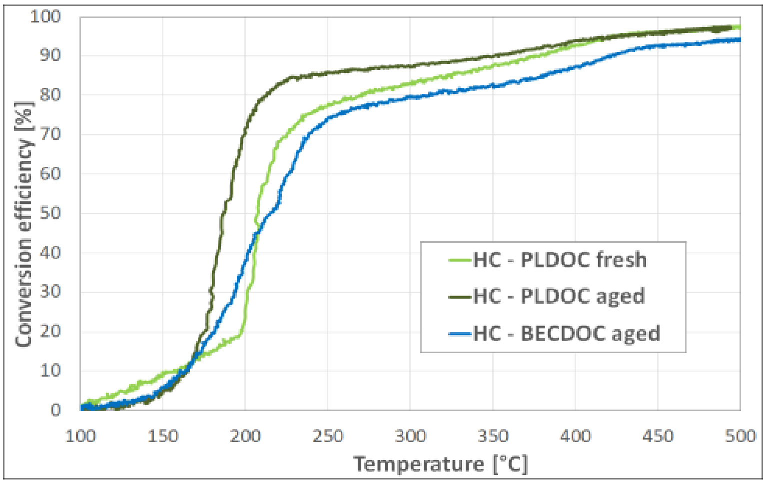

Figure 5.15: DOC light-off test: HC conversion efficiencies

The recycled catalysts have unusual behaviour in terms of T50 – normal results is that it increases with temperature whereas the recycled catalysts show stable behaviour. Further investigation is required in identifying some of the impurities that work as a stabilizer for the washcoat of the catalyst preventing aggregation and or oxidation of the active catalytic sides. PLDOC shows good overall performances and are comparable to commercial ones with similar loading.

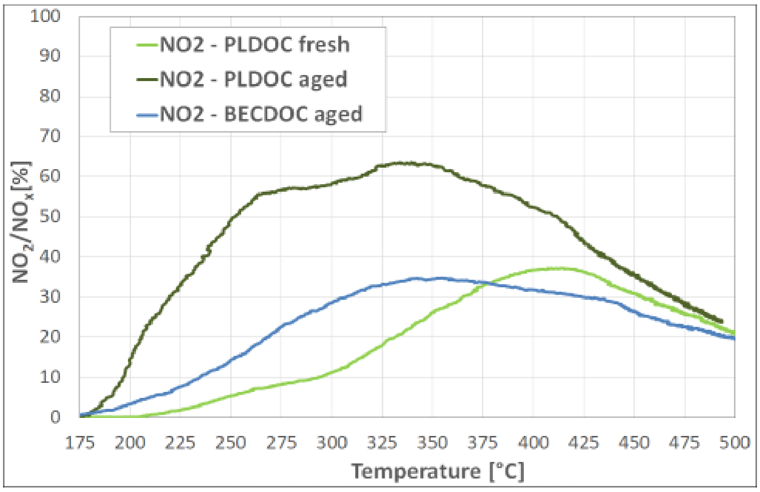

Figure 5.16: DOC: light-off test: NO conversion efficiencies

According to **Figure 5.16**, the NO_2 (nitrogen dioxide) formation at the outlet of the DOC, as another important key parameter is reported. It is the ability of the DOC to produce the desired amount of NO_2, available for the downstream devices in the after treatment system. Usual good values are $NO_2/NO_x = 50\text{-}60\%$.

5.5. Conclusions

In this chapter, a holistic approach of the circular economy model of valorizing spent automotive catalysts, in order to prepare new ones, is presented from experimental and technical aspect. The synthesis of nanocatalytic particles and the impregnation of cordierite carrots for three way catalyst TWC and diesel oxidation catalysts DOC were described in detail. The catalyst Pt, Pd and Rh solution, were extracted from spent automotive catalysts, where they were processed in PLATIRUS H2020 project (www.platirus.eu). The content of the PGM and impurities in these solutions were determined with ICP analysis. With respect to the concentration of these solutions, appropriate carrots were extracted from cordierite units and were impregnated in order to obtain TWC with metal ration Pd:Rh, 55:5 and DOC Pt:Pd, 3:1. The metal loading and the morphology of the novel catalyst were determined with XRF and optical microscopy. The effect of the aging on the structure of the catalyst was also studied with BET analysis, determining the pore size variation. The impregnation method was successfully implemented, since the desired loading of the catalyst TWC and DOC was obtained, while clocked cells were avoided.

The catalytic efficiency for the conversion of CO, HC and NO in DOC catalyst for diesel vehicles and TWC for petrol ones, under fresh and aged conditions, was also examined and compared to benchmark ones. Regarding TWC, the full conversion efficiency behaviour of the samples obtained from PGMs recycled are in line with commercial catalysts with similar loading. While, benchmark catalysts have shown slightly poorer performances. The elevated performance of TWC recycled catalyst, could be attributed to the impurities that are included in the solution such as Ce, which could probably affect the O_2 storage capacity of the catalyst. On the other hand, DOC recycled catalyst, both as fresh and aged, exhibited poorer performance, with respect to the benchmark one, probably, due to possible PGM impurities in the recycled solution or there is a slight possibility that capillary effects may cause uneven distribution of the catalytic powder at the carrot body caused by the high external surface of the carrot.

In conclusion, new monolithic catalysts incorporating recycled (impure) solutions as PGM precursors were synthesized successfully. The recycled catalysts exhibited similar or better catalytic efficiency performance with the benchmark catalysts (synthesized by using commercial PGM precursors and the same manufacturing parameters) and similar performance with the full scale commercial catalysts.

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6th Chapter

6. New PGM Secondary Sources: Heavy Duty Diesel Oxidation Catalysts and Catalyzed-Diesel Particulate Filters

6.1. Introduction of Heavy Duty DOC and c-DPFs

Heavy-Duty Vehicles are defined as trucks, buses, trains, ships, tractors, which are vital for the economy of a country. Most heavy-duty vehicles are powered by diesel engines which, in this case, provide technical advantages over petrol engines. The growth of the transport sector has led to a rapid increase in the fleet of heavy vehicles, increasing emissions of harmful gases. The main compounds of diesel exhausted contain carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2), water vapour (H_2O), sulfur compounds (SOx), hydrocarbons (CxHx) and particulate matter (PM) of size under 10μm *(Emission Standards: Europe)*.

According to Euro I, the first heavy-duty vehicle emissions standards of the EU, catalytic devices were not mandatory to be installed, whereas in Euro II, the installation of DOC was obligatory. Later in 2005, the Diesel Particulate Filters (DPF) technology was adopted by Euro IV legislation. In **Figure 6.1**, a typical catalytic system of heavy-duty vehicles for the reduction of pollutants emissions is presented [1, 2] for Euro V and Euro VI regulations.

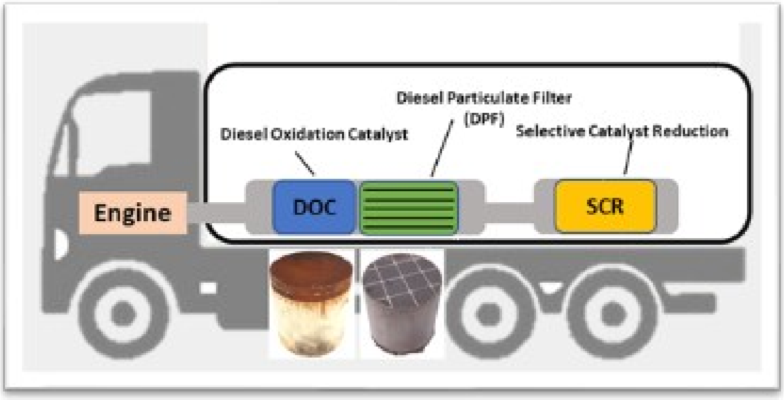


Figure 6.1: A typical schematization of DOC, c-DPF, and SCR systems in Diesel Heavy-Duty Vehicles (HDVs)

Catalytic converters were also developed to achieve the increasingly stringent emissions regulations in the EU. The exhausted aftertreatment devices that are applied to vehicles are Diesel Oxidation Catalysts (DOC), Diesel Particulate Filters (DPF), and Selective Catalytic Reduction (SCR). The Diesel Oxidation Catalysts (DOCs) are used for the oxidation of hydrocarbons and carbon monoxide to carbon dioxide (eq.1-2), while SCR are used for NO reduction to NO_2. Finally, the soot emissions and particulate matter are captured by DPF. The DOCs usually contain Pt as an active catalyst with excellent efficiency on oxidation reactions. Furthermore, Pd is also used as a supplement to Pt or as a substitute for it. These filters are made of the ceramic honeycomb (cordierite, silicon). DPF is mainly cordierite substrate with alternately plugged channels and the aim of this structure is the collection of the particulate mass emission (PM) of soot and ash. The Pt coated catalyzed Diesel Particulate Filters (c-DPFs) contribute to the further oxidation of CO and HC and the formation of NO_2 (3), helping in the SCR catalyst operation. Finally, the SCR is free of PGMs and contains as catalytic compounds vanadium, tungsten, iron, or copper and converts nitrogen oxide (NOx) to nitrogen (N_2) and water (H_2O) [3, 4].

$$[C_v H_{2v+2}] + O_2 = CO_2 + H_2O \ (1)$$

$$CO + O_2 = CO_2 \ (2)$$

$$2NO + O_2 = 2NO_2 \ (3)$$

DOC and DPF devices (catalyzed or non-catalyzed) suffer from the high concentration of carbon C depositions due to lack of maintenance or failure of the engine. As a result of engine malfunction, poisonous Pb could also be present on DPF and DOC services as deposition. For these findings, that is high C content and occasionally Pb, recycling companies avoid collecting and recycling these devices because pretreatment is required to avoid toxic gases emissions [5].

As already mentioned, there are many companies involved in the recycling of autocatalysts based on the pyrometallurgical process. That method includes the melting of the ceramic catalyst with the addition of fluxes and metal collectors at high temperatures (1500 – 1900°C) [6]. Despite the widespread use of this method, it faces various challenges. It requires large, specialized equipment with continuous operation at high temperatures and high energy consumption. During combustion, toxic emissions are released, and the other metals they contain, such as Ce, Al, Zr, are rejected in slag. Therefore, it is crucial to develop a more environmental and sustainable method based on hydrometallurgy. The advantage of the hydrometallurgical process instead of pyrometallurgical is that the process is performed in batches according to the market supply and demand. Also, the hydrometallurgical process is performed at lower temperatures and lower energy consumption is required. Although, the hydrometallurgical process has been studied extensively for recovering PGMs from Three Way Catalyst (TWC), none of the studied methods has been applied on an industrial scale.

The literature review has indicated that the Pt recovery from DOC with the hydrometallurgical method had been studied only by Ilyas *et al.* [7], while there are no reports on the recycling of Pt from c-DPF. However, several studies related to the recycling of PGMs from three-way catalytic or other types of catalysts contain PGMs [5, 8, 9]. The pretreatment of spent catalysts in the leaching process had been studied by multiple researchers. The thermal pretreatment or hydrogen pretreatment has been used to remove organic compounds and carbon from the surface of PGMs in order to facilitate the leachability of them. The most common studied lixiviant in the leaching process is the hydrochloric acid (HCl) with the addition of an oxidizing agent such as hydrogen peroxide (H_2O_2), nitric acid (HNO_3) and hypochlorite (ClO^-) or perchlorate (ClO_4^-) acid. The environmental imprint and the safety issues must be taken under consideration about using these strong reagents [7]. Also, the introduction of an additional Cl^- source has been already studied in Chapter 3. The effect of NaCl, $AlCl_3$ and $CuCl_2$ has extensively been studied to improve the PGMs dissolution, attempting partial substitution of high acidity, with the NaCl to be the most efficient.

The recovery of Pt from spent DOC and c-DPF, in this chapter, was studied with an acidic solution (HCl), an environmentally friendly oxidizing agent H_2O_2, and the addition of Cl^- source (NaCl). A thermal pretreatment step prior to leaching was performed in order to remove the deposited organic compounds and carbon in order to facilitate Pt extraction and easier handling of the leaching process.

6.2. Materials and Methods

6.2.1. Materials

In order to study the leachability of Pt from Heavy Duty Vehicles HDVs catalytic devices, a spent DOC catalyst and a spent catalyzed filter c-DPF were collected and used for the treatment and characterization. These devices were made of cordierite $(Mg,Fe)_2Al_3(AlSi_5O_{18})$. The Pt content range of DOC and c-DPF was determined with XRF analysis, in spectral range 2900-3200 ppm and 1600-1700 ppm, respectively. Leaching solution was prepared with hydrochloric acid (HCl supplied by Merk, purity

37%) as a leaching agent, the hydrogen peroxide (H_2O_2 supplied by Merk, purity 30%) as an oxidizing agent, and sodium chloride (NaCl supplied by Merk, purity 99.5%) as providing Cl^- were used for the leaching experiments.

6.3. Methods

6.3.1. Preprocessing and Thermal Pretreatment

The spent or deactivated Heavy-Duty Catalysts and Filters, DOC and c-DPF, were collected and provided by Monolithos collection route. Metallic parts were removed, and ceramic parts were grinded and milled under 250μm particulate size. The powder was homogenized, and the particle size was determined with 250μm granulometry sieving. The used sieves of Endcotts Ltd. in London of England were from steel frame with a diameter of 21cm and aperture size 250μm.

The final batches produced of about 9kg of DOC and 14kg of c-DPF, were homogenized. Appropriate sampling was performed for XRF analysis to take place in order to determine PGM content. Before the elemental quantification, the samples were dried in a furnace at 120°C for 2h to remove the humidity avoiding interference in the XRF results. The method of preprocessing and appropriate sampling has been described in detail in previous chapters [10] **(Figure 6.2).**

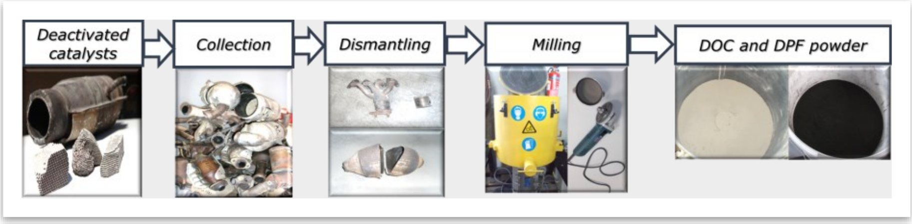


Figure 6.2: Flowsheet preprocessing of DOC and c-DPF

Before the leaching process, catalysts and filters in powder form were subjected to a calcination process in order for organic compounds to be removed, at 600 – 900°C for default time (2-15h), with a heating rate of 10°C/min. XRF analysis was performed in order for the PGMs content to be determined, before and after treatment, so as for the recovery yield to be determined with high accuracy. The effect of calcination on the mass loss was also calculated.

6.3.2. Leaching Procedure

Catalyst or filter powder was dried in the drying furnace at 120°C for 2h for the humidity to be removed and for the Pt content to be determined accurately with XRF analysis. Suitable amount of the catalyst was weighted and then added to the beaker. Reagents of HCl, H_2O_2, NaCl, and H_2O were added in a variety of concentrations to obtain certain experimental conditions (HCl 2-9M, H_2O_2 0.5-3% vol, NaCl 3-6M). Distilled water was added for the pH to be adjusted. Leaching temperature was controlled to remain at 70°C for a particular time (0.5-4h) under stirring. After leaching, the leachate and solid residue were separated via filtration. The wet solid residue was washed repeatedly to remove acidic content and dried overnight in order for the water content to be removed and avoid humidity interference in XRF analysis.

In **Figure 6.3** the flowsheet for the proposed hydrometallurgical process for the recovery of Pt from Diesel Oxidation Catalysts (DOC) and catalyzed Diesel Particulate Filters (c-DPF) is presented. The DOC and c-DPF were calcined at 800°C for 2h, prior to the leaching process, to remove the deposit organic compounds and coke and facilitate Pt extraction. In the leaching process, HCl, NaCl, and H_2O_2 were used as leaching agents.

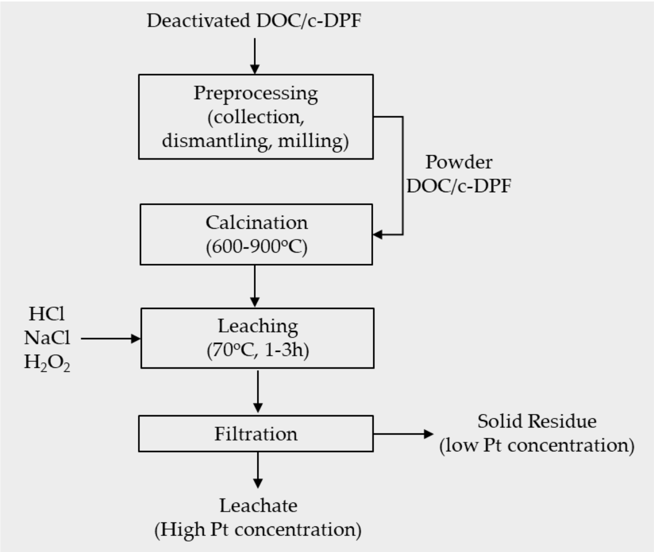


Figure 6.3: Flowsheet of the proposed hydrometallurgical process for Pt recovery from DOC and c-DPF

6.4. Analytical Methods

6.4.1. Optical Microscope

The morphology, structure, and dimensions of the filters (c-DPF) and catalysts (DOC) channels were determined by optical microscopy analysis. An optical microscope of AmScope in California, U.S.A., ME520 Series Optical Microscope, was used for the performed analysis. Images were obtained with a total microscope magnification of 5x.

6.4.2. X-ray Fluorescence (XRF) analysis

As for the qualitative and quantitative PGMs loading analysis of samples, X-ray Fluorescence spectrometer (portable VANTA Olympus 2017, Waltham, MA, USA) (**Figure 6.4**) and software (Olympus OOSA, version 3.8.540.0) have been used. X-ray fluorescence (XRF) analysis provides accurate, fast, non-destructive, repeatable measurements, as well as no chemical preparation is required. Prior to XRF measurement, the dried sample is milled to obtain particular granulometry (< 250μm). The XRF spectrometer was internally calibrated by the manufacturer, precisely measuring Pt in spent catalysts of average Pt concentrations region 900-1100 ppm. Additionally, X-ray Fluorescence (XRF) analyzer was calibrated, performing an additional calibration in two concentration regions, one in high concentrations (600-2800ppm) and one low concentration (< 600ppm), to improve the accuracy of XRF measurements further, before and after leaching process. This additional calibration would facilitate the accurate measurement and calculations of recovery yield.

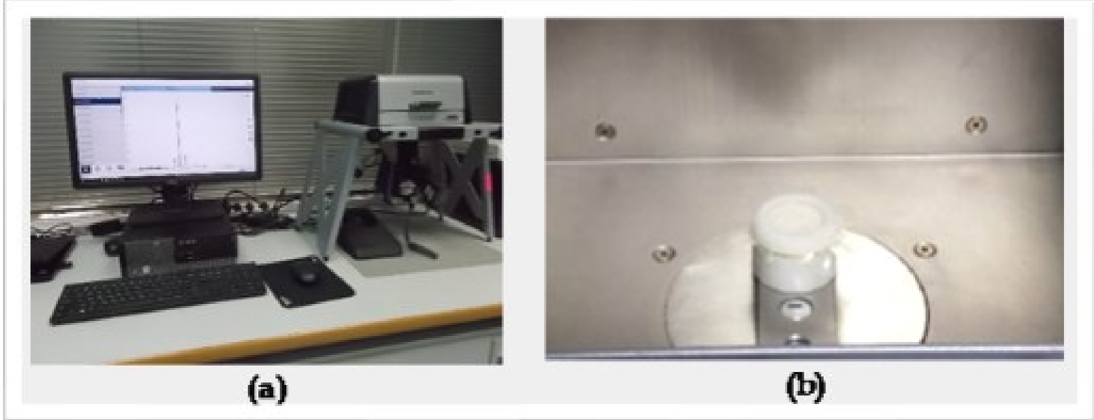

(a) (b)

Figure 6.4: Portable XRF analyzer (VANTA OLYMPUS) (b) a sample in the measuring position

6.4.3. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was conducted to determine the optimum temperature for calcination of the spent Diesel Oxidation Catalysts and Diesel Particulate Filter in order to remove organic compounds. The measurements were performed in flowing air at a heating rate of 10°C/min from 25°C to 1000°C. The samples remained at 1000°C for 200min.

