



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

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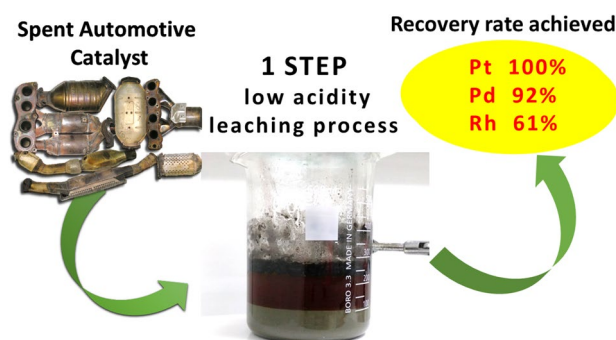
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Abstract

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 H₂O₂). 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

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Introduction

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 57% of PGM supply is used in catalytic converters. Processing 2 mg of spent automobile catalysts to recover PGMs can prevent the mining of 150 kg of their ores [1]. 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 plants 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 [2]. 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 [3].

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 hydrometallurgy 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.

The most common, traditional leaching solutions contain aqua regia and cyanide systems. Concerning aqua regia [4], leaching at temperatures above 70 °C is considered hazardous in plant scale, due to the aggressive nature of the solution and the decomposition of gaseous products (NO_x , Cl_2 , acid fumes). As for cyanide leaching, huge amount of waste is produced, and specialized equipment is required. It is inferred that the leaching process should be in line with green chemistry principles. State-of-the-art leaching systems, such as HCl, H_2SO_4 , NaCN, HNO_3 , combined with oxidizing agents and chloride salts, enhance the leaching efficiency, following greener approaches. Aberasturi et al. [5] claimed that 95% of PGMs have been recovered from spent catalysts, via dissolution in HCl (12 M), H_2SO_4 (18 M), H_2O_2 leaching system at 90 °C for 6 h, after thermal pre-treatment at 250 °C for 22 h. Mahmoud used acid agent 60% H_2SO_4 and reduction agent NaCl (0.1 M) achieving 95% Pt, 85%Rh, 85% Pd recoveries [6]. In this case, the noble metal extraction follows the order $\text{Pd} > \text{Pt} > \text{Rh}$ at low acid concentration ($< 50\% \text{H}_2\text{SO}_4$), but at higher acid concentrations the order was somewhat reversed $\text{Pt} > \text{Rh} > \text{Pd}$. Serife Sariog et al. [7] used milder reagents and less hazardous leaching conditions, where 98% Pd has been extracted from spent catalyst, using mixture of HCl (10%) and H_2O_2 (5%) at 90 °C for 3 h, and precipitation with NaBH_4 . Paiva et al. [8], recovered 84% of Pd, using a leaching solution of HCl (2 M), H_2O_2 (1 M) at 25 °C for 1 h, where the oxidizing agent H_2O_2 accelerated the dissolution after 10 min of reaction. The same leaching system is examined [9], giving significant recovery rates, namely Pt 88%, Pd 99%, Rh 77%, which seem to be improved with the partial substitution of HCl (5M) with NaClO (3%vol), obtaining lower acidity conditions without changing the dissolution efficiency. In one-step leaching reported by Harjanto et al., reduction pretreatment (350 °C, 3 h) was conducted, affecting the dissolution rate of Rh. An even more appropriate alteration of the leaching system HCl- H_2O_2 is conducted [10], where dissolution of Pt is maximized, after roasting pretreatment (700–900 °C, 10 °C/min), using HCl (10%), oxidizing agent H_2O_2 (1%), at 70 °C for 2 h. Further chloride leaching media examined conclude $\text{Cu}^{2+}/\text{HCl}$ [11], HCl/HNO_3 [12], HCl/HClO_4 [12], $\text{HCl}/\text{FeCl}_3/\text{NaCl}$ [13]. Additional sources of chlorines, namely NaClO, NaCl, AlCl_3 , CuCl_2 , improve the PGMs dissolution, tending to partially substitute high acidity reagents (HCl, aqua regia).

