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Hydrometallurgical recovery of platinum group metals from spent automotive converters

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Abstract: This work presents studies on the recovery of platinum group metals (PGM), especially platinum and rhodium, from spent automotive converters using hydrometallurgical techniques such as leaching and liquid-liquid extraction. The XRD analysis confirmed the presence of indialite – the high-temperature hexagonal form of cordierite (the main catalyst building material) in the solid samples. The influence of time and temperature on the leaching of PGM from spent automotive converters was investigated. The largest amounts of Pt(IV) and Rh(III) were leached with freshly prepared aqua regia and a mixture of HCl, H₂SO₄, and H₂O₂. Further, liquid-liquid extraction with quaternary phosphonium ionic liquid (Cyphos IL 101) was applied to recover PGM from the leach solutions (after leaching with a mixture of HCl, H₂SO₄, and H₂O₂) and to separate Pt(IV) from Rh(III).

Keywords: leaching, platinum group metals (PGM), recovery, spent automotive converters, liquid-liquid extraction, ionic liquid, Cyphos IL 101

1. Introduction

The rapidly growing demand for metals is a consequence of very fast technological development, particularly in the field of electronics and energy sources and storage. Modern technologies need a great number of elements in increasing quantities, e.g. lithium and cobalt for Li-ion batteries, rare earth elements (REE) for petrochemical catalysts, new generation batteries, wind turbines, or platinum group metals (PGMs) for automotive converters (Rzelewska and Regel-Rosocka, 2018; Supanchaiyamat and Hunt, 2019). As a result of the growing demand, a significant increase in PGM prices (except platinum price) has been noted for the last ten years until the COVID-19 epidemic (Table 1). The recent dramatic decrease in PGM prices (except ruthenium price) is caused by the global crisis due to COVID-19. However, currently, a high increase in rhodium price is observed, because of the rapidly growing number of produced cars. Depletion of natural metal resources and the increasing environmental requirements encourage scientists and industry to look for opportunities to reuse and recycle waste streams, e.g. end-of-life consumer and industrial products, closing the loop of the products lifecycle (a waste-to-resources concept of the circular economy) (Gao et al., 2018; European Commission, 2020).

In circular economy spent automotive converters (catalysts) are considered an important and concentrated (compared to natural ores) resource of PGMs. Ceramic catalysts are made of ceramic support covered with an alumina intermediate layer and an active substance (specific catalyst), i.e. noble metals, mainly Pt, Pd, and Rh (Saternus and Fornalczyk, 2009; Wołowicz, 2013, Saternus et al., 2020). Hydrometallurgical operations, such as leaching from solid materials or extraction from pregnant leach solutions, have been proposed recently for the recovery of metal ions, PGM particularly, from spent catalysts. These operations let concentrate PGMs or precipitate their oxides and, thus, recycle these valuable metals. Efficient leaching of PGMs needs oxidative conditions, thus hydrogen peroxide or aqua regia are applied as the leaching solutions (Jimenez de Aberasturi et al., 2011; Fornalczyk et al., 2016; Lu et al., 2020). Some authors have proposed the use of copper salt as an oxidizing agent to recover

Table 1. Average prices of PGM in 2010, 2015 and 2020 (1 oz = 28.35 g) (bankier.pl; infomine.com; www.platinum.matthey.com)

Year	Price \$/oz			
	Pt(IV)	Pd(II)	Rh(III)	Ru(III)
2010	1512	430	2500	185
2015	1175	810	1180	56
2020 before COVID-19	982	2540	11146	250
March 2020 after COVID-19	771	2171	10625	250
July 2020 after COVID-19	871	2064	8600	270
October 2020 after COVID-19	889	2367	13700	270

palladium and rhodium from spent catalysts (Nogueira et al., 2014). After leaching, the dissolved metals can be selectively recovered from the mixture by liquid-liquid extraction. Various compounds have been proposed for PGM extraction from, mainly, model solutions (Ortet and Paiva, 2015; Costa et al., 2016). Our team has proposed a scheme of selective extraction and stripping of Pd(II), Pt(IV), Ru(III), and Rh(III) from model chloride solutions with phosphonium ionic liquids as extractants (Rzelewska-Piekut and Regel-Rosocka, 2019). Most of the presented systems are model or cover only one operation, i.e. leaching or extraction. Thus, in this article, we investigate leaching of noble and non-noble metals from spent automotive catalysts with acids and an inorganic salt as oxidizing agents and combine it with liquid-liquid extraction of the selected metal ions with phosphonium ionic liquid (Cyphos IL 101). The results of the investigation can be the basis for the development of a PGM recovery process in the future.