6.4.4. X-ray diffraction (XRD)

The samples of DOC and c-DPF before and after calcination at 800°C for 2h were characterized by X-ray diffraction (XRD) (operation modes: 5-35° 2θ range, 0.04° step size and 2s step time), in order to establish any structural changes that may occur after thermal pretreatment, XRD analysis was performed on DOC and c-DPF before and after calcination step.

6.5. Leaching Results and Discussion

6.5.1. Optical Microscopy analysis

The Diesel Oxidation Catalytic converters consist of a monolith honeycomb and the washcoat containing platinum group metals, as shown in **Figure 6.5**. The exhausted gases contact the catalyst, and the pollutants are converted into harmless substances. The honeycomb structure with many small parallel channels of the DOC catalyst and the substrate contained Pt is confirmed by the optical microscope images.

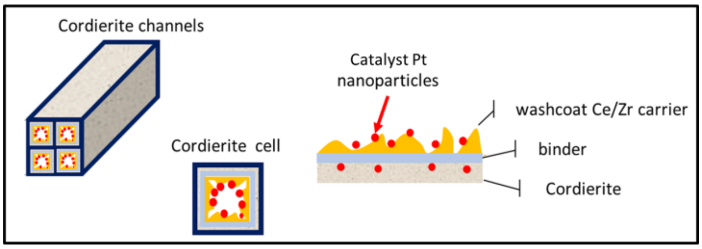
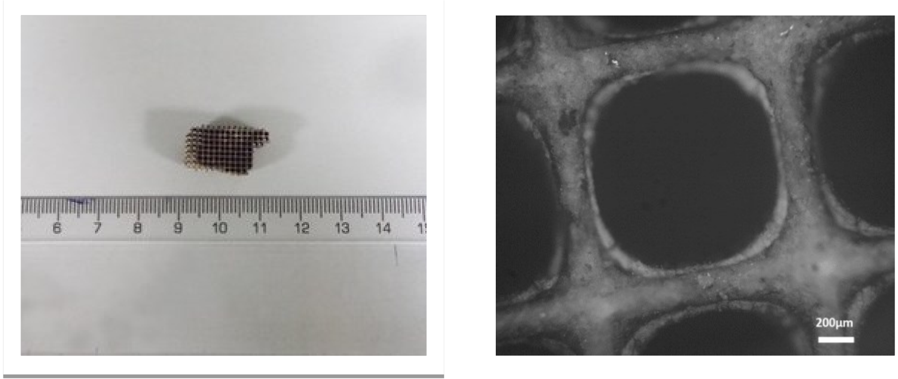


Figure 6.5: Structure of a Diesel Oxidation Catalyst

According to microscope images (**Figure 6.6**) obtained from the catalysts and the DPF internal part, the cell walls are described in detail. The DOC cell size is 0.1cm x 0.1cm, and the wall width was in the range from 0.1524mm to 0.2253mm. The washcoat was thinner than the cell wall and measured from 0.0341mm to 0.1059mm.



(a) (b)

Figure 6.6: (a) Small piece of part catalyst (DOC), (b) Image from the optical microscope in 5x magnification

The catalyzed Diesel Particulate Filters (c-DPF) exhibit a honeycomb structure, such as DOC catalysts, but contain alternate channels plugged at opposite ends; however, the channels have a larger diameter and porous walls. Exhaust gases go through the porous walls leaving larger particles trapped within the connected channels, as shown in **Figure 6.7**.

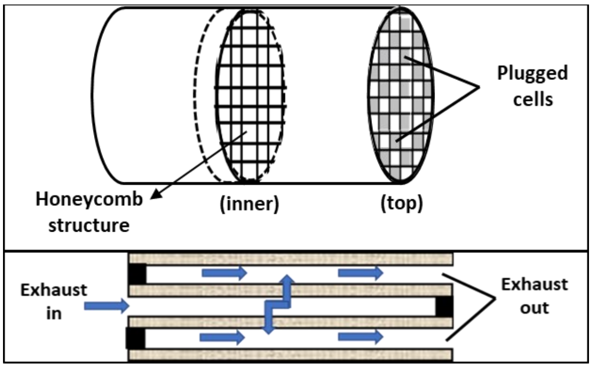
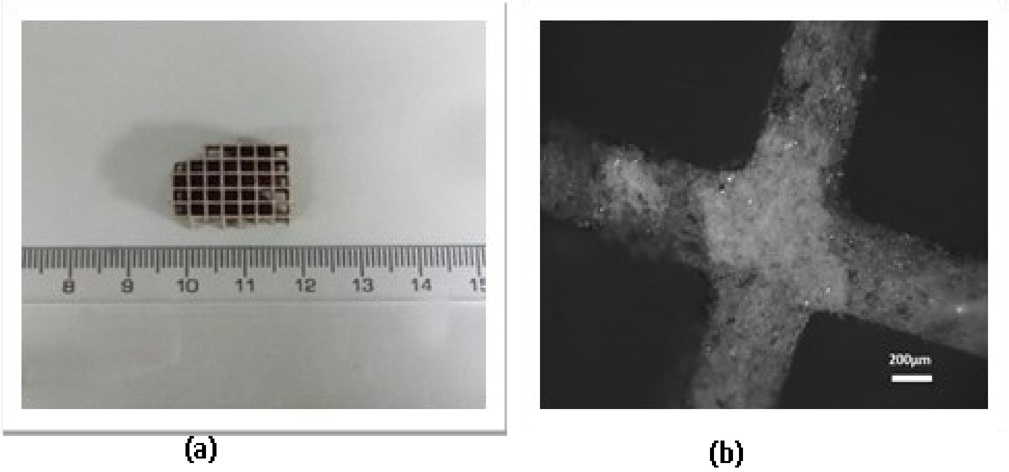


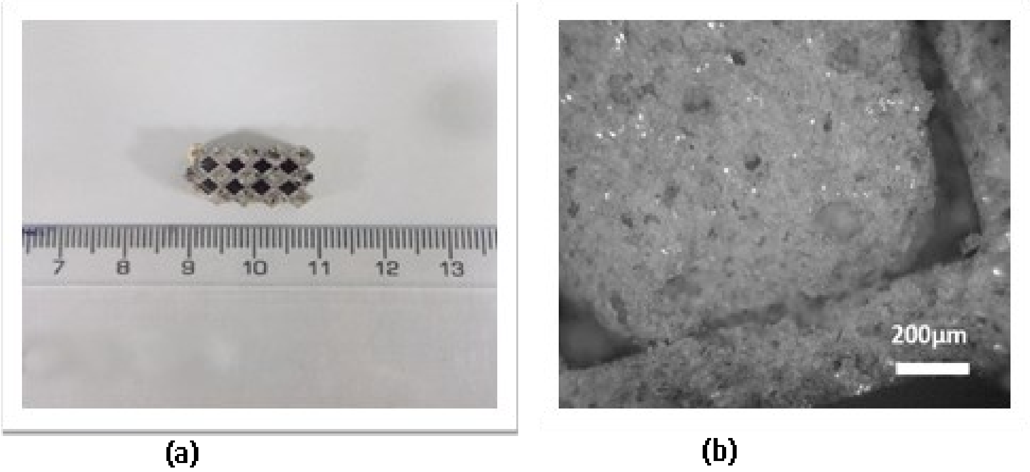
Figure 6.7: Schematic representation of the structure of a Diesel Particulate Filter (DPF)

Due to the particular structure of the filter, different cross-section parts were collected for the surface characterization, one from top/bottom and one from the inner main body of the filter (**Figures 6.8 and 6.9**). The cell of c-DPF was 0.3cm x 0.3cm, and the width of the wall ranged from 0.4365mm to 0.4787mm, measured in both samples.



(a) (b)

Figure 6.8: (a) The analyzed small piece of the inner part of filter (c-DPF), (b) Image from the optical microscope in 5x magnification



(a) (b)

Figure 6.9: (a) The analyzed small piece of the top or bottom surface of the filter (c-DPF), (b) the image from the optical microscope in 5x magnification

The washcoat of the DOC catalyst was observed by optical microscopy with the width in the range from 0.0341 mm to 0.1059 mm. On the other hand, the washcoat fundamental elements such as Ce and Zr were detected with XRF analysis, however the washcoat layer was not easy to be detected and measured with optical microscopy. The latter finding indicates that either a fine and homogeneous precursor of the washcoat has been mixed with the cordierite powder upon c-DPF fabrication, or a very thin layer of Pt/Ce/Zr has been distributed on the walls of the c-DPF channels. The first candidate configuration of homogeneous mixing of Pt, Ce, Zr and the cordierite would be reasonable, taking into consideration that flu gas is transferred through the channels rather than across them (**Figure 6.10**).

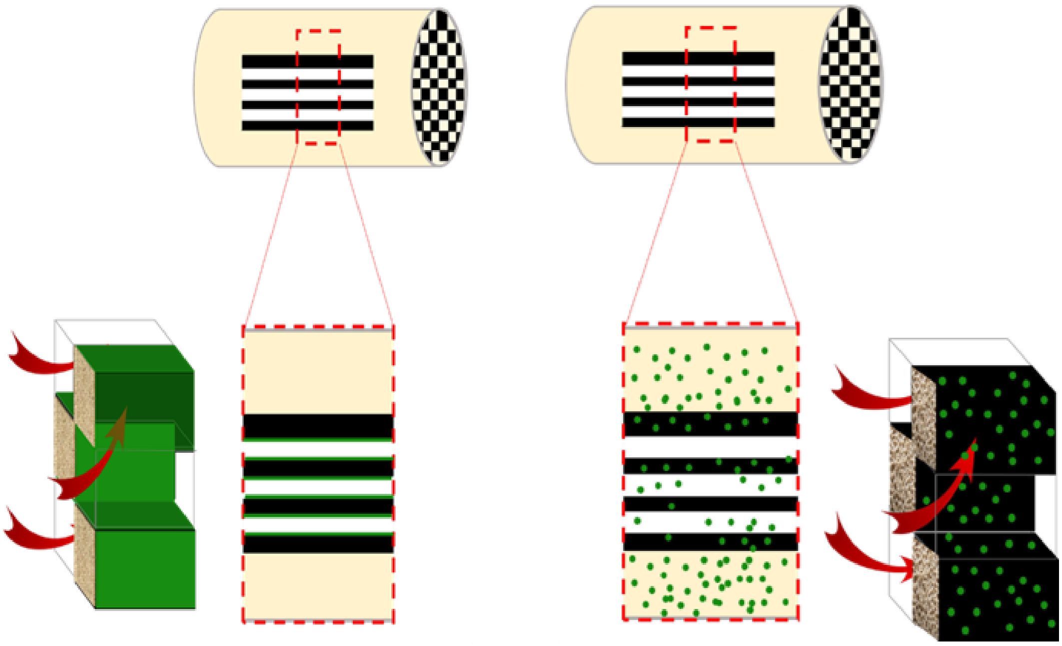


Figure 6.10: Possible Pt distribution configuration on c-DPF (a) Catalyst is homogeneously distributed on the cell surface, (b) Catalyst has been mixed with the cordierite material prior to the DPF fabrication

The cell density of DOC was measured 500cpsi, but the cell density of c-DPF was not measured because of its large channel. However, the washcoat of the c-DPF filter was not observed, but the washcoat Ce and Zr elements were detected by XRF analysis. The cell density of DOC was measured 500cpsi, while the cell density of c-DPF was determined 70cpsi.

6.5.2. Characterization of materials - Thermal pretreatment

The option of thermal pretreatment on Pt leachability was examined. Leaching experiments were performed with thermal pretreatment at different temperatures in catalyst (DOC) and filter (c-DPF) for Pt extraction. Initially, leaching experiments were performed with unpretreated DOC and c-DPF for extracting of Pt. In **Figure 6.11**, the Pt recovery rate reached only 48,5% and 70,5% for DOC and c-DPF, respectively. The low Pt extraction yield, and especially in the DOC, created the necessity of further pretreatment of the solids.

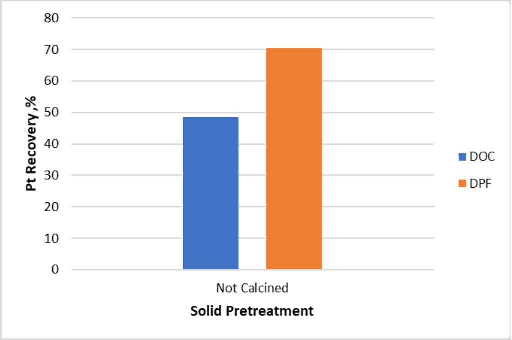
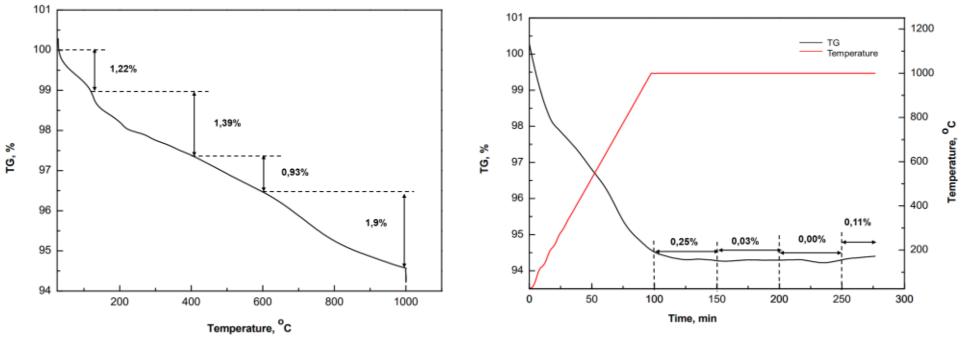


Figure 6.11: Pt extraction yield from unpretreated DOC and c-DPF, respectively

The end-of-life DOC and c-DPF contain carbon content, especially in the c-DPF case, may limit the leaching of Pt in mild conditions. So, thermogravimetric analysis of catalyst and DPF was performed to determine the proper calcination process before the leaching process for removing the carbon content and increasing the Pt leachability.

The performance of spent DOC during the calcination process under the air atmosphere conditions is presented in **Figure 6.12**. The TGA curve consisted of four weight-loss regions at 25-120°C, 120-400°C, 400-600°C, and 600-1000°C, respectively. The first weight loss region (between 25-120°C) and the second region (between 120-390°C) were attributed to the removal of the water content (1.22%) and hydroxyl water and volatile organic compounds (1.39%), respectively. In the third region (between 390-600°C), decomposition and combustion of organics were performed, releasing carbon dioxide (0.93%), and the final weight loss region (between 600-1000°C) was attributed to the combustion of the coke (1.9%).

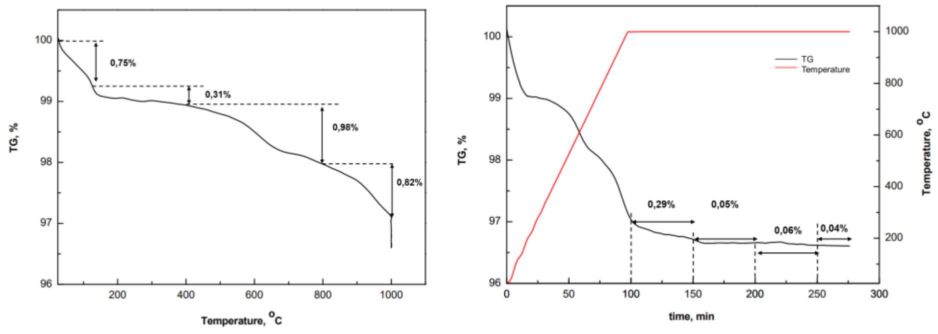
The sample remained at 1000°C for 200min to remove total organics compounds. The loss of mass was very low, and after 150min at 1000°C, it reached almost 0.00%. The total loss of the DOC sample was 5.44% from 25°C to 1000°C and increased only to 5.83% after 2hrs at 1000°C, indicating that the total amount of C content has been removed.



(a) (b)

Figure 6.12: (a) Thermogravimetric analysis (TGA) of DOC, (b) The weight variation at 1000°C for 200min

The spent c-DPF exhibits similar performance with DOC during calcination from 25°C to 1000°C. For TGA of c-DPF, four main steps were identified (**Figure 6.13**). The first one (from 25 to 120°C) corresponded to the loss of the water content of the DPF (0.75%). The second step (from 120 to 400°C) took place to remove the volatile organic compounds (0.31%). In the third step (between 400-800°C), the decomposition and combustion of organics were performed (0.82%) and in the last step (from 800-1000°C), the combustion of the coke (0.82%) took place. The sample of c-DPF remained at 1000°C for 200min. In the residence time at 1000°C, the loss mass almost was zeroed, which means that the total organic compounds and carbon were removed.



(a) (b)

Figure 6.13: (a) Thermogravimetric analysis (TGA) of the c-DPF, (b) the weigh variation at 1000°C for 200min

In both DOC and c-DPF cases, the temperature range for soot and coke removal was 400-900°C. During vehicle operation, active regeneration is performed when the accumulated soot and ash reach boundary limits. In this operation, the particulate soot is burned at an exhaust gas temperature of 600°C, unblocking the channels and reconverting the vehicle filter and engine to regular operation [13]. According to TGA analysis of DOC and c-DPF, the total removal of coke was performed at temperature 900°C. Therefore, thermal pretreatment temperatures were selected at 600°C, 800°C, 900°C.

The calcination effect was also observed by the color change on DOC samples that have been subjected to heat treatment in three different temperatures (600, 800, and 900°C). The color of raw spent DOC was dark brown and was progressively changed to white at 900°C (**Figure 6.14**).

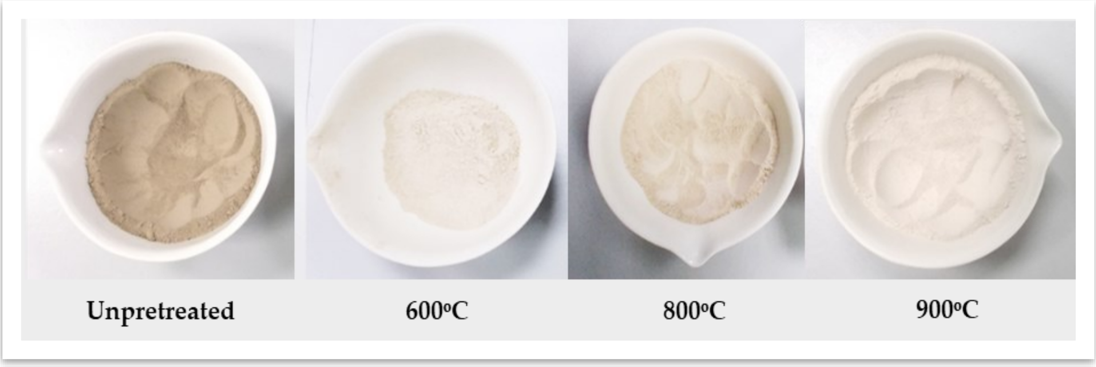


Figure 6.14: Change in color of the DOC catalysts during the calcination at 600°C, 800°C and 900°C respectively

An amount of c-DPF was calcined in three different temperatures (600, 800 and 900°C) and a change of color was also observed. The color of raw spent DPF was black and was slightly changed in light brown at 900°C (**Figure 6.15**).

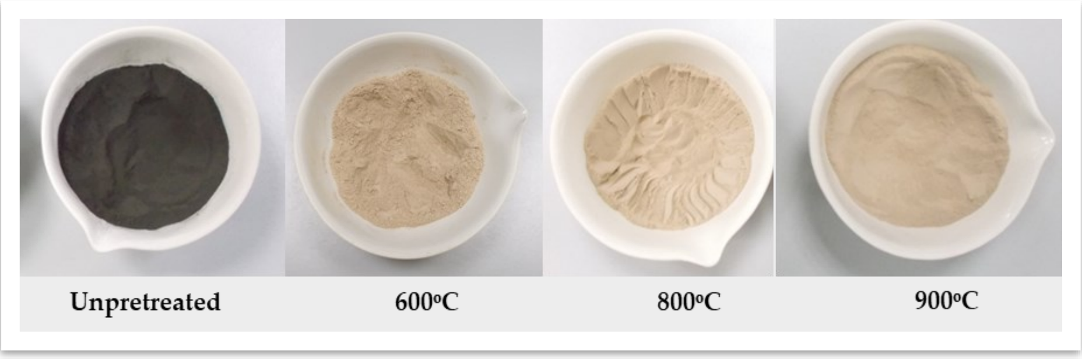


Figure 6.15: Change in color of the c-DPF during the calcination at 600°C, 800°C and 900°C respectively

The selected calcination temperatures were evaluated by leaching experiments both of the DOC and the c-DPF in stable leaching conditions: 3M HCl, 4.5M NaCl, 1% vol H_2O_2, S/L ratio 70% w/v at 70°C for 3h as suggested by Yakoumis *et al.* [8]. The results presented in **Figure 6.16** demonstrate the importance of calcination temperature on Pt leaching. In **Figure 6.16**, the recovery yield of Pt for DOC and c-DPF unpretreated and thermal pretreated samples at 600°C, 800°C and 900°C is also presented.