In this work, PGMs have been leached directly (no thermal or chemical pre-treatment is involved) under mild experimental conditions, by using low acidity reagents, namely the widely tested leaching system, $\text{HCl}-\text{H}_2\text{O}_2-\text{NaCl}$ at 70 °C for 2 h. As it can be deduced from the aforementioned

systems, 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 leached (70%) 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 brief kinetic evaluation of the leached catalyst sample has been conducted.

Experimental Procedure

Preparation of Homogenized Catalytic Converter Batch

In this work, a plethora of spent catalyst samples from a homogenized batch are processed and characterized. The prepared homogenized batch derived from 25 commercial spent catalytic converters (Table 1), producing a 20 kg batch of spent automotive catalyst powder. The method has been described in detail by Yakoumis et al. [14]. The final sample produced, about 20 kg of fine homogeneous powder from spent automotive catalytic converters enables authors 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 catalytic converter analytical samples (almost 1000 Euros per 100 g of sample). Furthermore, the use of a single homogenized batch is necessary, so that all dissolution/separation/recovery experiments followed are referring to a common sample of homogeneous monolith ceramic powder. The steps of spent catalyst mechanical pretreatment are represented in Fig. 1. The samples have been analyzed before and after leaching, determining their PGM concentrations. An external calibration has been obtained by MONOLITHOS Ltd to precisely determine the PGM concentration ranges, namely low concentrations (after leaching process) and higher concentrations (before leaching process).

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%), 1% v/v H_2O_2 (30%), NaCl (99.5%), deionized H_2O under magnetic stirring conditions (magnetic stirrer MSH-A analog up to 380 °C 1500 rpm, Witeg, Germany). 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 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 examined. Once leaching process has been completed, the solution is filtrated under vacuum, following the Buchner method, and several washes are followed. 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 confirming the confirm reproducibility of process and experiment conditions. X-ray fluorescence spectroscopy (XRF) measurements were recorded twice as well, in order to prevent significant variations.

Characterization Methods

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 its morphology and elemental analysis to be defined. These characterizations refer to before leaching catalyst sample. Scanning electron microscopy analysis (SEM) combined with energy-dispersive X-ray spectroscopy analysis (EDS) provides additional understanding of the surface material composition. The quantitative element determination, as well as semi-quantitative analysis are conducted in

Table 1 Models of 25 spent catalytic converters that were used for the batch formation