2. Materials and methods

2.1. Reagents and solutions

Spent automotive catalysts were provided by a Polish waste treating company. Generally, a spent automotive catalyst is made of ceramic support (Al_2O_3), which is covered with an active layer containing Pt or/and Pd and Rh. XRD analysis was used to determine the composition of the catalysts studied. A picture of the spent converter before and after grinding is presented in Fig. 1. The particle size of the powdered catalyst after sieving used for leaching was $<63 \mu\text{m}$.

Leaching solutions were prepared by mixing different inorganic acids (36% HCl, 98% H_2SO_4 , 65% HNO_3 , Chempur, Poland) and 30 wt% H_2O_2 (Avantor, Poland) and by the dissolution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Avantor, Poland) or $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Chempur, Poland) in 8 M HCl with or without 30 wt% H_2O_2 . The composition of the leaching solutions is presented in Table 2.

It is known that 36% HCl solution cannot leach PGM. HCl provides an acidic reaction medium and is a Cl^- donor but an oxidant is also needed. As PGMs are very resistant chemically, they need strongly

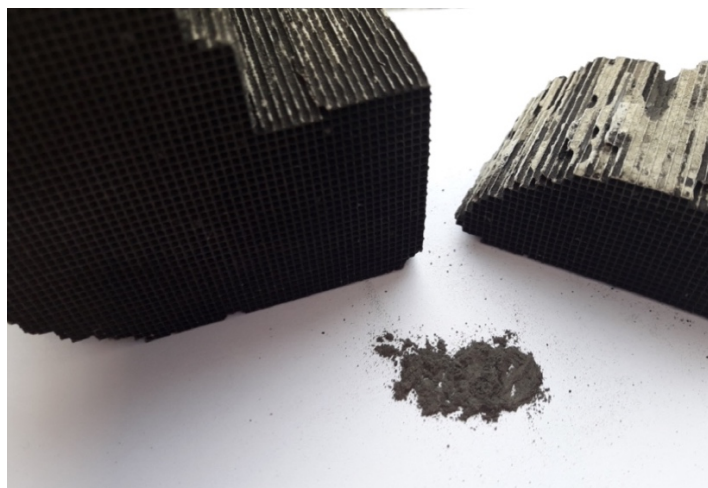


Fig. 1. A spent automotive converter before and after grinding

Table 2. Composition of the leaching solutions applied in the research

No.	Concentrations of the leaching solution components, M					
	HCl, cm ³	98% H ₂ SO ₄ , cm ³	65% HNO ₃ , cm ³	30% H ₂ O ₂ , cm ³	Cu(II), g/dm ³	Al(III), g/dm ³
1	40 cm ³ of 36% HCl	2.5	-	2.5	-	-
2	40 cm ³ of 36% HCl	-	2.5	2.5	-	-
3	33.75 cm ³ of 36% HCl	-	11.25	-	-	-
4	45 cm ³ of 8 M HCl	-	-	-	5	-
5	45 cm ³ of 8 M HCl	-	-	-	10	-
6	43 cm ³ of 8 M HCl	-	-	2	10	-
7	45 cm ³ of 8 M HCl	-	-	-	-	5
8	45 cm ³ of 8 M HCl	-	-	-	-	10
9	43 cm ³ of 8 M HCl	-	-	2	-	10

oxidative conditions to be dissolved. Thus, based on this knowledge and the literature (Jimenez de Aberasturi et al., 2011), a small amount of HNO₃ (in solution 1) or H₂SO₄ (in solution 2) with the addition of an oxidant H₂O₂ were added into the leaching solutions. Each of these solutions can be an alternative to aqua regia because is less corrosive than HCl:HNO₃ mixture.

An extractant (ionic liquid), Cyphos IL 101 (trihexyl(tetradecyl)phosphonium chloride), was supplied by Cytec Industries Inc. (USA) and diluted in toluene (Avantor, Poland) to form a 0.005 M solution of Cyphos IL 101.