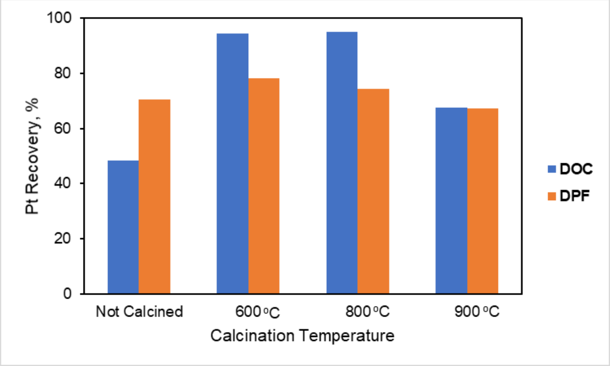


Figure 6.16: Pt extraction yield from unpretreated and thermal pretreated (600°C, 800°C and 900°C) DOC and c-DPF, respectively

According to **Figure 6.16** leaching efficiency of Pt was increased upon calcination at 600°C, for both c-DPF and DOC. Leaching efficiency was raised from 70.5% to 78% for c-DPF and from 48.5% to 94.6% for DOC. However, it was decreased to 67.2% and 67.6% for c-DPF and DOC, respectively, when the calcination temperature further increased at 900°C. The extraction Pt did not change significantly by increasing the calcination temperature from 600°C to 800°C. Therefore, the optimum calcination temperature was 800°C.

Although the DOC and c-DPF were calcined at 800°C for 2 hours in order to remove organic matter, the Pt extraction did not reach 100%. This could be in accordance with the assumption that Pt might be in the structure of the cordierite, indicating that additional pretreatment, probably a reduction step is required in order for the whole Pt content to be removed. Thus, X-ray diffraction (XRD) analysis was performed to evaluate the formed phases before and after the calcination at 800°C of DOC and c-DPF.

As shown in **Figure 6.17**, the main phase of DOC was identified as cordierite ($Mg_2(Al_4Si_5O18)$), which remained stable after thermal treatment at 800°C for 2h. In the same XRD pattern, some carbonate secondary crystallize phases were observed in raw DOC as Magnesium Aluminum Hydroxide Carbonate and Magnesium Oxide Carbonate. The absence of peak in these phases from the XRD pattern in calcined DOC is due to the carbonate decomposition of carbon dioxide.

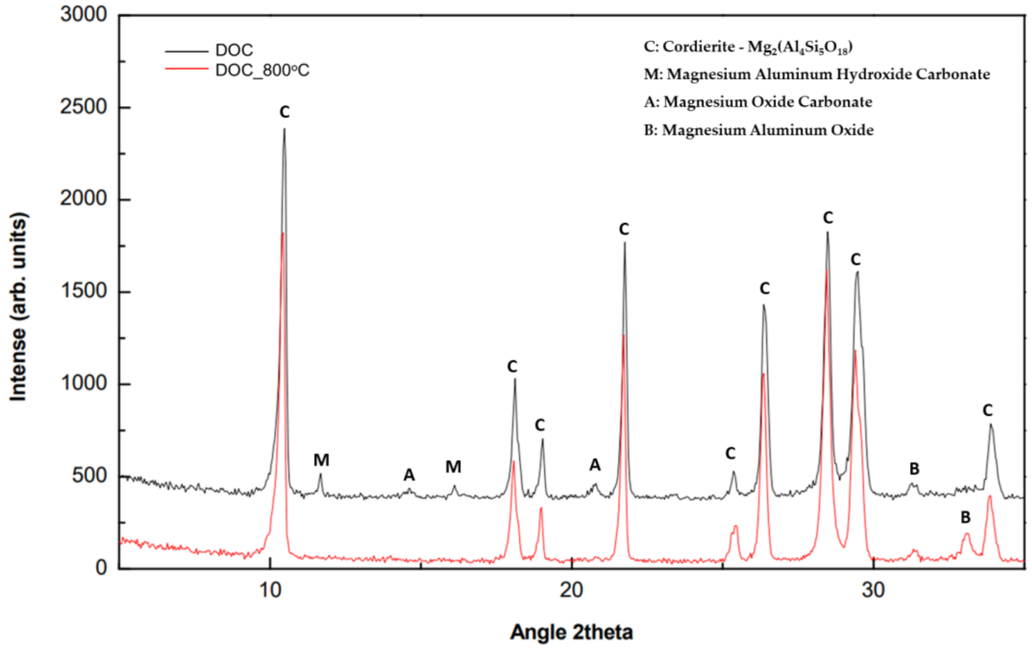


Figure 6.17: **XRD patterns of DOC before and after calcination at 800°C for 2h**

The similar behaviour of c-DPF before and after calcination at 800°C for 2h is shown in the XRD analysis (**Figure 6.18**). There were no apparent modifications in the main crystalize phase, cordierite, after thermal treatment, but only the absence of peak in the secondary carbonate phases, in which carbonate was decomposed after calcination.

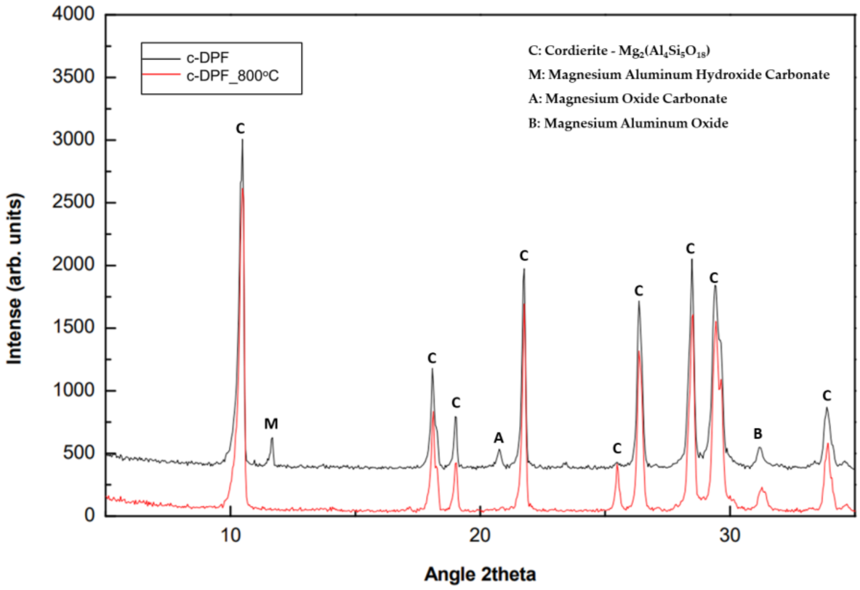


Figure 6.18: XRD patterns of c-DPF before and after calcination at 800°C for 2h

As shown in the XRD analysis of DOC and c-DPF before and after calcination at 800°C for 2h, there were no structural changes in the materials after calcination, which could obstruct the Pt leaching.

6.5.3. Leaching study

For the optimization of Pt leachability from DOC catalysts and c-DPF filters, the parameters of leaching process were evaluated. The main parameters of hydrometallurgical process were the solid to liquid (S/L) ratio, the acidity of the solution (HCl concentration), the oxidizing agent (H_2O_2 concentration), kinetics of the procedure (time) and the addition of a Cl^- source (NaCl concentration).

6.5.3.1. Effect of Solid to Liquid ratio

In order to develop an economically feasible, sustainable, and environmentally-sound recycling process, the generated wastes should be eliminated. Thus, the ratio of sample mass to the solvent required was studied in the range S/L 10%-80%. The evaluation of the Solid to Liquid (S/L) ratio was performed in order to design a more financially sustainable and environmentally friendly leaching process with lower generated liquid and solid waste. Leaching tests were conducted for both c-DPF and DOC systems, and leaching solution content is described in **Tables 6.1**, **6.2**, and **6.3**, respectively. The leaching experiments were performed at a stable temperature at 70°C for 3h.

In the case of DOC, the S/L ratio was studied with unpretreated powder, reducing the S/L ratio from 70% to 10% for considering the amount of solid to affect the Pt extraction yield (**Table 6.1**). The Pt extraction yield remained very low, even, after decreasing the amount of solid.

Diesel Oxidation Catalyst (DOC)					
Pretreatment	S/L ratio, g/ml	HCl	H_2O_2, vol	NaCl	Pt recovery, %
Not Calcined	10%	3M	1%	4.5M	33.9
Not Calcined	30%	3M	1%	4.5M	36.9
Not Calcined	50%	3M	1%	4.5M	30.2
Not Calcined	70%	3M	1%	4.5M	48.5

Table 6.1: Pt leaching efficiencies from unpretreated DOC obtained when using different S/L ratio

For this reason, leaching experiments with the calcined powder were performed. The Pt leaching was significantly increased by the thermal pretreatment at 800°C for 2h. As shown in **Table 6.2**, the Pt extraction yields were reached in 95.2% and 95.7% for the S/L ratio of 70% and 80%, respectively. Therefore, it is assumed that organic deposits hinder the extraction rate of Pt from catalysts.

Diesel Oxidation Catalyst (DOC)					
Pretreatment	S/L ratio, g/ml	HCl	H_2O_2, vol	NaCl	Pt recovery, %
Calcined 800°C	70%	3M	1%	4.5M	95.2
Calcined 800°C	80%	3M	1%	4.5M	95.7

Table 6.2: Pt leaching efficiencies from calcined DOC obtained when using different S/L ratio

In the case of c-DPF, the S/L ratio did not affect extraction of Pt with calcined at 800°C for 2h solid powder. The increase of the S/L ratio from 30% to 70% resulted in a slight decrease in Pt extraction yields from 76.5% to 74.4%%, respectively (**Table 6.3**).

Catalyzed Diesel Particulate Filter (c-DPF)					
Pretreatment	S/L ratio, g/ml	HCl	H_2O_2, vol	NaCl	Pt recovery, %
Calcined 800°C	10%	3M	1%	4.5M	76.0
Calcined 800°C	30%	3M	1%	4.5M	76.5
Calcined 800°C	50%	3M	1%	4.5M	76.2
Calcined 800°C	70%	3M	1%	4.5M	74.4

Table 6.3: Pt leaching efficiencies from calcined c- DPF when using different S/L ratio

Upon several tests, 80% S/L ratio for DOC and 70% S/L ratio for c-DPF, have been determined as the most efficient experimental conditions to treat these materials. Further evaluation of the other leaching conditions parameters would be validated based on this ratio.

On an industrial scale, the main goal is to recycle a large solid amount with high Pt recovery to develop an efficient process.

6.5.3.2. Effect of leaching solution acidity

The main parameter for the chosen industrial leaching process is the acidity of the used solution due to affect the qualitative of liquid waste and the safety of the process. The lesser concentrated the HCl solution is, the fewer water waste is generated from washing and neutralizing of waste steps. Thus, acidity should be minimized without compromising leaching yield. The HCl concentration of leaching systems DOC and c-DPF was tested at 70°C for 3h. The Pt extraction yields of DOC, with an S/L ratio of 70%, were not affected by increasing the HCl concentration from 3M to 4M (**Table 6.4**).

Diesel Oxidation Catalyst (DOC)					
Thermal Pretreatment	S/L ratio, g/ml	HCl	H_2O_2, vol	NaCl	Pt recovery, %
800°C	70%	3M	1%	4.5M	95.5
800°C	70%	4M	1%	4.5M	95.4

Table 6.4: Extraction yields of DOC for different HCl concentration with 70% S/L ratio

The acidity of the solution leaching of DOC was evaluated, increasing the S/L ratio to 80% (**Table 6.5**). The recovery of Pt was almost stable with slight differences, 95,7%, 95.3%, and 95.8%, for HCl concentrations 3M, 3.5M, and 6M, respectively.

Diesel Oxidation Catalyst (DOC)					
Thermal Pretreatment	S/L ratio, g/ml	HCl	H_2O_2, vol	NaCl	Pt recovery, %
800°C	80%	3M	1%	4.5M	95.7
800°C	80%	3.5M	1%	4.5M	95.3
800°C	80%	6M	1%	4.5M	95.8

Table 6.5: Pt extraction yields from DOC for different HCl concentrations with 80% S/L ratio

The same parameter was studied about c-DPF for various values of HCl concentration (**Table 6.6**). The rise of HCl concentration from 2M to 6M improves the Pt recovery from 74.3% to 77%, respectively. The further acidity increase (9M HCl) does not significantly affect process performance.

Catalyzed-Diesel Particulate Filter (c-DPF)					
Thermal Pretreatment	S/L ratio, g/ml	HCl	H_2O_2, vol	NaCl	Pt recovery, %
800°C	70%	2M	1%	4.5M	74.3
800°C	70%	3M	1%	4.5M	74.4
800°C	70%	6M	1%	4.5M	77.0
800°C	70%	9M	1%	4.5M	77.9

Table 6.6: Pt extraction yields of c-DPF for different HCl concentrations

For both DOC and c-DPF samples, the efficiency of the Pt recovery yields is not increased by the higher acidity of the solution. Therefore, the optimum HCl concentration is selected the 3M for developing an environmentally friendly leaching process for the DOC and c-DPF.

6.5.3.3. Effect of H_2O_2 oxidizing agent

The H_2O_2 contributes to the oxidation of PGMs for forming complexes with Cl^-, particularly of Pt, in the leaching system. The evaluation of this parameter was performed in various H_2O_2 concentrations with calcined starting material and an S/L ratio of 70% at 70°C for 3h. **Table 6.7** and **Table 6.8** show the values of all parameters and the Pt extraction yields for DOC and c- DPF, respectively.

Diesel Oxidation Catalyst (DOC)					
Thermal Pretreatment	S/L ratio, g/ml	HCl	H_2O_2, vol	NaCl	Pt recovery, %
800°C	70%	4M	0.5%	4.5M	96.2
800°C	70%	4M	1%	4.5M	95.4
800°C	70%	4M	1.5%	4.5M	95.5
800°C	70%	4M	3%	4.5M	95.4

Table 6.7: Pt leaching rate from DOC for different H_2O_2 concentrations

Insignificant variations were observed in the Pt recovery from DOC catalyst by the increase of H_2O_2. The slight decrease in Pt extraction cany be attributed to non-selective oxidizing of H_2O_2 at higher concentrations. Similar behaviour is observed in the leaching process of the c-DPF. The maximum Pt recovery was achieved in 96.2% with 0.5% vol H_2O_2 and 74.4% with 1% vol H_2O_2 for DOC and c-DPF, respectively.

Catalyzed-Diesel Particulate Filter (c-DPF)					
Thermal Pretreatment	S/L ratio, g/ml	HCl	H_2O_2, vol	NaCl	Pt recovery, %
800°C	70%	3M	0.5%	4.5M	73.0
800°C	70%	3M	1%	4.5M	74.4
800°C	70%	3M	1.5%	4.5M	73.5
800°C	70%	3M	3%	4.5M	73.5

Table 6.8: Pt leaching rate from c-DPF for different H_2O_2 concentrations

Therefore, as optimum H_2O_2 concentration for both materials in the current study 1% vol is selected.

6.5.3.4. Effect of leaching time

The kinetics analysis of the Pt leaching from DOC and c-DPF was investigated for 0.5-3h for DOC catalyst and 0.5-4h for the c-DPF filter at 70°C. The rest of the parameters remained constant for all tests. The experimental parameters of this study are described in **Tables 6.9 and 6.10.**

Diesel Oxidation Catalyst (DOC)						
Thermal Pretreatment	Time, h	S/L ratio, g/ml	HCl	H_2O_2, vol	NaCl	Pt recovery, %
800°C	0.5	80%	3M	1%	4.5M	56.0
800°C	1	80%	3M	1%	4.5M	94.8
800°C	2	80%	3M	1%	4.5M	95.3
800°C	3	80%	3M	1%	4.5M	95.1

Table 6.9: Pt leaching rate of DOC for different time

In the first hour of the leaching experiment, the Pt extraction yield from DOC is 94.8%. As shown in **Table 6.9,** the leachability of Pt was stabilized after 2 hours with Pt recovery of 95.3% and 95.1% at 3 hours. The increasing of Pt extraction is not important to keep the duration of the process above 2h.

Catalyzed-Diesel Particulate Filter (c-DPF)						
Thermal Pretreatment	Time, h	S/L ratio, g/ml	HCl	H_2O_2, vol	NaCl	Pt recovery, %
800°C	0.5	70%	3M	1%	4.5M	66.4
800°C	1	70%	3M	1%	4.5M	69.7
800°C	2	70%	3M	1%	4.5M	67.8
800°C	3	70%	3M	1%	4.5M	74.4
800°C	4	70%	3M	1%	4.5M	73.9

Table 6.10: Pt leaching rate of c-DPF for different time

On the other hand, the extraction of Pt from c-DPF is increased at a constant rate (**Figure 6.19** & **Table 6.10**). In the first hour, the Pt extraction is 66.4% and is stabilized at 74.4% at 3 hours. From 2h to 3h, the Pt recovery rate is slightly decreased from 74.4% to 73.9%, which may be attributed to the reprecipitate of the Pt.

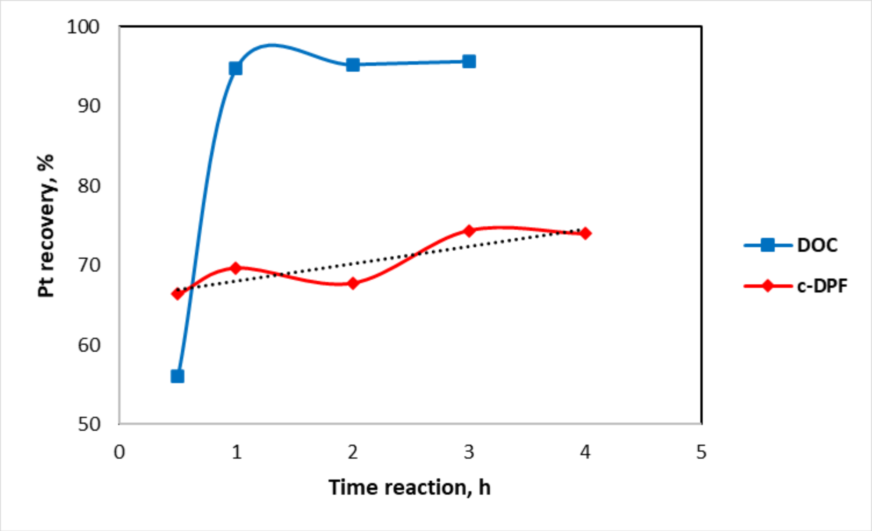


Figure 6.19: Pt kinetic behaviour of DOC and c-DPF for 0.5-3 leaching time

Therefore, according to **Figure 6.19**, the leaching reaction is completed and stabilized after 2h and 3h for DOC and c-DPD, respectively. The duration of a process on an industrial scale is a determinant parameter for its efficiency sustainability.

6.5.3.5. Effect of additional Cl-content

The reagent NaCl was used as an additional source for the formation of Cl-Pt complexes without raising the solution acidity. The study of this parameter was performed with calcined DOC and DPF at 70°C for 1h. The maximum Pt recovery from DOC, 95%, resulted from 6M NaCl, while the lower NaCl concentration 3M yielded Pt recovery 94.6%. The optimum value of NaCl concentration that was chosen was 4.5M with Pt extraction 94.8% (**Table 6.11**).

Diesel Oxidation Catalyst (DOC)					
Thermal Pretreatment	S/L ratio, g/ml	HCl	H_2O_2, vol	NaCl	Pt recovery, %
800ºC	80%	3M	1%	3M	94.6
800ºC	80%	3M	1%	4.5M	94.8
800ºC	80%	3M	1%	5M	93.8
800ºC	80%	3M	1%	6M	95.0

Table 6.11: Pt leaching yields of DOC for different NaCl concentrations

In leaching of c-DPF, the Pt extraction yield was almost stable for various tested NaCl concentrations (3-6M). The higher Pt recovery (74.4%) was achieved by adding 4.5M NaCl during the leaching experiment (**Table 6.12**).