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		

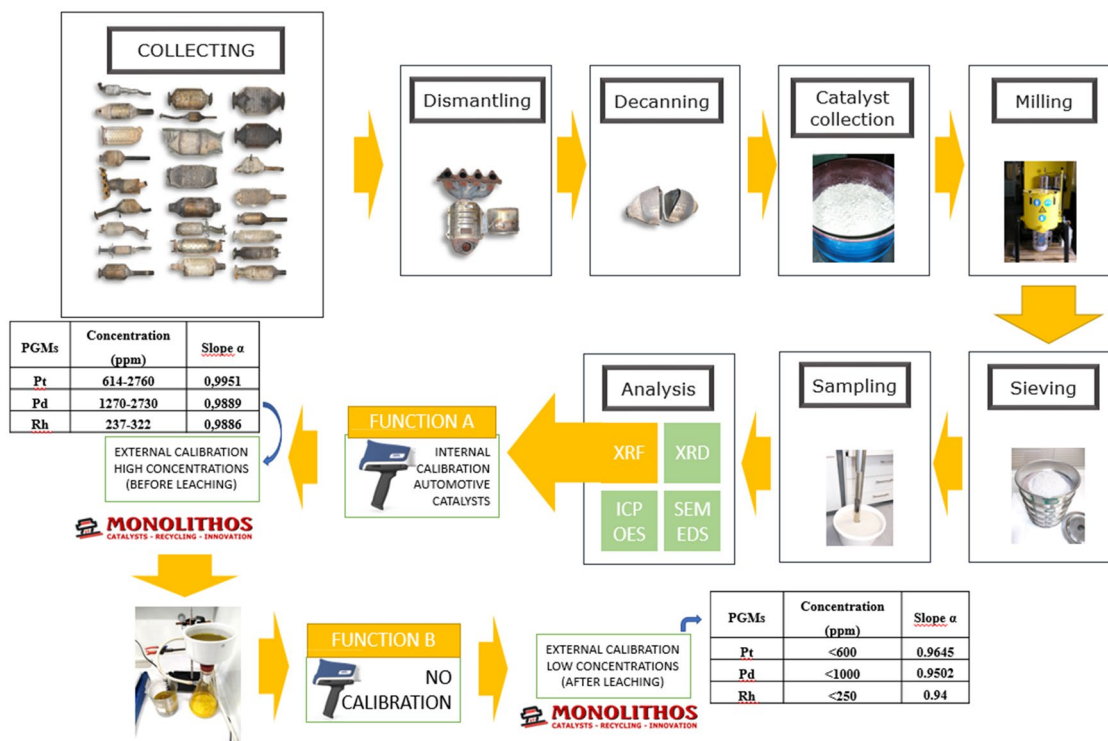


Fig. 1 Spent catalysts pre-process, leaching and analysis (Color figure online)

different sample areas under $\times 200$ magnification conditions. X-ray powder diffraction analysis (XRD) is used for the mineralogical characterization of sample. The crystallography of the PGMs, namely crystal lattice, crystallite size and shape, could be examined in case of significant PGM loading.

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 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, such as Spooren and Abo Atia [15] 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 before leaching sample and the after leaching one. Before any XRF measurement, the dried catalyst sample is milled into an analytical mill downsizing its' particle size,

then grounded, in order to obtain specific granulometry ($< 350 \mu\text{m}$) or pulverized, using an agate mortar. Under standard deviation lower than 5%, the concentration of the noble metals is 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 work, 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) in the laboratory scale we examined solid losses in the filter affecting the total mass of the solid residue.

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 anodic reactions of PGMs in $\text{HCl-H}_2\text{O}_2\text{-NaCl}$ systems ($E^\circ = -0.744 \text{ V}$ for Pt, $E^\circ = -0.620 \text{ V}$ for Pd, $E^\circ = -0.450 \text{ V}$ for Rh), it is

suggested that, compared to Rh complex, Pd and Pt chloro-complexes are more easily dissolved into the chloride media. It is expected that Rh should exhibit lower kinetics, due to its passivation layer and stereotactical structure.

Results

Leaching Parameters

In this one-step leaching method, noble metal oxidation and dissolution take place and PGM chloro-complexes are formed. In HCl media, the most stable species formed are PtCl_6^{2-} , PdCl_4^{2-} , RhCl_6^{3-} . The PGM-chloro-complexes get diluted in the acid chloride solution, by using H_2O_2 oxidizing agent. 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. [9], the addition of H_2O_2 by > 0.5 vol% increases the PGM dissolution, while the > 1 vol% addition does not result in a significant melioration. 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 vapors, 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.

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. [9]. Low leaching temperature minimizes energy consumption, leading to a cost-effective and environmentally friendly process.

Leaching Solution Acidity (HCl Molarity)

As illustrated in Table 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.

Balance of $C_{\text{NaCl}}/C_{\text{HCl}}$

As demonstrated in Table 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 chlorine anions introduced by different sources, chlorides salts mainly, 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 presented data of Table 3, 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.

Table 2 PGM leaching efficiencies obtained when using different HCl concentrations

S/L	HCl	H_2O_2	NaCl	Pt%	Pd%	Rh%
10	6 M	1% v/v	3 M	100	94.8	59.8
10	4.5 M	1% v/v	3 M	100	94	53.8

Table 3 PGM leaching efficiencies obtained when using different NaCl-HCl concentrations

S/L	HCl	H_2O_2	NaCl	Pt%	Pd%	Rh%
10	6 M	1% v/v	3 M	100	94.8	59.8
10	4.5 M	1% v/v	3 M	100	94	53.8
10	4.5 M	1% v/v	4.5 M	100	94	46
10	3 M	1% v/v	6 M	100	93	50

H₂O₂ Concentration

The oxidizing agent H₂O₂ is proved to ameliorate the leaching effectiveness, at a percentage of > 0.5 vol% [9]. 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% H₂O₂ has also been conducted (Table 4), ensuring that more than 1% v/v H₂O₂ affects reversibly the recovery.