2.2. Leaching and extraction procedure

0.5 g of the ground catalyst was placed in a reactor and then 45 cm³ of a leaching solution (Table 2) was added to keep the liquid to solid (L/S) ratio equal to 90. The leaching temperature was 70±2°C and the agitator rotation frequency was 300 rpm. Leaching was carried out for 180 minutes and 1 cm³ sample was taken after 10, 15, 30, 45, 60, 120, 180 min. The phases were separated after leaching and then the liquid phase was diluted two times to prepare samples for the determination of metal ions.

One-step extraction of metal ions from the leaching solutions was carried out in a typical way: 10 or 20 cm³ of the diluted leaching solution was mechanically shaken at 22±2°C for 20 min with 10 cm³ of an organic phase containing 0.005 M Cyphos IL 101 in glass separatory funnels. The volume ratio of the aqueous and organic phases (A/O) was equal to 1 or 2. The efficiency of metal ion extraction (*E*) was defined as a percentage extraction:

$$E = \frac{C_{\text{org}} \cdot V_{\text{org}}}{C_{\text{aq},0} \cdot V_{\text{aq},0}} \cdot 100\% \quad (1)$$

where *C*_{aq,0} is the initial concentration of metal ions in the aqueous feed (leach solution), *C*_{org} is the concentration of metal ions in the organic phase after extraction (calculated from mass balance as *C*_{org} = (*C*_{aq,0} - *C*_{aq}) · $\frac{V_{\text{aq}}}{V_{\text{org}}}$) of metal ions in the aqueous phase), *C*_{aq} means the concentration of metal ions in the aqueous phase after extraction, *V*_{org} and *V*_{aq} are volumes of the organic and the aqueous phases, respectively.

Stripping of metal ions from the loaded organic phases after extraction was carried out with 1 M HNO₃ in glass separatory funnels. The volume ratio of the organic and aqueous phases (O/A) was 1. The efficiency of metal ion stripping (*S*) was defined as a percentage stripping:

$$S = \frac{C_{\text{aq},S} \cdot V_{\text{aq},S}}{C_{\text{org}} \cdot V_{\text{org}}} \cdot 100\% \quad (2)$$

where *C*_{aq,S} is the concentration of metal ions in aqueous phase after stripping and *V*_{aq,S} is the volume of the stripping phase.

2.3. Apparatus

The composition of the spent catalyst was determined using X-ray powder diffraction (XRD) analysis. The diffraction patterns were performed using a TUR-M-62 horizontal diffractometer with goniometer

type HZG-3. Diffraction patterns of investigated samples were obtained using standard software. The measurements were taken using Cu-K α radiation ($\lambda=1.5418 \text{ \AA}$) with nickel filtering. The following parameters were applied: voltage 30 kV, anodic current 25 mA, angle range 2Θ : 3-80°, counting step (2Θ): 0.04°, counting time: 3 s, with remaining standard parameters. The tests were carried out at ambient temperature.

Identification analysis of the tested compounds was carried out using the XRAYAN program (Marciniak et al., 2014). This program is connected to the databases PDF-4+ ICDD (International Centre for Diffraction Data, USA).

Metal ion concentrations in the aqueous solutions were measured by atomic absorption spectrometer (ContrAA 300, Analytic Jena, Germany) at the following wavelengths: 265.9, 343.5, 248.3, 213.9, 285.2, 240.7, 232.0, and 271.0 nm for Pt(IV), Rh(III), Fe(III), Zn(II), Mg(II), Co(II), Ni(II) and Pb(II), respectively.

Standard deviations calculated for three repetitions of each step of the process did not exceed 5% for leaching and 8% for extraction.

3. Results and discussion

3.1. X-ray diffraction analysis of the spent automotive converter

The exact composition of the spent automotive converter provided by the company was unknown. X-ray diffraction was used for the identification of the composition of a powdered catalyst before and after leaching. The XRD diffractogram of the spent catalyst before leaching is presented in Fig. 2.