Catalyzed Diesel Particulate Filter (c-DPF)					
Thermal Pretreatment	S/L ratio, g/ml	HCl	H_2O_2, vol	NaCl	Pt recovery, %
800ºC	70%	3M	1%	3M	73.4
800ºC	70%	3M	1%	4.5M	74.4
800ºC	70%	3M	1%	5M	73.3
800ºC	70%v	3M	1%	6M	74.3

Table 6.12: Pt leaching yields of DPF for different NaCl concentrations

Thus, the optimal NaCl concentration for keeping off the low acidity in the leaching process that was selected was 4.5M.

6.6. Development and validation of the Catalytic Efficiency of Diesel Oxidation Catalysts prepared from Recycled/Impure Platinum

The recovered metals from EoL diesel oxidation catalysts DOC, containing Pt as oxidation catalyst, will be valorized in order to prepare fresh DOC catalyst, using the leachate solution. The method of wet impregnation that has been employed for catalyst realization has been validated via Scanning Electron microscopy, where fine nano-sized particles have been formed, while no effect has been detected on $CeZrO_2$ substrate upon the catalyst development. The new nanocatalytic powder will be embedded on $CeZrO_4$ in aiming in 1% metal loading on the substrate [12-14].

The extraction of Pt from milled DOC spent catalyst was performed in 5L glass jacketed reactor treating 1,5kg milled DOC catalyst. According to XRF analysis applied on the solid residue, after the filtration step, the Pt recovery yield was 95%, when applying the same experimental parameters **(Table 6.2)** as were applied on the 20g spent catalyst lab scale experiments, without further tunning. Furthermore, the content of Pt in the leachate solution after the filtration was determined with ICP-OES measurement and verified with XRF analysis, as well.

Figure 6.20: Scale up leaching process of 1,5kg of spent DOC catalyst to recover Pt metal.

According to the ICP-OES measurements of the leachate solution the concentration of the Pt was 1,3g Pt/L. For XRF analysis measurements, appropriate volume of the leachate solution 10ml was mixed with 10g cordierite powder adding 10ml of distilled water, to obtain better distribution of the leachate on the cordierite substrate, in order to prepare a powder like sample. The sample was prepared twice with corresponding amounts of 5ml leachate in 10g of cordierite and 15ml of 2D water. The dried powder sample was subjected to XRF analysis for Pt content determination (**Table 6.13**):

Prepared Samples	**Measure Pt (ppm)**	**Pt concentration (determined by XRF) g Pt/L**	**Pt concentration (determined by ICPOES) g Pt/L**
10ml leachate **10g of cordierite** **10ml of H_2O**	1327	1,33	1,3
5ml leachate **10g of cordierite** **15ml of H_2O**	669	1,34	

Table 6.13: Determination of the Pt content

The nanocatalytic powder for DOC catalyst application was prepared by impregnating the corresponding metal (***<u>in the form of pregnant leachate with no purification/pre-treatment step</u>***) onto $CeZrO_4$ via a wet impregnation method under ambient conditions on hot stirring plate.

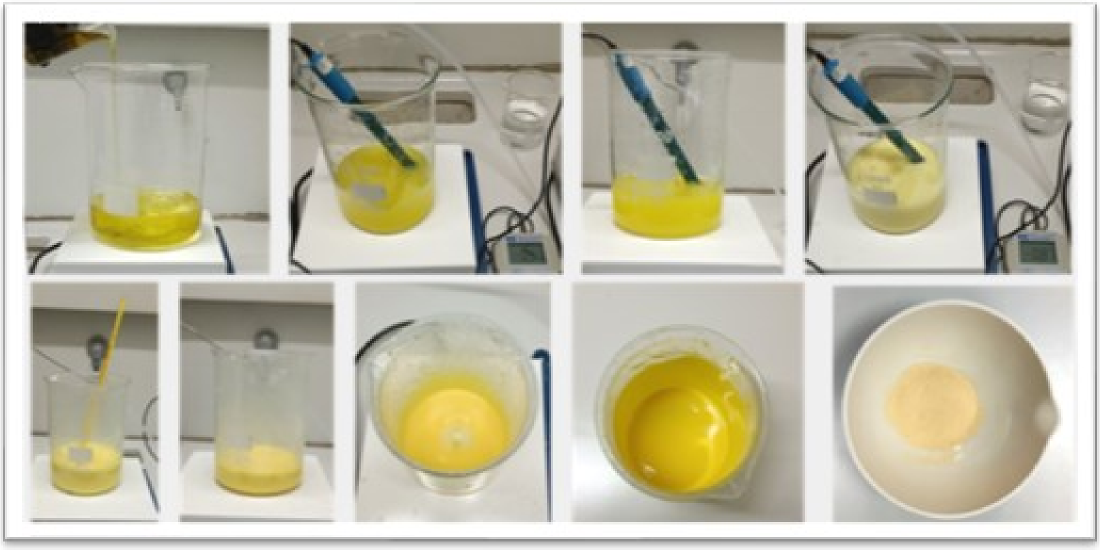


Figure 6.21: Synthesis steps of Pt /$CeZrO_4$ nanocatalyst from leachate solutions.

Water was removed with an evaporation step, avoiding filtration in order to preserve the Pt content prior to the calcination step. The nanocatalyst was received in powder form and subjected to the calcination step at 500°C for 1h, to stabilize Pt nanoparticles on the carrier. Final metal Pt loading and dispersion was determined with XRF analysis and found 1.1%.

The fresh nanocatalyst synthesized with the DOC leachate solution was further validated for its efficiency in CO, CH_4 and NO abatement under standard diesel exhaust testing conditions $\lambda = 1.03$.

In **Figure 6.22**, the light-off curves (conversion vs. temperature) for CO and CH_4 oxidation and for NO reduction in lean-burn catalytic conditions $\lambda = 1.03$ of the fresh catalyst prepared by the leachate solution are presented. The light-off curve is the conversion-temperature plot of CO oxidation, CH_4 oxidation and NOx reduction in different temperatures. The conversion for each gas component is calculated via mass balances of the oxidation of CO and CH_4, and the reduction of NOx, under given stoichiometry of the reactions and certain O_2 concentration in the gas stream for the oxidation and calculated formed CO_2 for NOx reduction. The conversion-temperature plot is recorded in O_2 rich and lean conditions, in order to validate the catalyst activity both under oxidizing and reducing conditions. In this study, only oxidizing lean burn conditions were measured since the DOC catalyst was validated for diesel exhaust gases conditions. Important activity indication values for catalyst characterization lean-burn catalytic conditions are summarized in **Table 6.14**.

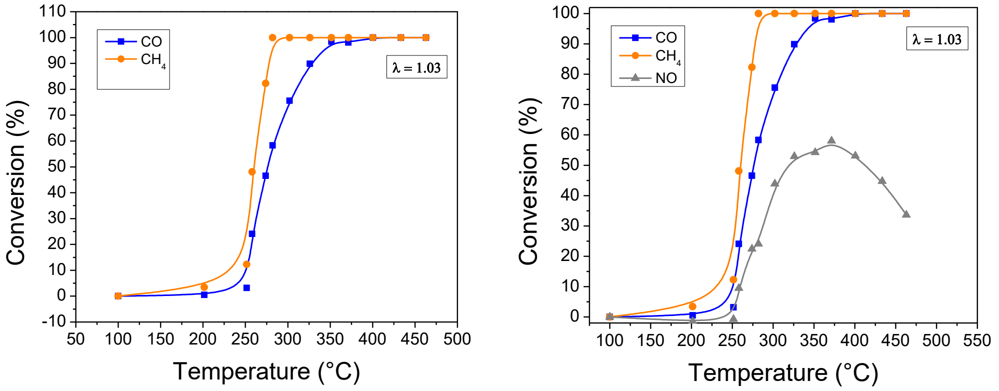


Figure 6.22: Light-off curves for the (%) conversion of: (a) CO (b) CH_4 (c) NO under lean-burn conditions ($\lambda = 1.03$)

The catalyst is exhibiting extraordinary catalytic efficiency, since it is capable of converting 100% of CO and CH_4, while the efficiency for NO reduction is 43%, despite the lean burn conditions of the experiment (excess oxygen).

CO Oxidation			CH_4 Oxidation			NO Reduction		
Efficiency: 99%			Efficiency: 100%			Efficiency: 43%		
T50	T90	T99	T50	T90	T99	T50	T90	T99
304	345	377	285	314	326	-	-	-

Table 6.14: T50 temperatures under lean-burn conditions (λ = 1.03) for fresh nanocatalyst prepared by DOC leachate solution.

6.7. Conclusions of Heavy Duty DOC and c-DPF

In this chapter, the extraction of Pt from Diesel Oxidation Catalyst (DOC) and catalyzed Diesel Particulate Filter (c-DPF) incorporating the HCl-H_2O_2-NaCl system was studied. The thermal pretreatment at 800°C for 2h, before the hydrometallurgical process, was found to remove the organic content and enhance the Pt extraction yield from DOC and c- DPF, from 48.5% to 94.6% and from 45% to 75%, respectively. The structure of samples was not affected after thermal treatment according to XRD analysis. In addition, the lack of washcoat observation may be attributed to the assumption of the Pt inside the c-DPF structure, which affects the leachability of Pt. In the leaching experiments, the different conditions (solid/liquid ratio, acid concentration, oxidizing agent concentration, additional Cl concentration, and the leaching time) were evaluated in order to optimize the Pt extraction yield. The low acidity (3M HCl), low reagents concentration (1% v/v H_2O_2 and 4.5M NaCl) at 70°C for 2 or 3h has resulted in an environmentally friendly process, while the leaching parameters are the same with the ones proposed by Yakoumis *et al.* [18] for Light Duty Vehicles catalysts.

Moreover, the pregnant leachate solution (with no purification/pre-treatment step) from Pt extraction was used to prepare fresh washcoat for DOC catalyst. The new catalyst was prepared with loading 1,1% on $CeZrO_4$ substrate, and catalytic performance was validated on lean burn conditions λ = 1.03. The results were extremely good, since total convention of CO and HC has been achieved, while the NOx efficiency is 43% (even though we have lean conditions – commercial catalysts do not exceed 20% efficiency for NOx in these conditions). The results are in accordance with the results of Chapter 5, proving that impure pregnant solutions could be used in order to produce new catalysts, with similar (or even better) catalytic efficiency results.

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7th Chapter

7. New PGM Secondary Sources: Hydrogen Energy Storage Devices and Electrocatalysts

7.1. Introduction of Renewable Energy Sources

Technological advantages have led to improved quality of life, increasing the world population and consequently energy demands. Almost 90% of consumed energy is provided by fossil fuels. Fossil fuels are considered non-renewable energy sources and become scare progressively. The dependency of a country on fossil fuel as the main power source can lead to serious economic and political issues. In addition, fossil fuels consuming produce greenhouse gases causing air pollution and global warming. The European Union targets for 2030 aims at reducing greenhouse gas emissions by 40% compared to 1990, increase the renewable share in energy consumption at least to 32% and improve the energy efficiency at least to 27%. To achieve the above, a rapid transition moving from fossil to sustainable fuels is required to meet the increased energy demands.

Renewable Energy Sources (RES) based on solar or wind energy have been used to produce renewable energy with minimal environmental impact and economic cost [1]. However, they cannot guarantee the undisturbed energy production because of unstable weather conditions. Electrochemical energy storage of hydrogen (H_2) is a promising option with the potential to provide low-carbon energy for all sectors of the economy.

7.2. Fuel Cell and Hydrogen (FCH) technologies

Hydrogen is one of the most promising clean, efficient and sustainable energy carrier. Hydrogen technology, having many attractive properties as high energy density (140 MJ/kg), can be produced from renewable and sustainable sources and its energy can be distributed continuously. A series of applications (industrial, transport/mobile, portable, stationary energy applications) including power generation in periods of increased demand, supplementation of the natural gas grid for increased efficiency, vehicle fueling or use as a feedstock for green generation of chemicals can be covered with H_2. Environmentally friendly electrochemical conversion of H_2 in fuel cells produces energy and water as a byproduct, without carbon dioxide (CO_2) emissions. The environmentally friendly byproducts are the main reason for the development of Fuel Cell and Hydrogen (FCH) technologies.

The replacement of fossil-based technologies by FCH systems is considered a pathway to reduce the dependence on fossil fuels, since these devices enable a low carbon energy economy, allowing the use and storage of renewable energy in the form of H_2 (**Figure 7.1**). FCH technologies belong to clean technologies and offer a significant reduction in CO_2 and NOx emissions. In a fuel cell, H_2 is consumed to produce energy (**Figure 7.1a & b**). On the other hand, in a water electrolyzer, energy is consumed to produce H_2 (**Figure 7.1c & d**).

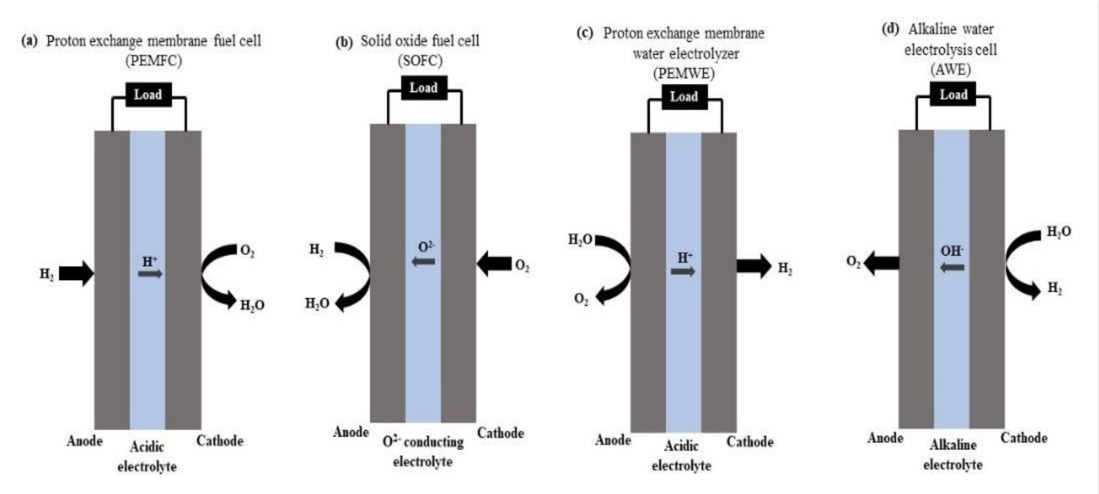

Figure 7.1: FCH technologies for energy production with H_2 consumption (a, b) and for H_2 production with energy consumption (c, d).

FCH technologies are proven and established in aerospace. For example, an Advanced Closed Loop System (ACLS) which recycles CO_2 on the Space Station into O_2 has been developed by European Space Agency (ESA) for human spaceflight. In ACLS, CO_2 exhaled by astronauts is used to produce water (Sabatier reaction). This water is then used to produce oxygen (by electrolysis) for the crew on the Space Station.

7.2.1. H_2 production in the Proton Exchange Membrane Water Electrolyzer (PEMWE)

Hydrogen production from water is an attractive route for costless renewable electricity. Water is abundant on earth's surface and can be used to meet the H_2 needs required for the sustainable production of fuels and chemicals. Among the water splitting technologies, electrolysis is the most efficient and mostly extensively studied [2]. In water electrolysis, water splits into H_2 and O_2 by supplying electrical energy. In a water electrolyzer, the latter reaction is divided into two sub reactions that take place on the anode and cathode, respectively, which are separated by a solid or liquid electrolyte (**Figure 7.2**). Catalysts are used in both electrodes to increase reactions rates. The main advantages of H_2 production through electrolyzers are low emissions, high efficiency, low energy consumption, easy start and stop recycling and easy transport. The main disadvantages are low scale application, limited lifetime, high cost (electrolyte, critical metal materials) and sensitivity towards impurities in the water.

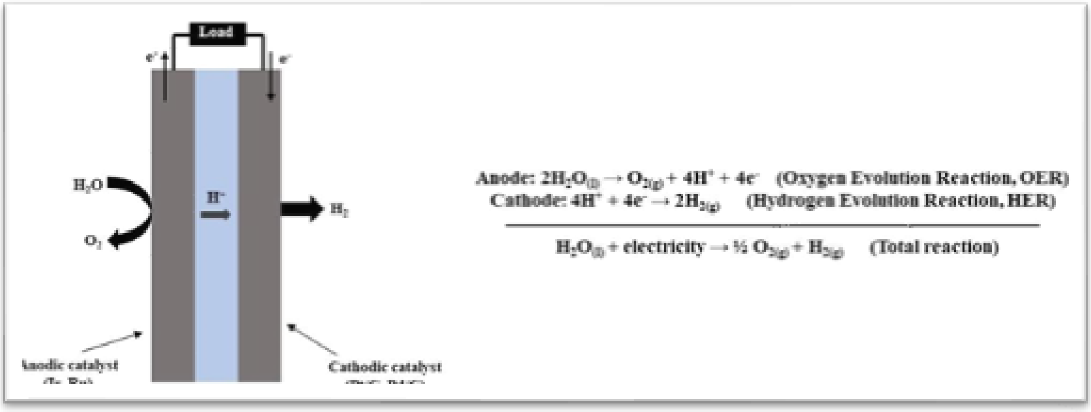

Figure 7.2: Proton exchange membrane water electrolyzer (PEMWE)

PEMWEs operate in a temperature range 20-100°C and use a thin solid polymer electrolyte membrane and noble metal-based catalysts electrodes [3]. In particular, in a PEMWE, water is supplied to the anode where it is oxidized to produce O_2, protons (H^+) and e-, according to the oxygen evolution reaction (OER) presented in **Figure 7.2**. Protons travel via the proton conducting electrolyte membrane to the cathode side. The electrons exit from the anode and reach the cathode through an external power circuit. In cathodic electrode, protons and electrons are re-combined to produce H_2, according to the hydrogen evolution reaction (HER).

7.2.2. Main components of a PEMWE

The major component of a PEMWE is the membrane electrode assembly (MEA),. MEA consists of the proton conductor polymer membrane sandwiched between two porous electrical conducting electrodes. Solid polysulfonated membrane (commonly NafionTM from Chemour) with typical thickness of 60-200 μm is used as an electrolyte [4]. These membranes have unique properties, such as high strength and efficiency, high oxidative and thermal stability, good durability, high proton conductivity and low electron conductivity. The hydration of the membrane should be preserved, so as for the proton conduction to be favored. Therefore, heat and water management systems are critical processes to ensure efficient operating conditions. On both sides of the membrane, thin electrodes (10 μm thick) are directly bonded to the surface. The SoA catalysts for PEMWE are platinum (Pt) or palladium (Pd) at the cathode and iridium oxide (IrO_2) or ruthenium oxide (RuO_2) at the anode [5]. Iridium is typically used for water oxidation, due to its high corrosion resistance. The MEA is clamped between two electrically conductive porous transport layers (PTLs). The transport layers are typically made of carbon paper and sintered titanium (Ti) foam or felt (280 μm thick) on the cathode and the anode side, respectively [6]. PTLs are responsible for effective mass transport and heat/water management and ensure electrical conductivity.

De-ionized water is supplied to the anode side of the cell by a flow field separator plate and diffused via current collector. Current collectors enable an electric current to flow between the electrodes and flow field plates, (**Figure 7.3a**). Due to severe acidic operational conditions and high overvoltage and concentration of O_2 at the anode side, metallic separator plates and current collectors are primarily used in PEMWE devices. Typically, Ti-based materials show outstanding strength, high thermal conductivity, low permeability, high electrical conductivity and corrosion resistance [5]. However, after long operation under high anodic potentials, Ti corrodes and an inert insulating oxide layer is formed. Thus, protection of the titanium plates using precious metal Pt and Ir coatings are used. At the cathode side a graphite flow field is usually used to transport H_2.

In order to achieve the desired electric power, multiple MEA are interconnected by bipolar plates (BPPs), (**Figure 7.3b**). Bipolar plates surface is designed with a set of channels that have the dual function of reactant delivery and coolant handling. A bipolar plate electrically connects adjacent cells, uniformly distributes H_2O and gases, separates oxygen in anode of one cell from the H_2 in cathode of the adjacent cell, removes heat from active areas and provides mechanical support to the MEA. Bipolar plates should exhibit low surface contact resistance, excellent corrosion resistance, high electrical and thermal conductivity, low gas permeability, good mechanical strength, low weight and low cost. BPPs are generally made of graphite, polymeric compounds or carbon-polymer composites. Titanium, aluminum and metal alloys, such as Cr-Ni steel, are also considered suitable given their high electrical conductivity and good mechanical properties. However, due to corrosion conditions, metallic bipolar plates need to be coated [6, 7].