Effect of Other Cl⁻ Sources

The effect of the anions of chloride salts other than NaCl, namely AlCl₃ and CuCl₂, has been studied and demonstrated in Table 5. In case of AlCl₃, 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 AlCl₃ into leaching media caused highly aggressive exothermal reaction, where the temperature was hardly controlled, even with the use of water bath.

In case of CuCl₂ salt, which introduces into the solution twice the number of Cl ions but less compared to AlCl₃, lower recovery values for Rh have been observed, with respect to AlCl₃ salt. Moreover, the leachate of CuCl₂ (4.5 M), HCl (4.5 M), 1% v/v H₂O₂ solution resulted in unstable dispersion, forming crust on the solutions' surface and aggregation. The cause for this destabilization might refer to CuCl₂ 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 has been further investigated.

Table 4 PGM leaching efficiencies obtained when using different H₂O₂ concentrations

S/L	HCl	H ₂ O ₂	NaCl	Pt%	Pd%	Rh%
10	6 M	1% v/v	3 M	100	93.7	60.9
10	6 M	2% v/v	3 M	87	93	47

Table 5 PGM leaching efficiencies obtained when using different chloride source leaching

S/L	HCl	H ₂ O ₂	NaCl	CuCl ₂	AlCl ₃	Pt	Pd	Rh
10	6 M	1% v/v	–	–	3 M	100%	94%	63%
10	6 M	1% v/v	–	3 M	–	100%	94%	53%
10	6 M	1% v/v	3 M	–	–	100%	94%	60%

Table 6 PGM leaching efficiencies obtained when using different S/L ratio

S/L	HCl	H ₂ O ₂	NaCl	Pt%	Pd%	Rh%
10	4.5 M	1% v/v	3 M	100	94	53.8
50	4.5 M	1% v/v	3 M	100	94	57
70	4.5 M	1% v/v	3 M	100	93	50
80	4.5 M	1% v/v	3 M	56	93	26.4

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, when S/L > 70% the solid cannot react properly with the leaching solvent. (Table 6).

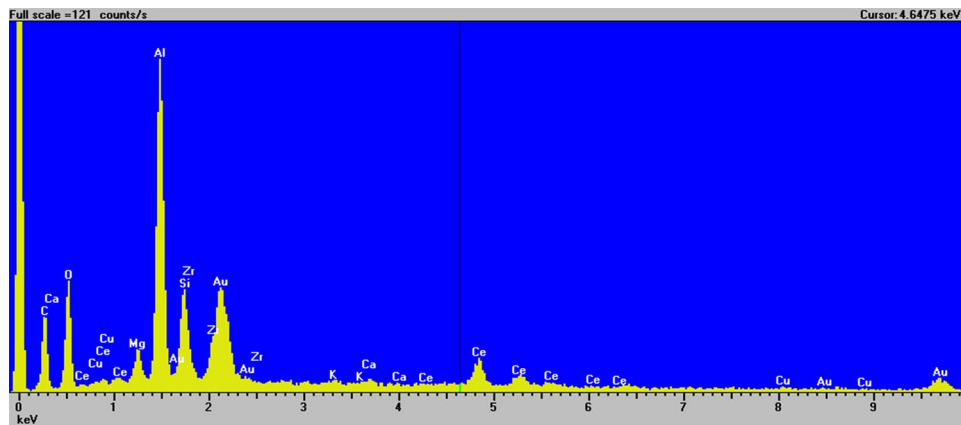
Process Optimization

According to the Table 6, the highest S/L ratio achieved is 70%, resulting in promising leaching yields for Pt (100%), Pd (93%) and Rh (50%). As is can be seen in Table 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 revealed, 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 H₂O₂ at 70 °C for 2 h gives promising recovery yields, following green chemistry rules. Reagents should be added in a specific order, namely