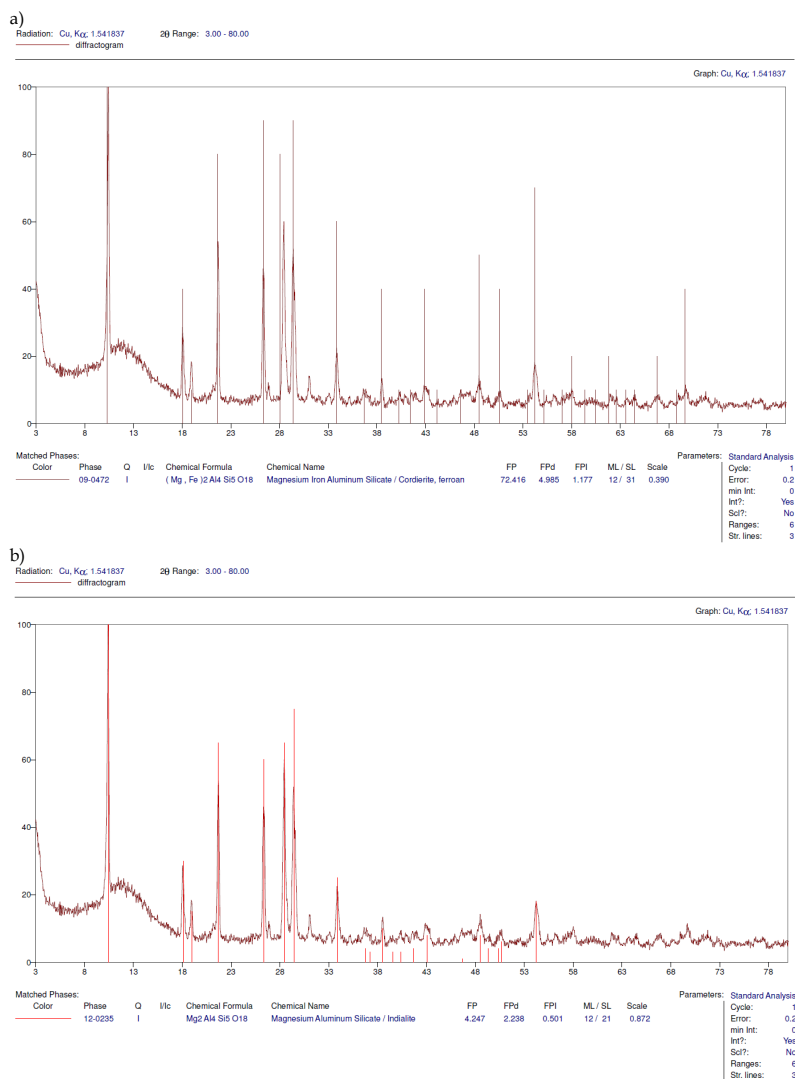


Fig. 2. X-ray diffraction patterns of the spent automotive converter confirming the presence of (a) cordierite and (b) indialite in the investigated sample (vertical lines are data from the database PDF-4+ICDD)

The literature (Saternus and Fornalczyk, 2009; Jimenez de Aberasturi et al., 2011; Rzelewska and Regel-Rosocka, 2018) indicates cordierite (magnesium aluminosilicate, 3–35% MgO, 32–35% Al₂O₃, 45–51% SiO₂ and 2–12% Fe₂O₃) as the main component of the automotive catalyst support (Serryet al., 2011). Cordierite has an orthorhombic structure and occurs in a number of structural states that are related to changes between (Si₅Al) and Al₃(Mg,Fe²⁺)₂ ions (Sampathkumar et al., 1995). The identification analysis shows that the presence of cordierite in the sample is confirmed (Fig. 2 a). However, the best fit was obtained for indialite (Fig. 2 b), which is the high-temperature hexagonal form of α -cordierite (Sampathkumar et al., 1995; Sorin et al., 2013). Structural studies show that these two minerals have a similar chemical composition. For this reason, a mixture of both minerals is present in the tested sample. Additionally, the Si/Al ratio equal to 1.25, both in cordierite and indialite, suggests that the support is made of X-type zeolite (Si/Al in the range from 1 to 1.5 represents X-type zeolite (Bahaloo-Horeh and Mousavi, 2020)).

The X-ray patterns of the catalyst sample before and after leaching are compared in Fig. A1 (in Appendix). These X-ray images are similar but the diffraction maxima differ slightly in intensity. This may be due to the loss of catalyst mass during leaching, associated with the extraction of various chemical compounds from the solid phase to the liquid phase.