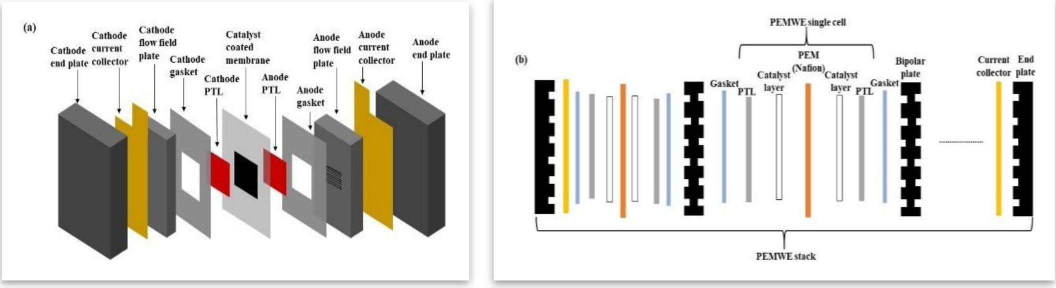

Figure 7.3: PEMWE (a) single cell and (b) stack.

For potential leaks to be prevented and ensure an optimal compression between the layers, gaskets (made up of silicon, TeflonTM, rubber, etc.) are interposed. The PEM stack is mechanically supported by two thick end plates. Due to the operating temperature and the presence of humidity, the materials that are used for end plates should exhibit high electrical insulation, high thermal conductivity, stability and rigidity, and corrosion resistance. Therefore, end plates are typically made of Al or steel.

7.3. Recycling CRMs from PEMWE

In terms of sustainability and environmental impact, PEMWE is considered as the most promising system for high pure efficient H_2 production from renewable energy sources. However, the increased development of PEMWE devices require high amounts of critical raw materials (CRMs) as electrocatalysts and corrosion coatings (Pt, Ru, Ir) and high cost materials (Ti) as BPPs and PTLs, (**Table 7.1**). For example, 1 MW PEMWE requires about 1.5 kg of Ir catalyst and annual production of Ir is about 3 -4 tons.

CRMs are identified in the EU according to two main aspects: 1) economic importance and 2) risk of supply disruption [8, 9]. The value chain of CRMs is not fully and homogeneously covered by the European industry. China is the principal global supplier of CRMs. To address the growing concern of securing CRMs for the EU economy, the Commission launched the European Raw Materials Initiative in 2008. One of the priority actions of the Initiative was to establish a list of CRMs at the EU level. The Commission established the first list in 2011 which contained 14 CRMs. After that, the list is revised every three years. In 2020, the list has been expanded to 30 materials.

The coronavirus pandemic has revealed Europe's dependencies in certain products, critical materials and value chains. For example, China is the main supplier for CRMs used into batteries, making European carmakers reliant on Chinese suppliers. As the pandemic triggers transport disruption between western capitals and China, and due to the lack of mineral deposits in Europe, there is an urgent need to secure the supply of vital materials. In order to reduce Europe's dependency on external importers, exploration, investment and improved recycling processes must be developed [10].

	Catalyst (mg/cm^2)	**Porous transport layer (mg/cm^2)**	**Bipolar plates (mg/cm^2)**
Anode	2-3 (Ir)	5 (CRMs-coated Ti)	**0.02-0.04 (CRMs on Ti)**
Cathode	0.2-0.5 (Pt)	5 (CRMs-coated Ti)	**0.02-0.04 (CRMs on Ti)**

Table 7.1: State-of-the-Art (SoA) CRMs loading in PEMWE

The most challenging barrier for PEMWE to overcome and become sustainable is the reduction of their cost without their performance to be compromised. Despite the significant progress in the last decade [8], economic issues still hamper their commercialization. In this respect, environmentally sustainable approaches to recover CRMs from PEMWE should be considered. The transition from a linear to a circular economy, where the value of CRMs is maintained in the markets for as long as possible, is a crucial parameter to develop a sustainable, low carbon and competitive EU economy.

7.3.1. Conventional methods

Nowadays, the simplest process with a negligible environmental impact contains mechanical steps to recycle a PEMWE stack such as the disassembly of the stack into its individual components. Recycling of the MEA and BPPs from PEMWE systems is challenging because specialized recycling processes are required. The recovery of precious metals and membrane from the MEA can be achieved by shredding the used MEA and delaminate the different layers [12].

Conventional methods for recovery Pt, Ru, Ir and Ti from composite materials are pyrometallurgy and hydrometallurgy [1]. According to the pyrometallurgical method, thermal treatment of the materials is carried out in a high-temperature furnace to bring about physical and chemical transformation and enable recovery of valuable metals. In pyrometallurgy processing mechanical pre-treatment is not required and high recovery rates can be achieved. However, it is energy-intensive, quite expensive and release highly toxic and corrosive hydrofluoric acid gas.

On the other hand, hydrometallurgy is the SoA process for Platinum Group Metals (PGMs) recovery. Hydrometallurgical method chemical reactions are carried out in aqueous or organic solvents for metal recovery. The process consists of the following general steps: (i) leaching, (ii) solution concentration, purification and precipitation, and (iii) metal recovery/refining (Duclos et. al, 2016).

In the solution concentration and purification step, PGMs anions in solution are separated by different techniques. Sulfides, hydroxides and carbonates are widely used for metals precipitation (Singh, 2009). Pt can be precipitated as $(NH_4)_2PtCl_6$ salt using NH_4Cl and reused with carbon powder for new catalysts to be recycled [1]. A refining step is required in order to achieve high purity metals in separate solutions. Hydrometallurgical process exhibits higher selectivity, lower energy consumption and more environmentally friendly with respect to pyrometallurgical method. The main drawback of the method is the use of large volume of solvents and the generation of toxic wastewater.

Platinum group metals can be extracted from the catalytic layers of PEMWE with a leaching process. However, pre-treatment to delaminate the layers of the MEA is mandatory. On the other hand, in the case of PGMs extraction with pyrometallurgy, pre-processing is not required (Valente et. al, 2019). Although, pyrohydrometallurgy exhibits higher recovery efficiency than hydrometallurgy, safety and environmental issues raise, due to demanding and severe working conditions.

Recycling methods for Ti recovery could provide an important cost reduction in PEMWE technology. Ti, which is not a natural element, is normally produced by a Kroll process. In general, Ti can be recovered through conventional existing processes based on physical separation (size reductions and magnetic separation). However, when

Ti is combined with other elements, a more complex recovery method is required. THE Main disadvantages of the latter method are the large material and energy expenditures for the process and remain of Ti in the processed materials. Chloride and fluoride recycling technologies can also be used for Ti recovery.

7.3.2. Novel methods

Recycling of precious electrocatalysts (Pt, Ir) used in PEMWE systems using the above existing methods is usually inefficient or essentially nonexistent due to design constructions, unavailable recycling technologies and the thermodynamics of separation [15,18]. Duclos *et al.*, proposed hydrometallurgy to recover Pt from catalyst coated membrane (CCM) MEA of a PEM fuel cell system. A series of leaching solutions and separation techniques were examined, obtaining 76% of Pt recovery yield. However, further processing is required to manage remaining solid waste and HCl neutralization.

However, apart from pyrometallurgical and hydrometallurgical processes for CRMs recovery from MEAs, novel recovering technologies has also been developed [11]. The designing of a single process where the entire unit of the stack is subjected to, in order for the precious metals and other valuable materials to be recovered, is highly desirable. Novel methods usually show advanced technical, economic and environmental performance. Selective electrochemical dissolution method is proposed for Pt and carbon support recovery from cathodic compartment of MEAs [16]. Although, high purity Pt is recovered in high yield under mild conditions, reconditioning of carbon support is required in order to be reused. Acid process is proposed for Pt and membrane recovery from MEAs [17]. The main advantages of the method are high Pt recovery yield and low pollution emissions. However, acid process is a time-consuming method and high pH conditions are also required. Recently, M. Carmo *et al.*, proposed ultrasonication to recover both noble metal catalysts materials and ionomer separately without any harmful and pollutant emissions from MEA in PEMWE. The membrane free from catalysts is separated, dried and reused to fabricate new MEAs. Pt and Ir are separately recovered and reused. This is an environmentally friendly and fast process and high recovery yield (> 90%) can be achieved.

7.3.3. Low acidity hydrometallurgical method for Pt recovery from spent MEAs

Main manufacturing process of MEA is spray coating. The spray-coating method is widely used for catalyst fabrication. Typically, the catalyst ink is coated on the gas diffusion layer or cast directly on the membrane (**Figure 7.4**). The application apparatus can be a manual spray gun or an auto-spraying system with programmed X–Y axes, movable robotic arm, an ink reservoir and supply loop, ink atomization, and a spray nozzle with adjustable flux and pressure.

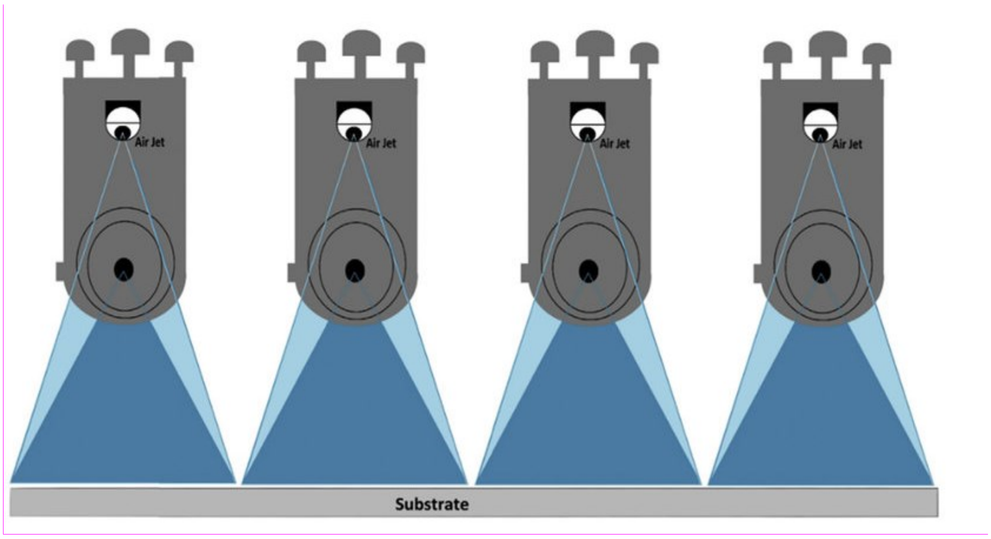

Figure 7.4: PEMWE MEA spraying method

Catalyst Pt or Ir/C ink was sprayed directly onto the membrane, and an infrared light was used simultaneously to evaporate the solvents. The concentration of the catalyst on each electrode side of the MEA could reach 2 μg/cm^2. The resultant MEAs prepared by this method yielded very high performance and homogeneous distribution of the catalyst Pt or Ir/C on the Nafion membrane. The novel hydrometallurgical method that has been described in Chapter 3 has also been applied with very promising results on the extraction of Pt and Ir catalyst from spent MEAs (**Figure 7.5a**). The carbon layer containing the Pt and Ir catalysts was initially dispatched from the Nafion membrane using an alcoholic solution (**Figure 7.5b**). The catalyst suspension was dried and the collected powder (**Figure 7.5c**) was subjected to single step hydrometallurgical process for the recovery of the PGM metals. The aqueous:alcohol solution with various concentrations was used for the separation of the Nafion membrane (**Figure 7.5d**) in order to recover C electrodes and the membrane to remain intact (**Figure 7.5d**).

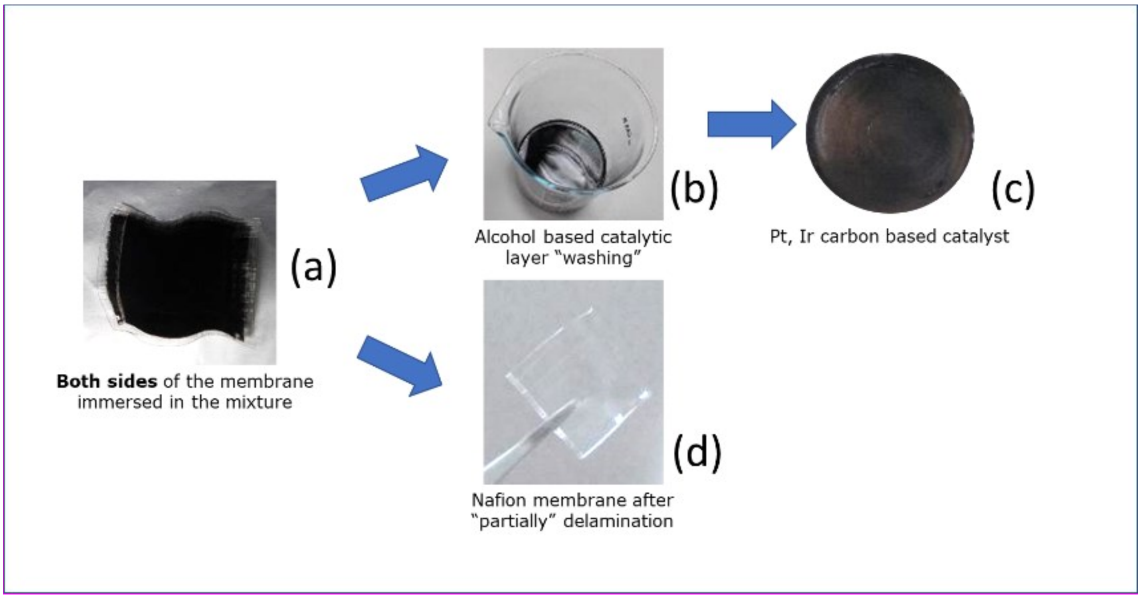

Figure 7.5: Pre-processing of the MEAs membrane, before subjected to low acidic hydrometallurgical recycling

In order to separate anode from cathode electrode, another method was also tested to separate electrodes from Nafion membrane, obtaining two separate alcoholic solutions containing Pt and Ir, individually. According to **Figure 7.6**, the Nafion MEA (**Figure 7.6a)** brought into contact with alcoholic solution from cathodic electrode side **Figure 7.6b,c**, so as for Pt and C electrode to be dispatched and dissolved in it (**Figure 7.6d**). Then, the dried one-electrode Nafion Membrane (**Figure 7.6e**) brought into contact with alcoholic solution from cathodic side (**Figure 7.6f,g**), so as for Ir and C anodic electrode to be dispatched and dissolved in the solution (**Figure 7.7h**). Then, the membrane, remained intact (**Figure 7.6i**).

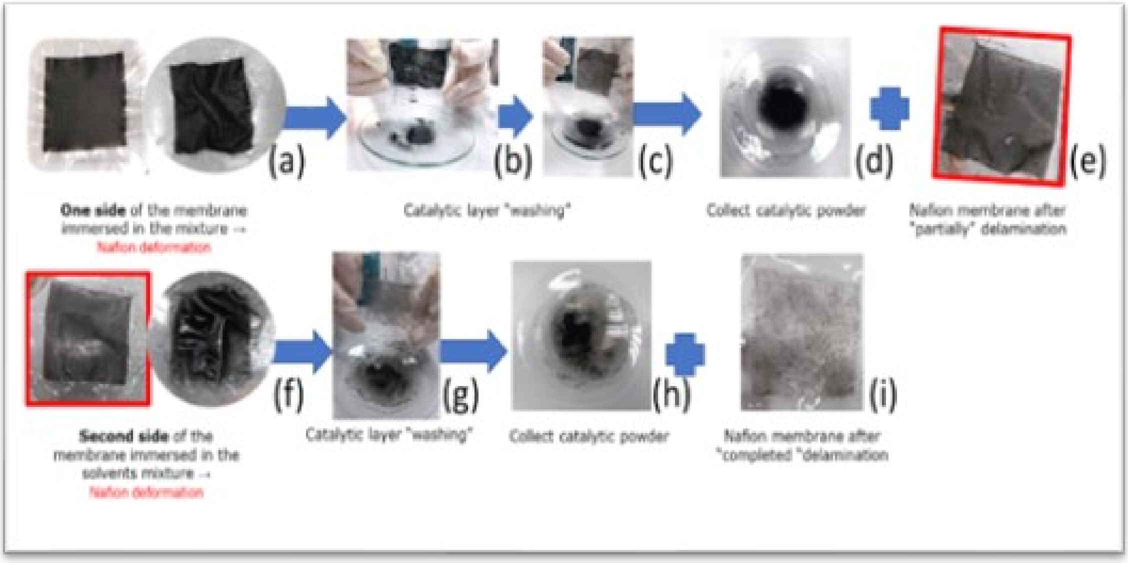

Figure 7.6: Pre-processing of the MEAs membrane, before subjected to low acidic hydrometallurgical recycling separating anode and cathode catalyst

The Pt/C cathodic powder (**Figure 7.6d**) obtained was then subjected into hydrometallurgical single step extraction method, in order for S/L ratio, temperature, solution acidity and reaction time to be examined in detail. Preliminary results indicates, that low content of alcohol solution is sufficient for the separation of polymer-organic assembly. Moreover, the extraction rate of Pt was higher than 99% with low acidity 3.5M solution, 4M NaCl, 70^{o}C and 3h under stirring conditions. Similar recovery process was applied for Ir anodic electrode C powder, where recovery rate was 60%.

The experimental parameters, such as the type of solvents (mild organic/inorganic solvents), the solvent ratio, and the electrode detachment/peeling from carbon paper or cloth method (soaking a liquid under stirring or ultrasonication to achieve effective catalyst separation) during membrane-electrode delamination step, as well as the acidity of the HCl solution, the concentration of oxidation agent, the reaction time and temperature during the leaching process, will be studied to describe the optimum conditions for recycling of CRMs (e.g., Pt, Ir, Ru and Ti) from MEAs in high recovery yields. The method and the process for separating electrodes and membrane were also submitted for a patent in **Hellenic Industrial Property Organization** (245-0004386313) under the title “Recovery of CRMs from electrochemical stack devices via hydrometallurgical process” for recycling process of CRMs from electrochemical devices stacks using its hydrometallurgical leaching method.

7.4. Conclusions of Renewable Energy Sources

The growth of required energy and the increase in fossil fuel resource depletion, have led to the development of alternatives systems for sustainable production of fuels and green energy. H_2 is proposed as a promising alternative source of energy. Eco-friendly and high purity H_2 production by PEMWE has attracted great scientific attention as an effective option to reduce greenhouse gas emissions. PEMWE systems have been already used to produce oxygen for the crew on the Space Stations. Nowadays, the increased development of PEMWE devices that require high purity CRMs (Pt, Ir, Ru, Ti), together with the low availability of these metals compromise their economic feasibility. In this regard, there is an urgent need for an efficient, low cost and environmentally friendly recycling EoL strategy for the recovery of CRMs and high cost materials from PEMWE. The low cost, single step hydrometallurgical process for PGMs recovery developed by the current Phd was applied for the recovery of Pt and Ir from MEAs from PEMWE stacks in 99% and 60% respectively.

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8th Chapter

8. Market Analysis

8.1. Introduction

Catalytic converters are currently the most effective emission control devices for vehicles to comply with the emission control regulations set by the EU (currently at EURO 6). These devices utilize Platinum Group Metals (PGMs) e.g., Pt, Pd, Rh for the effective oxidation and reduction of the harmful gases emitted from the vehicles exhausts (CO, NOx, HC). With the disposal of vehicles, catalytic converters are also disposed, wasting significant amounts of PGMs. The EU is currently facing a dual challenge i) an increasing PGMs supply/demand gap ranging at 44 tn (2019) combined with the fact that autocatalysts are the highest PGMs consuming application, and ii) the insignificant production of PGMs in the EU as ~84% of the supply comes from South Africa and Russia.

The specific chapter focuses on the dual objective to manufacture automotive catalytic converters (ACC) integrating 100% recycled PGMs, while simultaneously decreasing the PGM quantity via partial substitution by a low-cost and politically less sensitive transition metals such as copper.