Table 7 Leaching system optimization

S/L	HCl	H ₂ O ₂	NaCl	Pt%	Pd%	Rh%
70%	4.5 M	1% v/v	3 M	100	93	50
70%	4.5 M	1% v/v	4.5 M	100	93	56
70%	3 M	1% v/v	4.5 M	100	92	61

Fig. 2 Energy dispersive X-ray spectroscopy analysis (EDS) of spent catalyst sample (Color figure online)

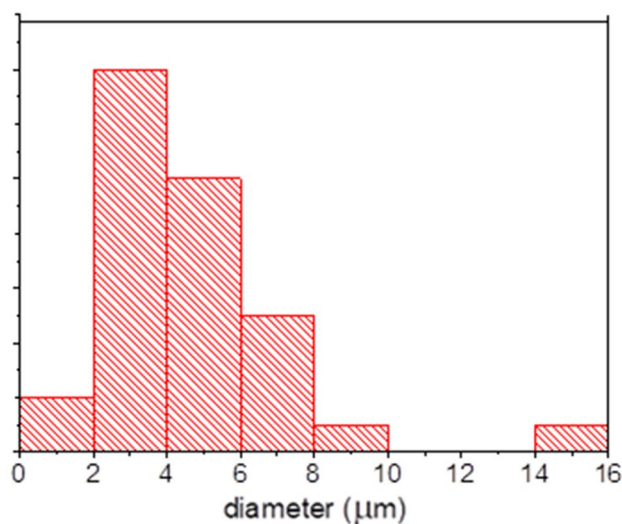
catalyst powder, HCl, 1% v/v H₂O₂, NaCl and deionized water. As for the sample preparation before the leaching process, fine grinding affects the total recovery rate by increasing the leaching efficiency.

Compared to previous studies, the low concentration of HCl achieved minimizes the production of Cl₂ 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, more washing is required to remove chlorine anions from the leaching residue. Thus, chloride sources need to be minimized in an adequate for the leaching percentage.

Morphological Characterization of the Catalyst Sample

As it can be seen from 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%) (Fig. 2). This result is expected, as the sample derived from spent automotive catalyst, where cordierite monolith contains Mg, Al, Si, O, with the formula of (Mg,Fe)₂Al₃(Si₅AlO₁₈) to (Fe,Mg)₂Al₃(Si₅AlO₁₈). Furthermore, the cordierite has been impregnated with alumina, or silica or ceria washcoat.

SEM image (SE, magnification of × 5000, × 10,000) illustrates the surface topography of the spent catalyst sample, that derives from mixed monoliths of distinct PGMs concentrations. The structure analysis has been performed using Image J program. According to the

**Fig. 3** Histogram of particle size distribution (Color figure online)

histogram drawn by OriginLab (Fig. 3), a slightly heterogeneous 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 might be distinguished, which have nano-dimensions (× 10,000 magnification). (Fig. 4).

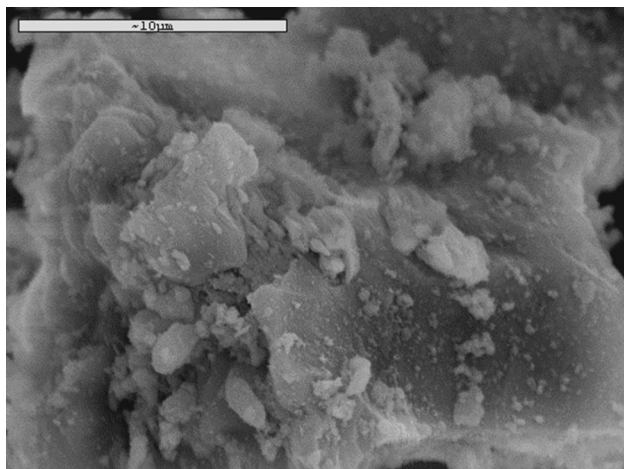


Fig. 4 Small PGMs prills on ceramic grain ($\times 10,000$)

According to the XRD pattern (Fig. 5), the main peaks correspond to indialite (syn- $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) and cerianite (Ce, syn- CeO_2). Moreover, crystal phase of potassium magnesium aluminum silicate ($\text{KMg}_2\text{AlSi}_4\text{O}_{12}$) 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, because of 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, can not be detected.