The specific analysis is mainly based on the automotive market and the subsequent catalytic converters market analysis which is the major solution provided today to the automotive industry for emission control for both light-duty and heavy-duty vehicles. The project targets to the introduction into the market of a novel technological device which reduces the CO, HC and NOx emissions generated by both light and heavy-duty vehicles. The target market is the whole automotive industry, including the automotive original equipment manufacturing (OEM) and the aftermarket, to be fitted on light-duty vehicles (e.g., passenger cars, SUVs and pickup trucks) and heavy-duty vehicles (e.g., cargo trucks and buses) running on petrol and diesel.

8.2. Automotive Industry

Globally, in 2019 the automotive industry accounted for 1.25 Trillion EUR generated by vehicles sales of a total of 88,194,000 vehicles sold. The specific market is expected to reach ca 2.11 Trillion EUR in size by 2027, growing at a CAGR of 7.1% during the period 2020-2027.[1] The largest vehicles producers are:

Light duty vehicles (81,342,000 vehicles in 2019): Toyota followed by the Volkswagen group, Hyundai, General Motors, Ford, Nissan, Honda, Fiat Chrysler Automobiles, Renault and PSA.[2] Heavy duty vehicles (6,852,000 vehicles in 2019): Daimler, Volvo, Volkswagen group which owns Scania and MAN SE, and Paccar.[3]

The sales of each vehicles segment for the years 2013-2020 are shown in **Figure 8.1**. Based on the performances of those years, projections were made for 2021 and beyond, taking into account also the COVID-19 impact, which is expected to bring a slight drop in vehicles sales in the years 2020-2023. However, recovery of the market is projected from 2023 onwards.

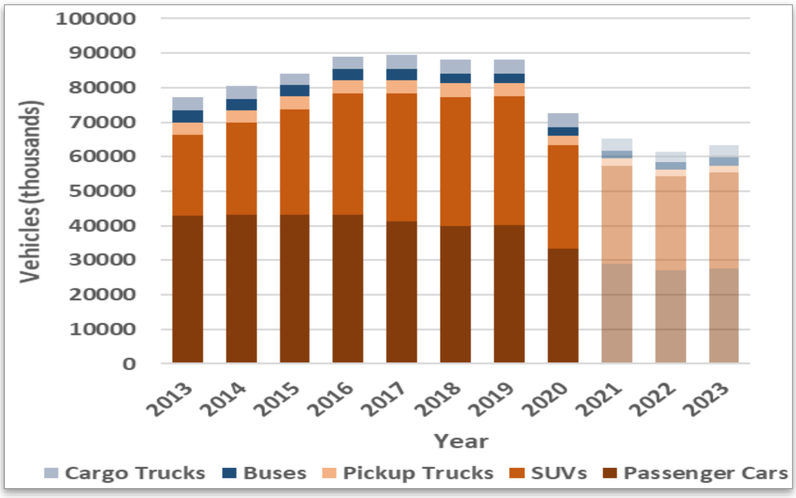

Figure 8.1: Light and heavy-duty vehicles sales by sub-segment[4]

The specific Thesis targets to constitute a commercial emission control device mainly for the automotive aftermarket which refers to automotive replacement parts for vehicles and has a market share of ca. 10% of the whole automotive market, produced by hydrometallurgically recycled PGMs.

8.2.1. Autocatalysts market

In 2019, the corresponding global autocatalysts market accounted for EUR 10 Billion and is projected to reach EUR 19 Billion by 2025, growing at a CAGR of ca. 7.2% during the forecasted period.[5] The specific market consists primarily of the production of the below devices with their market share.

- Three-Way-Catalysts, consisted of three different PGMs (Pt, Pd, Rh).
- Diesel Oxidation Catalysts, consisted of PGMs (Pt, Pd) and aiming particularly for combustion engines running on diesel.
- Catalyzed-Diesel Particulate Filters consisted of Pt and aiming in the removal of ash and soot from the exhaust emissions of diesel combustion engines.

The autocatalysts industry is very crucial for Europe's prosperity since the sector represents the largest private investor in research and development (R&D). The growth of the sector can be attributed to the increasingly stringent global emission standards. Currently, the EURO 6 emission control regulation is in force and pushes vehicles manufacturers to utilize autocatalysts in vehicles and end-users to maintain and replace them if needed. In addition, greater stress on improving vehicle efficiency and reducing toxic emissions is a major factor driving the automotive catalyst market. The automotive industry is currently trying to adjust to the Paris Agreement and reduce the CO_2 emissions at 20% with the use of state-of-art commercial autocatalysts giving a great market potential to constitute the primary emission control devices for light and heavy duty vehicles.

The Asia-Pacific region, which was the dominating region adopting autocatalysts in 2019, is also expected to grow at a fast pace due to the sheer volume of cars being sold. China is expected to occupy a significantly high market share by the end of 2025 in the Asia-Pacific market. Improving economic conditions in the region, increasing disposable income and preference towards automatic transmission are also expected to fuel the growth. Also, stringent emission norms and fuel-efficiency standards in the form of Bharat Stage VI will see lighter and more fuel-efficient vehicles to be developed, further driving the market growth. The expected growth of catalytic converters at different parts of the world is shown in **Figure 8.2.**

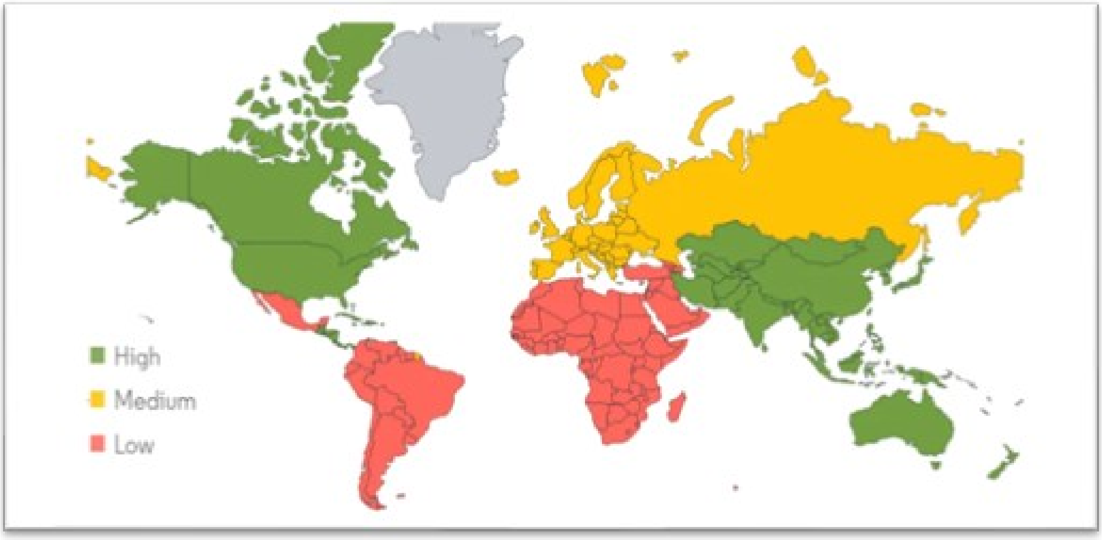

Figure 8.2: Automotive Catalytic Converters and PGMs Market-Growth Rate By Region (2020-2025)

The global Automotive Catalytic Converter Market is an almost consolidated market which gives moderate freedom to new players to enter the market. BASF Catalysts LLC is the world's leading supplier of automotive catalysts. The company developed the first catalytic converter in 1970 and it upholds the line of emission catalysts even today. FUTABA INDUSTRIAL CO. LTD. and Benteler International AG have upheld their significant position in the competitive landscape along with the other prominent companies. This is anticipated to positively influence the global market as these companied are expected to drive market innovation and development in the coming years.

Worldwide Key Players:

BASF SE, FUTABA Industrial CO LTD, Benteler International AG, Johnson Matthey, Umicore, Tenneco Inc., CDTi Advanced Materials, Inc., Cummins Inc., Eberspächer, Ecocat India Pvt. Ltd., Klarius Products Ltd., Clariant, Faurecia SA, Marelli SPA, Yutaka Giken Company Limited.

Table 8.1: Automotive Catalytic Converters Manufacturers

Different shapes of catalytic converters are available in the market due to different needs in automotive vehicles size, fuel type and consumption. Prices usually range between 800 EUR to 2000 EUR per piece, depending upon the vehicle type and model.

A custom handmade catalytic converter usually utilized by racing/sport vehicles can cost more than 2000 EUR/piece.

The automotive catalytic converter market is driven by investments made by major manufacturers and research and development in the market. In April 2018, Tenneco Inc., an auto parts manufacturer, has agreed to acquire Federal-Mogul from Icahn Enterprises L.P. in cash and stock deal valued at USD 5.4 billion. In April 2019, Faurecia S.A. of France announced that the company will produce catalytic converters at Clarion's Koriyama Plant in Fukushima, Japan. Manufacturing equipment will be installed in October 2019, with production starting around August to September 2020. This will be the first synergetic effect achieved after Faurecia's acquisition of Clarion. Faurecia intends to expand business with Japanese automakers by establishing a manufacturing system in Japan.

8.3. Heavy Duty Vehicles Market Catalysts

Specifically, the current (state-of-the-art) emission control system of these vehicles include i) the diesel oxidation catalyst (DOC), ii) the diesel particulate filter (DPF), and iii) the selective catalytic reduction (SCR), containing valuable PGMs. In the framework of this work, the DOC and c-DPF have been targeted as high PGMs sources to take full benefit of the potential of end-of-life HDVs.

In 2019, 6,852,000 heavy duty vehicles were sold, comprising sales from the sub-segments of heavy duty cargo trucks and the buses/coaches. A dedicated market analysis of them is presented below.

A) Cargo Trucks

The specific sub-segment of the automotive HDVs was valued at EUR 370 Billion in 2019 generated from the sales of 4,142,000 vehicles and is projected to reach EUR 445 Billion in 2026, growing at a CAGR of 3.2% between the period of 2020-2026.[8] Sustainable growth is expected in Asia, Europe and the North America **(Figure 8.3)**, driven by proliferating infrastructure and construction projects initiated across the globe. Furthermore, to fight major problems like traffic congestion, population explosion, high manufacturing costs and ageing transportation infrastructure, developed economies are now investing heavily in infrastructure development in developing economies such as India. These factors are boosting the sales of heavy-duty trucks across the globe. Asia pacific countries exhibits the fastest economic growth rates in the entire world. The Asia-Pacific region is expected to be a major market propelling the global construction industry, with augment construction activities in countries, such as India and ASEAN (Association of Southeast Asian Nations) countries. China's One Belt One Road initiative is a highly ambitious project that serves the purpose of constructing a unified market with geographies around World through road, rail and sea routes.

Figure 8.3: HDVs Catalytic Converters and PGMs Market-Growth Rate By Region (2020-2025)

Significant rise is expected also in the US with the high-speed railway project aiming at connecting 8 of the 10 largest cities of California from San Diego to San Francisco. The project is scheduled to be completed by 2029.

The European market is mainly driven by the robust network of national and state highways for road transportation, supported by the increasing transportation needs of food items and other consumer goods between European countries. Road accounts for the largest share of EU freight transport performance among the three inland transport modes, accounting for over 75.3% of the total inland freight transports. Several benefits provided by heavy-duty trucks, such as durability, extremely long range, and high volume-carrying capacity, are increasing their adoption for freight transportation in Europe.[10]

The heavy emissions coming out of heavy duty cargo trucks has slowly turned the interest into developing hybrid (fuel-electric) and HDVs running on natural gas.[11]

8.3.1. Buses and Coaches

The specific sub-segment of the automotive HDVs was valued at EUR 30 Billion in 2019 generated from the sales of 2,500,000 vehicles and is projected to reach EUR 46 Billion in 2025, growing at a CAGR of 7.6% between the period of 2020-2025.[12] Buses worldwide are classified in the below categories:

- School buses: They are specially designed to safely transport students to and from educational facilities and are also known as “conventional” school buses.
- Transit buses: Buses designed to efficiently move passengers within metropolitan areas. These buses are also used in other applications.
- Motor coaches: Used to transport passengers between cities or regions and tend to be uniquely designed with comfortable seats and large luggage storage space at wheel level.

Much of the gains are expected to arise from the Asia-Pacific region with lead driver being China (**Figure 8.4**) and will be attributable to school buses, because of safety concerns about other types of buses currently used to transport students. Growth in demand for motor coaches, transit buses, and all other buses will be much more moderate.

However, transit bus sales will rise at the next fastest rate behind school buses, boosted by efforts to i) reduce traffic congestion and improve air quality as urban populations continue to grow; ii) reduce volatile fuel costs, making bus transportation more attractive to commuters; iii) the ongoing development of public transportation infrastructures, including bus rapid transit systems, in a number of developing countries.

The market for motor coaches, which currently accounts for the largest portion of global bus demand, will increase at a slower pace, fueled by rising per capita income and vacation travel spending. Sales of all other buses, which include shuttles and other smaller vehicles based on a medium-duty chassis, will register the slowest gains, supported by a pickup in tourism and travel spending.

The US is projected to record above average increases, as bus demand rebounds following a dramatic drop in sales from 2006 to 2011. Product demand in Western Europe and Japan will also recover from recent lows (mostly due to COVID-19 pandemic). Bus sales in these areas will be stimulated by generally healthy economic conditions and higher tax revenues, providing government agencies with the revenues needed to replace older vehicles and expand current fleets for national and international connecting bus services.

Figure 8.4: Buses and Coaches market growth rate by region (2020-2025)

The market for buses is a fragmented one, with the major players holding a significant share of the market due to their developed products and network of various dealers. The major player in the market is Zhengzhou Yutong Bus Co. with almost 90% of the market, followed by Xiamen King Long United, Daimler AG, Volvo, Traton (Man, Scania, etc.), Tata Motors, Ashok Leyland, etc.

8.4. PGMs Market

The Platinum Group Metals (PGMs) value chain is based on the supply and utilization of six metals: platinum, rhodium, palladium, iridium, ruthenium, and osmium. The platinum group metals market has been witnessing substantial prospects most notably from the numerous uses of platinum and palladium. They are used extensively in jewelry making and in manufacturing medical and electronics devices. Key applications of PGMs include the autocatalysts manufacturing (utilizing Pt, Pd and Rh), chemicals, fuel cells, glass, electrical and electronics, ceramics, paints and pigments, etc. The precious metals market, in which PGMs are included together with Au and Ag, was valued at 152 Billion EUR (2019) in revenue and is expected to grow at a CAGR of 9% between 2020-2027.[15] Only for the PGMs market, in 2019, the global supply was 447 tons, among them 180 tons Pt, 210 tons Pd and 20 tons for Rh, while the rest accounted for 37 tons. The corresponding gross demand for applications reached 679 tons, creating an annual supply-demand gap of 232 tons.

Europe is already the world's largest consumer of PGMs in industrial applications with a share of ca. 23% of the global demand. Reportedly, autocatalysts consume the highest amounts of PGMs among all applications (**Figure 8.5**). In 2019 the European demand of PGMs,[16,17] was estimated at ~71.5 t Pd, 78.7 t Pt and 4 t Rd, (~154 t of PGMs worth ~7.5 B€ with current PGMs prices[18]) with ~ 90%, 54% and 80% respectively channeled to the production of automotive catalysts (~110 t of PGMs).[2,9]

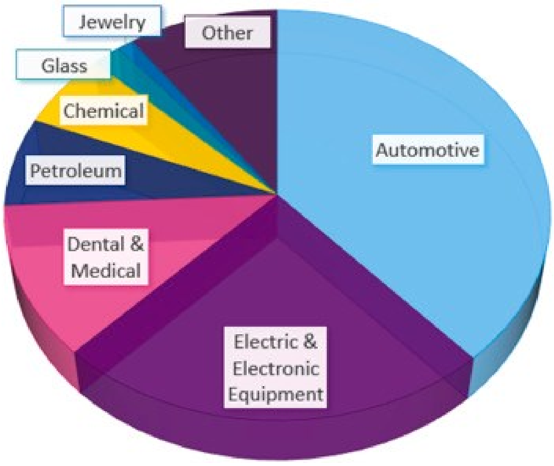

Figure 8.5: Industrial applications of PGMs

The main challenge with the current situation in the EU is twofold: i) PGMs are very expensive materials (i.e., Rh for instance is about 10 times more expensive than gold, and Pd is almost twice more expensive then gold) that are currently experiencing a serious risk of supply as the PGMs market was in deficit in 2019, and all-time highs were seen in PGMs prices in 2020 (3X since 2016 for Pd, 6X since 2016 for Rh), and ii) the primary production of PGMs in the EU is insignificant; ~84% of the primary supply comes from South Africa and Russia, countries-major producers of PGMs (**Figure 8.6**) but also with suboptimal geopolitical stability which makes Europe entirely dependent on this import. Therefore, the current situation is causing a significant increase on the cost of commercial catalytic converters used by the automotive sector. It is therefore well understood that the demand of PGMs is expected to rise within the next few years, and the situation is becoming very critical to have sufficient PGMs supply for those markets.

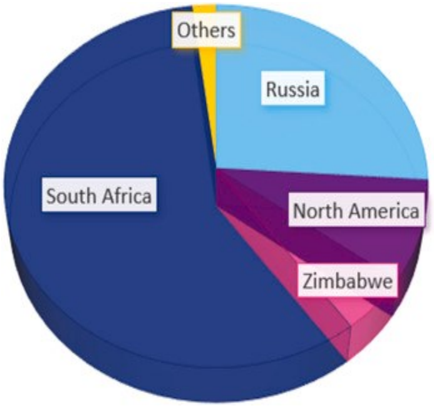

Figure 8.6: Geographical areas of PGMs mining ores

As mentioned above, the highest amount of PGMs is utilized for the production of autocatalysts (70%) and the utilization of the latter also drives the demand for the former, making the two elements highly connected in terms of market demand and growth. As a result, PGMs demand is expected to grow in regions where autocatalysts demand is also growing. Furthermore, many major PGMs producers are also highly involved in the autocatalysts manufacturing chain making the market highly consolidated, with the top five players controlling nearly 88% share of the market. The major companies include Anglo American Platinum, Norilsk Nickel, Impala Platinum, Lonmin, and Northam Platinum Limited. A bigger list of PGMs producers is shown in **Table 8.2**.

Worldwide Key Producers:

Anglo American Platinum, Norilsk Nickel, Impala Platinum, Lonmin, Northam Platinum Limited, Sino-platinum, Sedibelo, Incwala, Wesizwe, Zimplats, Jinchuan, Aquarius, Platina, Caisson Laboratories, Royal Bafokeng, Eastplats, BASF SE, Heraeus, Umicore

Table 8.2: PGMs biggest producers

In the European area the market is concentrated in 7 key companies, with Johnson Matthey owing the 39% of the market, producing ca. 43 tn of PGMs annually.

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9th Chapter

9. Conclusions

9.1. Introduction

In this chapter, the final conclusions of the PhD, as well as proposals for future steps will be presented.

9.2. Conclusions

In this thesis, an optimized single-step leaching process for PGMs has been developed, following the well-tested HCl–H_2O_2–NaCl system for the valorization of Platinum Group Metals from Spent Automotive Catalysts. Comparing with previous studies on the same system, pretreatments, such as reduction or pre-concentration, have been avoided in this novel approach. The leaching yields obtained are 100%, 92% and 61% for Pt, Pd and Rh, respectively, using low acidity reagents, namely 3 M HCl, 4.5 M NaCl, 1%v/v H_2O_2, under mild temperature conditions (70°C). Furthermore, the highest S/L ratio achieved (S/L = 0.7) leads to high catalyst mass dissolution, thus significant PGMs dissolution by direct leaching. The high S/L ratio of the proposed process offers significant advantages in industrial design, as smaller plant installation may be required and low amount of waste is generated. Undoubtedly, improvements in liquid waste management should be proposed to minimize waste treatment expenses. Both mild acidity and leaching temperature of the proposed leaching system led to the presumption that an environmentally friendly approach has been implemented. Further leachate analysis must be performed to evaluate the sustainability of the process design followed by PGM separation studies.

The specific system, applying the same operation parameters, has been tested for the valorization of Platinum from New PGM containing secondary sources, like the MEA of Hydrogen Devices containing electocatalysts and Heavy Duty Vehicles Emission Control Devices, namely the Pt containing DOC and catalyzed-DPFs. The leaching efficiency of the method was extraordinary for all new secondary sources leading tested since the Pt leaching efficiency reached > 99% for MEAs, 95% for Heavy Duty DOCs and 75% for Heavy Duty c-DPFs.