Kinetic Approach

A brief kinetic investigation about the optimized leaching system, namely 3 M HCl—4.5 M NaCl—1% v/v H_2O_2 at 70°C , is represented (Fig. 6). According to Fig. 6, 2 h leaching duration is appropriate for the PGMs dissolution, as concentrations do not further increase (3-h leaching period). Concerning the findings, PGMs chlorides formation accelerates from 0 to 0.5 h, while after 0.5 h there is a stabilization period. Leaching time 0.5 h is inadequate for the PGMs dissolution, especially in case of Rh. In case of Pd, after 0.5 h a plateau is observed, where Pd total dissolution occurs. In case of Pt, fast kinetics can be seen between 0.5 and 1 h, while Pt plateau appears between 1 and 2 h. Both Pt and Pd reach equilibrium values up to 2 h, while Rh dissolution decreases after around 2 h of leaching. A further investigation should be held, about the Rh relation to the catalyst matrix system, in order to fully understand Rh kinetic chloro-formation. 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, due to its' stereo tactical structure and passivation layer formed in acid conditions.

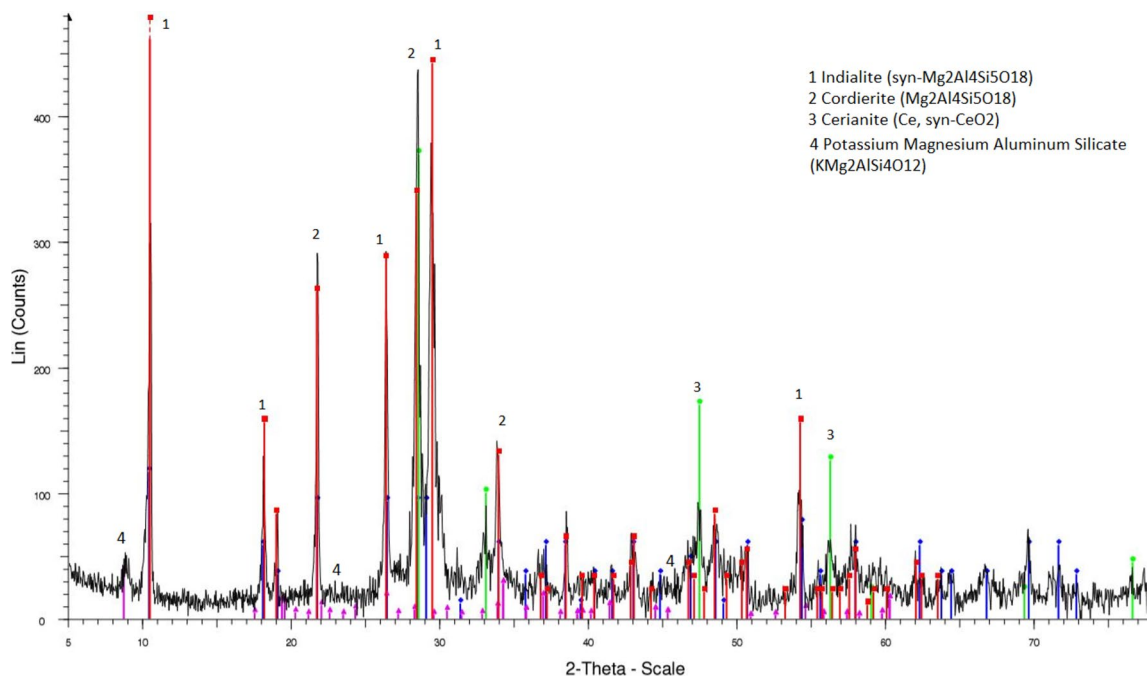


Fig. 5 X-ray powder diffraction pattern for spent catalyst batch samples (Color figure online)