The specific industrially driven Thesis is suggesting an integrated circular economy model for the valorization/re-use of recycled/leached PGM for producing new catalytic converters. According to the model, PGM recovered from passenger vehicle catalytic converters via hydrometallurgical processes (irrespectively of the method employed), can be used as secondary raw material source for the preparation of novel autocatalysts. The latter are designed in order to support the sustainability of the described circular economy model that accounts for the actual recycling rate of spent autocatalysts and the achieved PGM recovery yields. From the collected spent catalysts and the leachable PGMs, innovative catalysts were developed and measured for their catalytic efficiency. More precisely, both Three-Way-Catalyst and Diesel Oxidation Catalyst were manufactured using recycled (impure) PGMs as precursors. CRFiat (Center Research Fiat) tested the catalysts vs commercial testing protocols (both as fresh and after hydrothermal ageing) and concluded that the have similar catalytic efficiency with commercial and benchmark catalysts of the same PGM loading.

Last, a market analysis was conducted to investigate the market potential of the proposed thesis. According to the findings, catalytic converters are currently the most effective emission control devices for vehicles to comply with the emission control regulations set by the EU (currently at EURO 6). These devices utilize Platinum Group Metals (PGMs) e.g., Pt, Pd, Rh for the effective oxidation and reduction of the harmful gases emitted from the vehicles exhausts (CO, NOx, HCs). With the disposal of vehicles, catalytic converters are also disposed, wasting significant amounts of PGMs. The EU is currently facing a dual challenge: i) an increasing PGMs supply/demand gap ranging at 44 tn (2019) combined with the fact that autocatalysts are the highest PGMs consuming application, and ii) the insignificant production of PGMs in the EU as ~84% of the supply comes from South Africa and Russia, driving to a tremendous raise of PGM prices in the recent (i.e., 1500% raise in Rh price in the last five years).

9.3. Next steps

As the next steps from the present thesis, the following activities are proposed:

- Upscaling of the proposed process in large scale reactors (1,000lt batch reactor) in order to evaluate the efficiency of the process.

- Development of the full scale-catalysts and fitting them in real passenger cars to investigate the efficiency as well as the behaviour comparing to the commercially available catalysts.

- Comparison of the PGMs leaching process with the existing solutions and executing a feasibility study to investigate whether this process is economically viable for further industrialization.

- Investigation of application of the specific process for other metals and other sources of metals (e.g., rare earths).

- Apply hydrometallurgical recovering method on heavy duty vehicles catalyst in large scale.

Annex with Publications

Annex 1

Yakoumis I.V., Panou M., Moschovi A.M., Panias D., 2021, “Recovery of platinum group metals from spent automotive catalysts: A review”, *Cleaner Engineering and Technology*, 3, 100112 (https://doi.org/10.1016/j.clet.2021.100112)

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

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ABSTRACT

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

1. Introduction

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

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

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

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Annex 2

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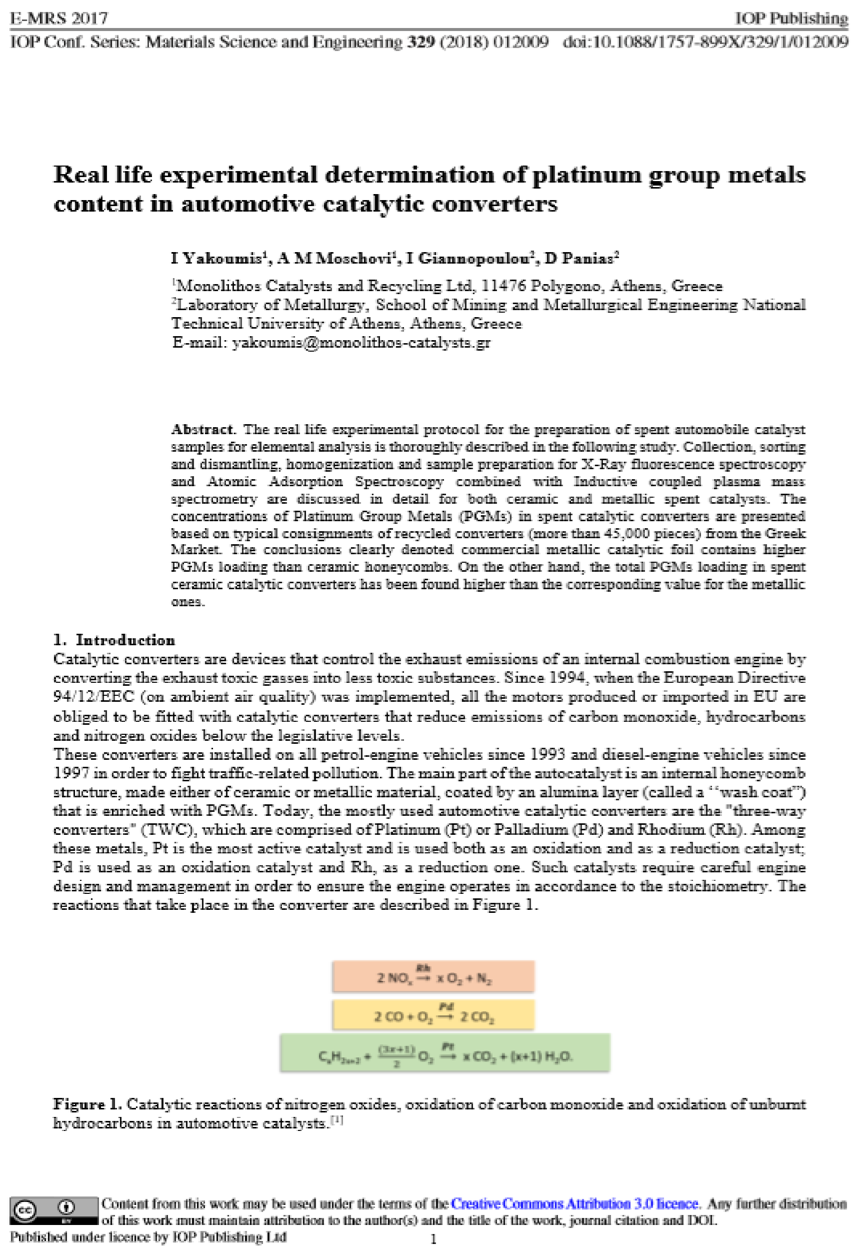

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Real life experimental determination of platinum group metals content in automotive catalytic converters

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Abstract. The real life experimental protocol for the preparation of spent automobile catalyst samples for elemental analysis is thoroughly described in the following study. Collection, sorting and dismantling, homogenization and sample preparation for X-Ray fluorescence spectroscopy and Atomic Adsorption Spectroscopy combined with Inductive coupled plasma mass spectrometry are discussed in detail for both ceramic and metallic spent catalysts. The concentrations of Platinum Group Metals (PGMs) in spent catalytic converters are presented based on typical consignments of recycled converters (more than 45,000 pieces) from the Greek Market. The conclusions clearly denoted commercial metallic catalytic foil contains higher PGMs loading than ceramic honeycombs. On the other hand, the total PGMs loading in spent ceramic catalytic converters has been found higher than the corresponding value for the metallic ones.

1. Introduction

Catalytic converters are devices that control the exhaust emissions of an internal combustion engine by converting the exhaust toxic gasses into less toxic substances. Since 1994, when the European Directive 94/12/EEC (on ambient air quality) was implemented, all the motors produced or imported in EU are obliged to be fitted with catalytic converters that reduce emissions of carbon monoxide, hydrocarbons and nitrogen oxides below the legislative levels.

These converters are installed on all petrol-engine vehicles since 1993 and diesel-engine vehicles since 1997 in order to fight traffic-related pollution. The main part of the autocatalyst is an internal honeycomb structure, made either of ceramic or metallic material, coated by an alumina layer (called a ‘‘wash coat”) that is enriched with PGMs. Today, the mostly used automotive catalytic converters are the "three-way converters" (TWC), which are comprised of Platinum (Pt) or Palladium (Pd) and Rhodium (Rh). Among these metals, Pt is the most active catalyst and is used both as an oxidation and as a reduction catalyst; Pd is used as an oxidation catalyst and Rh, as a reduction one. Such catalysts require careful engine design and management in order to ensure the engine operates in accordance to the stoichiometry. The reactions that take place in the converter are described in Figure 1.

$$2\,NO_x \xrightarrow{Rh} x\,O_2 + N_2$$

$$2\,CO + O_2 \xrightarrow{Pd} 2\,CO_2$$

$$C_xH_{2x+2} + \frac{(3x+1)}{2}O_2 \xrightarrow{Pt} x\,CO_2 + (x+1)\,H_2O.$$

Figure 1. Catalytic reactions of nitrogen oxides, oxidation of carbon monoxide and oxidation of unburnt hydrocarbons in automotive catalysts.[1]

Annex 3

Yakoumis I.V., Moschovi A.M., Panou M., Panias D., 2020, "Single-Step Hydrometallurgical Method for the Platinum Group Metals Leaching from Commercial Spent Automotive Catalysts." *J. Sustain. Metall.,* 6, 259–268 (https://doi.org/10.1007/s40831-020-00272-9)

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RESEARCH ARTICLE

Single-Step Hydrometallurgical Method for the Platinum Group Metals Leaching from Commercial Spent Automotive Catalysts

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Abstract

Platinum group metals (PGMs) are considered critical raw materials, thus their recycling and re-use is of outmost importance. Among the PGMs, platinum (Pt), palladium (Pd) and rhodium (Rh) are the basic metals used in catalytic converters. Concerning the stringent EU standards for emission control imposed to car manufacturers (Euro 6d nowadays), the worldwide demand for PGMs is being increased. As for PGM recovery methods, research is focusing on greener, plain recovery techniques, which utilize milder reagents and offer energy efficiency. In this work, a state-of-the-art hydrometallurgical process is proposed resulting in recovery rates for Pt, Pd and Rh, namely 100%, 92% and around 60%, respectively. A batch of more than 20 commercial spent catalyst samples has been mechanically pre-processed (i.e. sorted, decanned, milled, grinded, homogenized and characterized), in order for a 20 kg sample of homogenized fine pent catalytic powder to be derived. The proposed hydrometallurgical method does not involve any kind of thermal pre-treatment or chemical reduction, thus energy consumption is minimized, while the use of chemicals has been restricted to simple and cheap inorganic solvents (namely HCl, NaCl and H_2O_2). The aforementioned recovery rates have been validated through X-ray fluorescence spectroscopy analysis (XRF). The equipment used has been successfully calibrated to measure low PGM concentrations (less than 50 ppm for each metal). The kinetics of the hydrometallurgical process have also been studied, in short intervals, and spent catalyst material has been characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy analysis (EDS) and X-ray powder diffraction (XRD).

Graphical Abstract

Keywords Platinum group metals · Hydrometallurgy · One-step leaching · Spent automotive catalysts · XRF calibration

Introduction

Platinum group metals (PGMs) are widely used in various industrial areas, being part of exhaust catalytic system, electronics, photovoltaics, dental materials, pharmaceuticals,

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Extended author information available on the last page of the article

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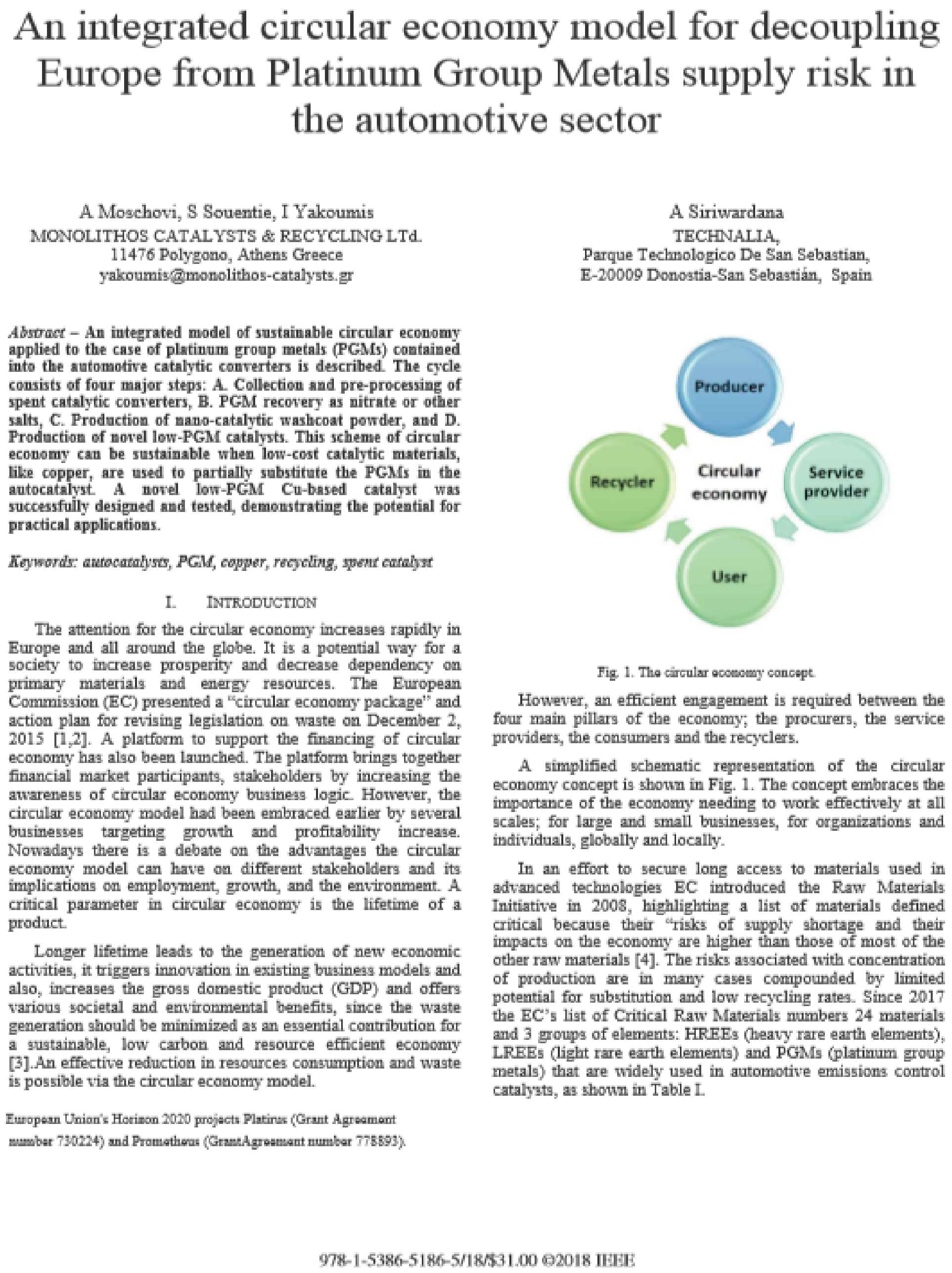
Annex 4

Moschovi A.M., Souentie S., Yakoumis I.V., Siriwardana A., 2018, “An Integrated Circular Economy Model for Decoupling Europe from Platinum Group Metals Supply Risk in the Automotive Sector”, *2018 IEEE International Conference on Environment and Electrical Engineering and 2018 IEEE Industrial and Commercial Power Systems Europe (EEEIC / I&CPS Europe)* pp. 1-5 (DOI: 10.1109/EEEIC.2018.8493824).



An integrated circular economy model for decoupling Europe from Platinum Group Metals supply risk in the automotive sector

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***Abstract* – An integrated model of sustainable circular economy applied to the case of platinum group metals (PGMs) contained into the automotive catalytic converters is described. The cycle consists of four major steps: A. Collection and pre-processing of spent catalytic converters, B. PGM recovery as nitrate or other salts, C. Production of nano-catalytic washcoat powder, and D. Production of novel low-PGM catalysts. This scheme of circular economy can be sustainable when low-cost catalytic materials, like copper, are used to partially substitute the PGMs in the autocatalyst. A novel low-PGM Cu-based catalyst was successfully designed and tested, demonstrating the potential for practical applications.**

Keywords: autocatalysts, PGM, copper, recycling, spent catalyst

I. INTRODUCTION

The attention for the circular economy increases rapidly in Europe and all around the globe. It is a potential way for a society to increase prosperity and decrease dependency on primary materials and energy resources. The European Commission (EC) presented a “circular economy package” and action plan for revising legislation on waste on December 2, 2015 [1,2]. A platform to support the financing of circular economy has also been launched. The platform brings together financial market participants, stakeholders by increasing the awareness of circular economy business logic. However, the circular economy model had been embraced earlier by several businesses targeting growth and profitability increase. Nowadays there is a debate on the advantages the circular economy model can have on different stakeholders and its implications on employment, growth, and the environment. A critical parameter in circular economy is the lifetime of a product.

Longer lifetime leads to the generation of new economic activities, it triggers innovation in existing business models and also, increases the gross domestic product (GDP) and offers various societal and environmental benefits, since the waste generation should be minimized as an essential contribution for a sustainable, low carbon and resource efficient economy [3].An effective reduction in resources consumption and waste is possible via the circular economy model.

Fig. 1. The circular economy concept.

However, an efficient engagement is required between the four main pillars of the economy; the procurers, the service providers, the consumers and the recyclers.

A simplified schematic representation of the circular economy concept is shown in Fig. 1. The concept embraces the importance of the economy needing to work effectively at all scales; for large and small businesses, for organizations and individuals, globally and locally.

In an effort to secure long access to materials used in advanced technologies EC introduced the Raw Materials Initiative in 2008, highlighting a list of materials defined critical because their “risks of supply shortage and their impacts on the economy are higher than those of most of the other raw materials [4]. The risks associated with concentration of production are in many cases compounded by limited potential for substitution and low recycling rates. Since 2017 the EC’s list of Critical Raw Materials numbers 24 materials and 3 groups of elements: HREEs (heavy rare earth elements), LREEs (light rare earth elements) and PGMs (platinum group metals) that are widely used in automotive emissions control catalysts, as shown in Table I.

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Annex 5

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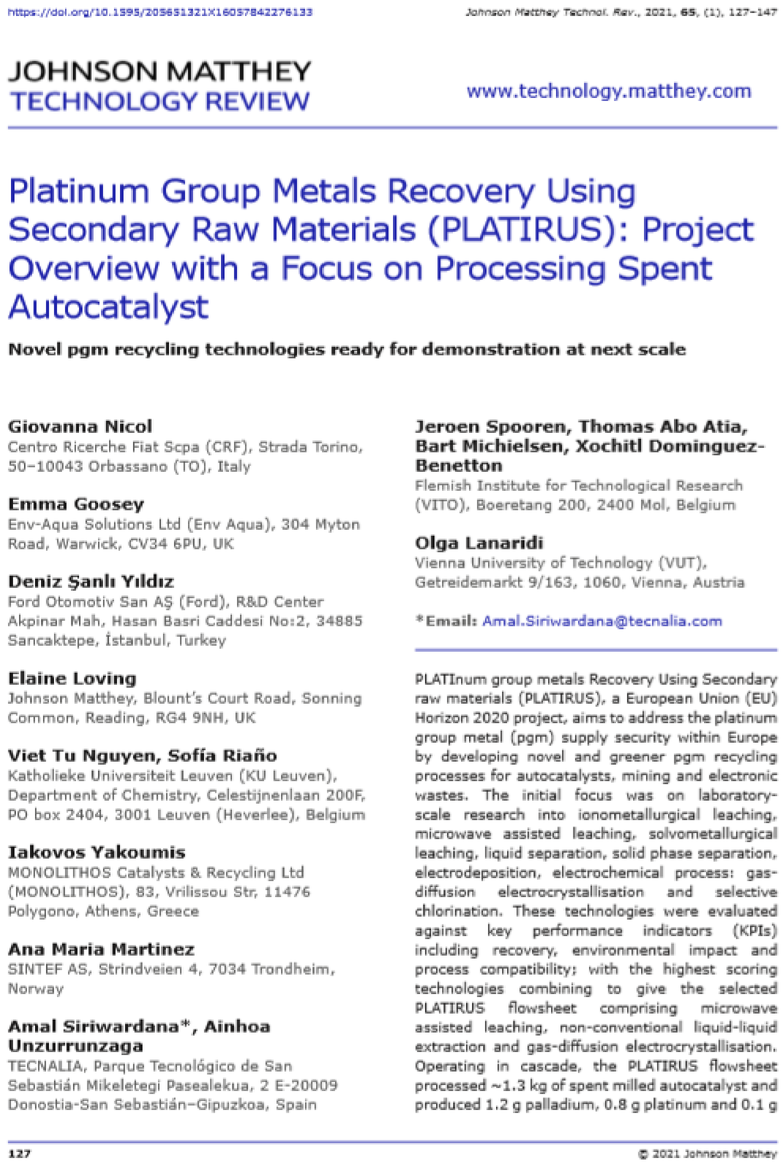

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Platinum Group Metals Recovery Using Secondary Raw Materials (PLATIRUS): Project Overview with a Focus on Processing Spent Autocatalyst

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

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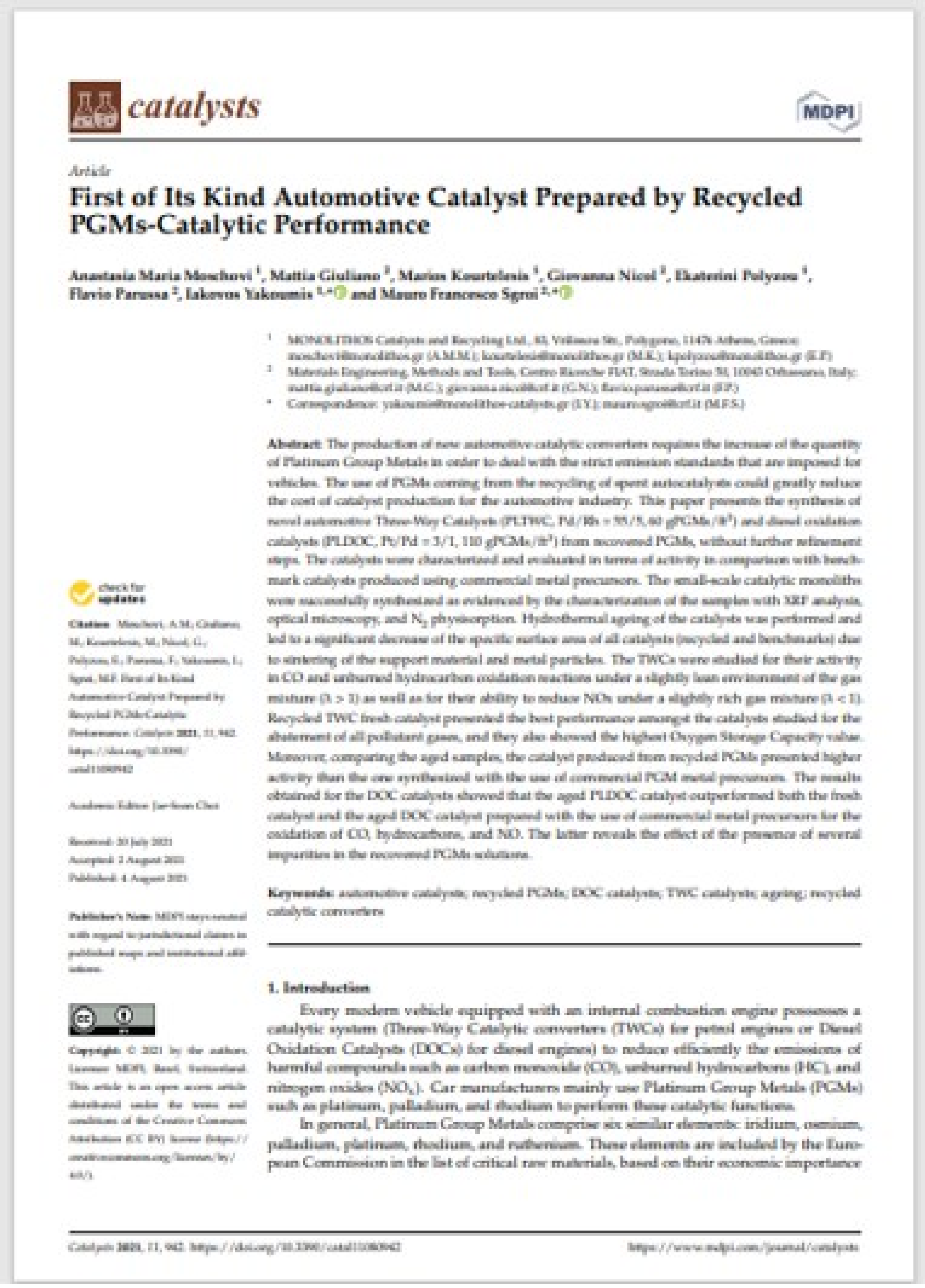
Annex 6

Moschovi A.M., Giuliano M., Kourtelesis M., Nichol G., Polyzou E., Parussa F., Yakoumis I.V., Sgroi M.F., 2021, "First of its kind automotive catalyst prepared by recycled/impure PGMs solutions", *Catalysts,* 2021, 11(8), 942; https://doi.org/10.3390/catal11080942



Article

First of Its Kind Automotive Catalyst Prepared by Recycled PGMs-Catalytic Performance

Anastasia Maria Moschovi [1], Mattia Giuliano [2], Marios Kourtelesis [1], Giovanna Nicol [2], Ekaterini Polyzou [1], Flavio Parussa [2], Iakovos Yakoumis [1,*] and Mauro Francesco Sgroi [2,*]

Abstract: The production of new automotive catalytic converters requires the increase of the quantity of Platinum Group Metals in order to deal with the strict emission standards that are imposed for vehicles. The use of PGMs coming from the recycling of spent autocatalysts could greatly reduce the cost of catalyst production for the automotive industry. This paper presents the synthesis of novel automotive Three-Way Catalysts (PLTWC, Pd/Rh = 95/5, 60 gPGMs/ft^3) and diesel oxidation catalysts (PLDOC, Pt/Pd = 3/1, 110 gPGMs/ft^3) from recovered PGMs, without further refinement steps. The catalysts were characterized and evaluated in terms of activity in comparison with benchmark catalysts produced using commercial metal precursors. The small-scale catalytic monoliths were successfully synthesized as evidenced by the characterization of the samples with XRF analysis, optical microscopy, and N_2 physisorption. Hydrothermal ageing of the catalysts was performed and led to a significant decrease of the specific surface area of all catalysts (recycled and benchmarks) due to sintering of the support material and metal particles. The TWCs were studied for their activity in CO and unburned hydrocarbon oxidation reactions under a slightly lean environment of the gas mixture ($\lambda > 1$) as well as for their ability to reduce NOx under a slightly rich gas mixture ($\lambda < 1$). Recycled TWC fresh catalyst presented the best performance amongst the catalysts studied for the abatement of all pollutant gases, and they also showed the highest Oxygen Storage Capacity value. Moreover, comparing the aged samples, the catalyst produced from recycled PGMs presented higher activity than the one synthesized with the use of commercial PGM metal precursors. The results obtained for the DOC catalysts showed that the aged PLDOC catalyst outperformed both the fresh catalyst and the aged DOC catalyst prepared with the use of commercial metal precursors for the oxidation of CO, hydrocarbons, and NO. The latter reveals the effect of the presence of several impurities in the recovered PGMs solutions.

Keywords: automotive catalysts; recycled PGMs; DOC catalysts; TWC catalysts; ageing; recycled catalytic converters

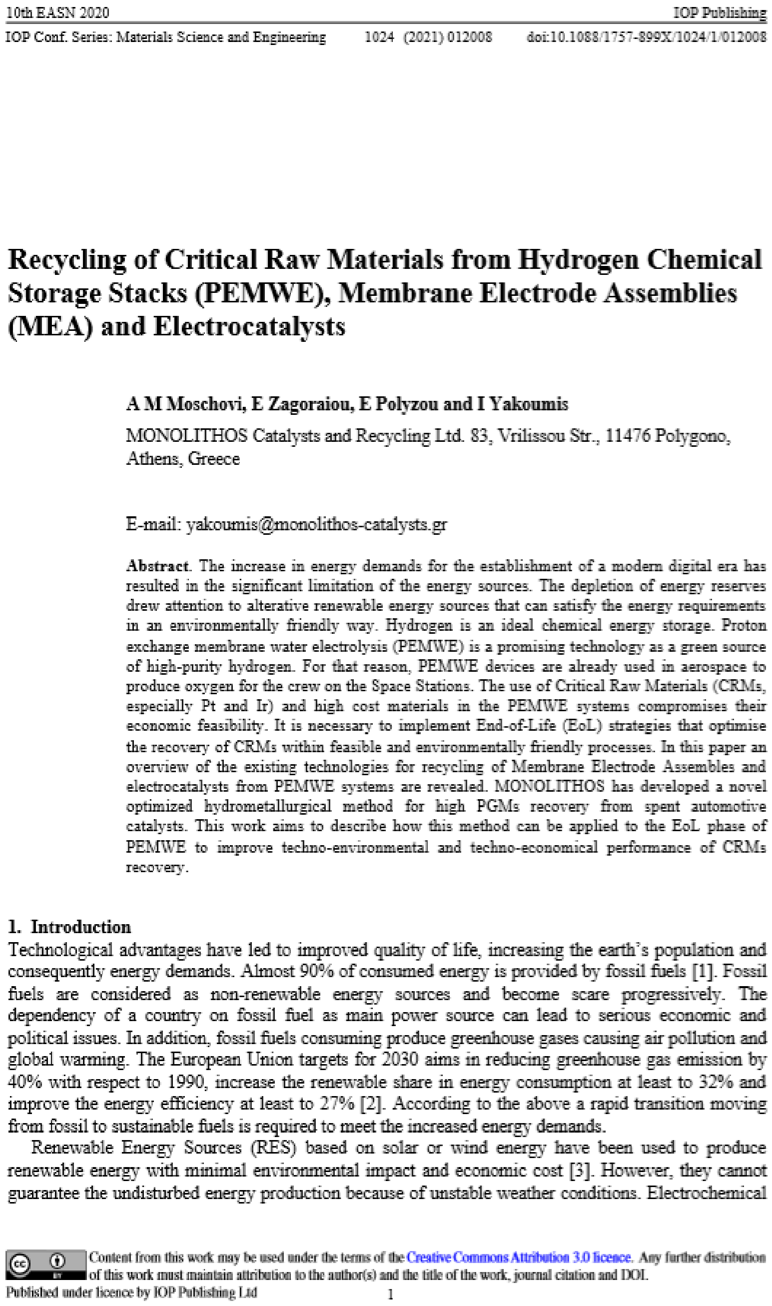
1. Introduction

Every modern vehicle equipped with an internal combustion engine possesses a catalytic system (Three-Way Catalytic converters (TWCs) for petrol engines or Diesel Oxidation Catalysts (DOCs) for diesel engines) to reduce efficiently the emissions of harmful compounds such as carbon monoxide (CO), unburned hydrocarbons (HC), and nitrogen oxides (NO_x). Car manufacturers mainly use Platinum Group Metals (PGMs) such as platinum, palladium, and rhodium to perform these catalytic functions.

In general, Platinum Group Metals comprise six similar elements: iridium, osmium, palladium, platinum, rhodium, and ruthenium. These elements are included by the European Commission in the list of critical raw materials, based on their economic importance

Annex 7

Moschovi A.M., Zagoraiou E., Polyzou E., Yakoumis I.V., 2021, "Recycling of Critical Raw Materials from Hydrogen Chemical Storage Stacks (PEMWE), Membrane Electrode Assemblies (MEA) and Electrocatalysts", *IOP Conf. Ser.: Mater. Sci. Eng.*, 1024 012008 (DOI: 10.1088/1757-899X/1024/1/012008)



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Recycling of Critical Raw Materials from Hydrogen Chemical Storage Stacks (PEMWE), Membrane Electrode Assemblies (MEA) and Electrocatalysts

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Abstract. The increase in energy demands for the establishment of a modern digital era has resulted in the significant limitation of the energy sources. The depletion of energy reserves drew attention to alterative renewable energy sources that can satisfy the energy requirements in an environmentally friendly way. Hydrogen is an ideal chemical energy storage. Proton exchange membrane water electrolysis (PEMWE) is a promising technology as a green source of high-purity hydrogen. For that reason, PEMWE devices are already used in aerospace to produce oxygen for the crew on the Space Stations. The use of Critical Raw Materials (CRMs, especially Pt and Ir) and high cost materials in the PEMWE systems compromises their economic feasibility. It is necessary to implement End-of-Life (EoL) strategies that optimise the recovery of CRMs within feasible and environmentally friendly processes. In this paper an overview of the existing technologies for recycling of Membrane Electrode Assembles and electrocatalysts from PEMWE systems are revealed. MONOLITHOS has developed a novel optimized hydrometallurgical method for high PGMs recovery from spent automotive catalysts. This work aims to describe how this method can be applied to the EoL phase of PEMWE to improve techno-environmental and techno-economical performance of CRMs recovery.

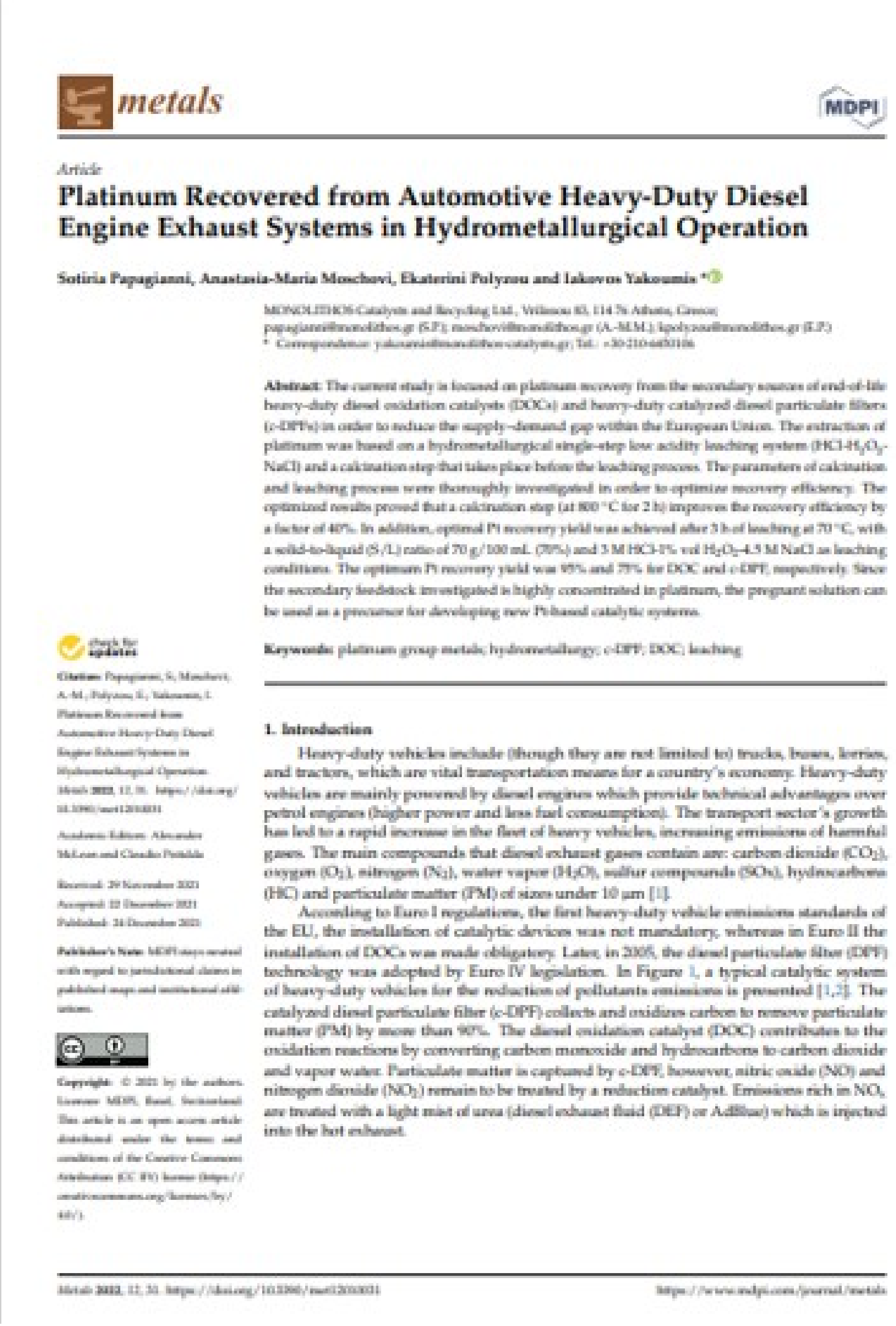
1. Introduction

Technological advantages have led to improved quality of life, increasing the earth's population and consequently energy demands. Almost 90% of consumed energy is provided by fossil fuels [1]. Fossil fuels are considered as non-renewable energy sources and become scare progressively. The dependency of a country on fossil fuel as main power source can lead to serious economic and political issues. In addition, fossil fuels consuming produce greenhouse gases causing air pollution and global warming. The European Union targets for 2030 aims in reducing greenhouse gas emission by 40% with respect to 1990, increase the renewable share in energy consumption at least to 32% and improve the energy efficiency at least to 27% [2]. According to the above a rapid transition moving from fossil to sustainable fuels is required to meet the increased energy demands.

Renewable Energy Sources (RES) based on solar or wind energy have been used to produce renewable energy with minimal environmental impact and economic cost [3]. However, they cannot guarantee the undisturbed energy production because of unstable weather conditions. Electrochemical

Annex 8

Papagianni S., Moschovi A.M., Polyzou E., Yakoumis I.V., 2021, “Platinum Recovery for Heavy Duty Vehicles Diesel Oxidation Catalysts and catalyzed Diesel Particulate Filters”, *Metals*, 2022, 12(1), 31; https://doi.org/10.3390/met12010031



metals

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Article

Platinum Recovered from Automotive Heavy-Duty Diesel Engine Exhaust Systems in Hydrometallurgical Operation

Sotiria Papagianni, Anastasia-Maria Moschovi, Ekaterini Polyzou and Iakovos Yakoumis *

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Abstract: The current study is focused on platinum recovery from the secondary sources of end-of-life heavy-duty diesel oxidation catalysts (DOCs) and heavy-duty catalyzed diesel particulate filters (c-DPFs) in order to reduce the supply–demand gap within the European Union. The extraction of platinum was based on a hydrometallurgical single-step low acidity leaching system (HCl-H_2O_2-NaCl) and a calcination step that takes place before the leaching process. The parameters of calcination and leaching process were thoroughly investigated in order to optimize recovery efficiency. The optimized results proved that a calcination step (at 800 °C for 2 h) improves the recovery efficiency by a factor of 40%. In addition, optimal Pt recovery yield was achieved after 3 h of leaching at 70 °C, with a solid-to-liquid (S/L) ratio of 70 g/100 mL (70%) and 3 M HCl-1% vol H_2O_2-4.5 M NaCl as leaching conditions. The optimum Pt recovery yield was 95% and 75% for DOC and c-DPF, respectively. Since the secondary feedstock investigated is highly concentrated in platinum, the pregnant solution can be used as a precursor for developing new Pt-based catalytic systems.

Keywords: platinum group metals; hydrometallurgy; c-DPF; DOC; leaching

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1. Introduction

Heavy-duty vehicles include (though they are not limited to) trucks, buses, lorries, and tractors, which are vital transportation means for a country’s economy. Heavy-duty vehicles are mainly powered by diesel engines which provide technical advantages over petrol engines (higher power and less fuel consumption). The transport sector’s growth has led to a rapid increase in the fleet of heavy vehicles, increasing emissions of harmful gases. The main compounds that diesel exhaust gases contain are: carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2), water vapor (H_2O), sulfur compounds (SO_x), hydrocarbons (HC) and particulate matter (PM) of sizes under 10 μm [1].

According to Euro I regulations, the first heavy-duty vehicle emissions standards of the EU, the installation of catalytic devices was not mandatory, whereas in Euro II the installation of DOCs was made obligatory. Later, in 2005, the diesel particulate filter (DPF) technology was adopted by Euro IV legislation. In Figure 1, a typical catalytic system of heavy-duty vehicles for the reduction of pollutants emissions is presented [1,2]. The catalyzed diesel particulate filter (c-DPF) collects and oxidizes carbon to remove particulate matter (PM) by more than 90%. The diesel oxidation catalyst (DOC) contributes to the oxidation reactions by converting carbon monoxide and hydrocarbons to carbon dioxide and vapor water. Particulate matter is captured by c-DPF, however, nitric oxide (NO) and nitrogen dioxide (NO_2) remain to be treated by a reduction catalyst. Emissions rich in NO_x are treated with a light mist of urea (diesel exhaust fluid (DEF) or AdBlue) which is injected into the hot exhaust.