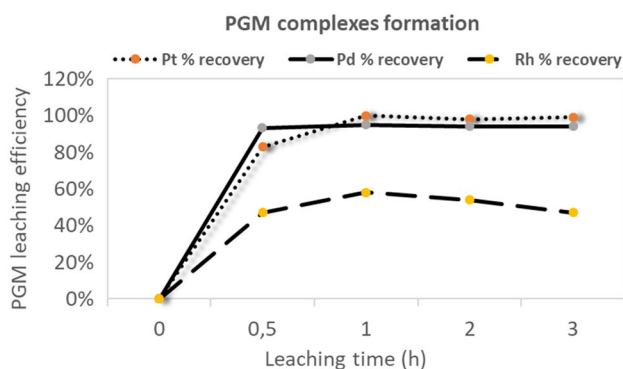


Fig. 6 PGMs kinetic behavior for 0.5–3 h leaching time (Color figure online)

Discussion

The present leaching method, is based on the Harjanto et al. [9] study, focusing on industrialization and further optimization. Harjanto et al. claimed, that promising leaching yields, namely 95.5%, 100% and 85.6% for Pt, Pd and Rh, respectively, have been received via HCl–H₂O₂–NaClO system. Harjanto’s one-step leaching refers to one leaching solution, which consists of HCl, H₂O₂ and partial substitution of HCl by NaClO. Nevertheless, hydrogen treatment (350 °C, 3 h) is included, affecting the dissolution rate of Rh (77%). In the present leaching system, no pre-concentration or reduction stage has been preceded. It is suggested that the described leaching process, will reduce process cost (OPEX), as less energy is consumed, and green reagents in low-acidity environment are used. Moreover, in terms of industrialization, high S/L ratio assists in smaller industrial installations affecting the investment cost (CAPEX). However, leachates’ waste management should be considered referring to the cost efficiency of this method. As for environmental aspect, milder acidity reagents may prevent waste generation in a significant extent.

In terms of catalyst’s samples preparation, the requirement of a large homogenized batch has been fulfilled. Aiming to receive a large batch of PGMs secondary resource, 25 commercial spent catalysts have been collected, sorted, preprocessed, milled, and analyzed for their noble metal content. Moreover, the spent catalyst batch has been characterized using XRD, SEM_EDS and XRF techniques. Almost 20 catalyst samples were used, which derived from the catalysts batch, and have been leached, following at least one repetition for each experiment to confirm recovery yields. The leaching efficiency of PGMs has been verified by X-ray fluorescence analysis (XRF), providing accurate, fast, non-destructive, repeatable measurements, without necessity of chemical preparation. The use of X-ray fluorescence spectroscopy enables the precisely elemental and quantitative analysis of the catalyst sample

batch, as the same sample is examined both before and after leaching process.

The accuracy of XRF measurements is further improved by external calibration mode, by MONOLITHOS Ltd. 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 small variations may affect the leaching procedure. In this respect, external calibration using two different elemental analysis techniques has been performed, comparing values received by XRF and Inductively coupled plasma—optical emission spectrometry (ICP-OES). Referring to the samples before dissolution, calibration curve covers PGMs concentration ranges of 614–2760 ppm, 1270–2730 ppm, 237–322 ppm for Pt, Pd, Rh respectively. Another calibration has been obtained for lower PGM concentrations, namely 50–600 ppm, 50–1000 ppm, 50–250 ppm for Pt, Pd, Rh, respectively, referring to solid residues received after leaching.

Conclusion

In this work, an optimized single-step leaching process for PGMs has been developed, following the well-tested HCl–H₂O₂–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 H₂O₂, 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 lead 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.

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