In research works on the composition of automotive catalysts (Jiang et al., 2013; Hofmann et al., 2015) X-ray maxima at 2Θ approximately 40 and 46° are reported to be characteristic for platinum crystalline structure, while at 2Θ 34.5 for PdO. In the X-ray diffraction patterns, these maxima do not occur, which could be associated with the absence of platinum and palladium in crystalline form (PGM determination impossible in the case of the catalyst before leaching) or with the presence of these structures in trace amounts. Low loading of PGM on the catalyst monolith, particularly compared to the support amount, and the absence of their patterns in XRD analysis has been reported by some researchers (Hofmann et al., 2015; Bahaloo-Horeh and Mousavi, 2020). On the other hand, the lack of diffraction reflections from platinum metals after leaching can also be explained by the depletion of the catalyst.

3.2. Leaching of metal ions from spent automotive converters

3.2.1. The influence of leaching time

At first, the influence of time on the leaching of non-precious metal ions (Fe(III), Mg(II), and Zn(II)) from spent automotive catalysts was investigated and the results for leaching with four selected solutions are shown in Fig. 3. Figures for other leaching solutions are included in the Appendix (Fig. A2).

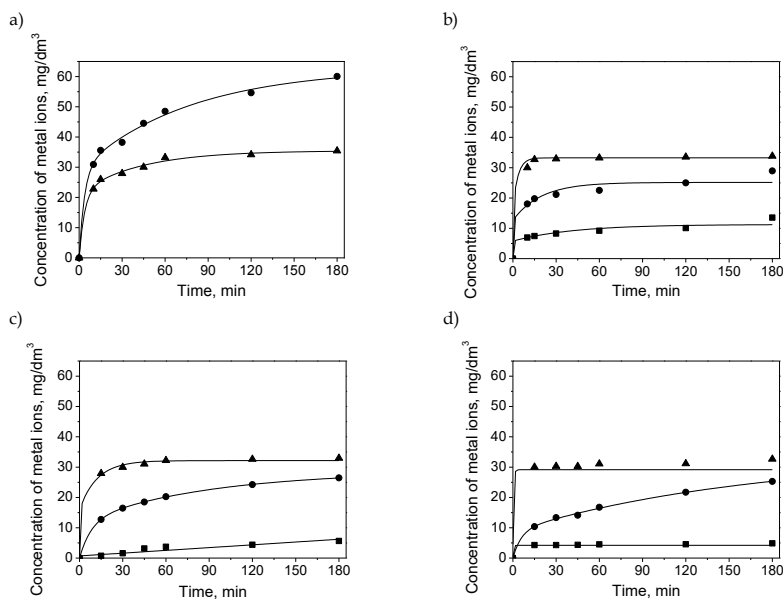


Fig. 3. Influence of time on leaching of non-precious metal ions from spent automotive converters (■) Fe(III), (●) Mg(II), (▲) Zn(II) (temperature: $70 \pm 2^\circ\text{C}$, leaching solutions: a) solution 6, b) solution 9, c) solution 3, d) solution 1

Leaching for longer than 30 min did not affect changes in the leaching system (Fig. 3 b and d). Regardless of the type of the leaching solution, the amount of Zn(II) in the solution after leaching is in the range of 30-35 mg/dm³ (Fig. 3 a-d). After 180 minutes the leaching solutions without Cu(II) addition contain about 25 mg/dm³ of the leached Mg(II) (Fig. 3 b-d). It is noteworthy that leaching with a mixture of 0.06 M CuCl₂, 8 M HCl, and 0.44 M H₂O₂ (solution 6, Fig. 3 a) leads to two-fold higher Mg(II) concentration than in other tested solutions. The amount of Fe(III) in the solutions after leaching is less than 10 mg/dm³ (Fig. 3 b-d) or even Fe(III) does not occur (Fig. 3 a).

3.2.2. The influence of temperature

For two selected solutions: aqua regia (solution 3, Fig. 3 c) and the mixture of 40 cm³ HCl, 2.5 cm³ H₂SO₄, and 2.5 cm³ H₂O₂ (solution 1, Fig. 3 d) leaching of non-precious metals was investigated at 40°C and the results are shown in Fig. 4.

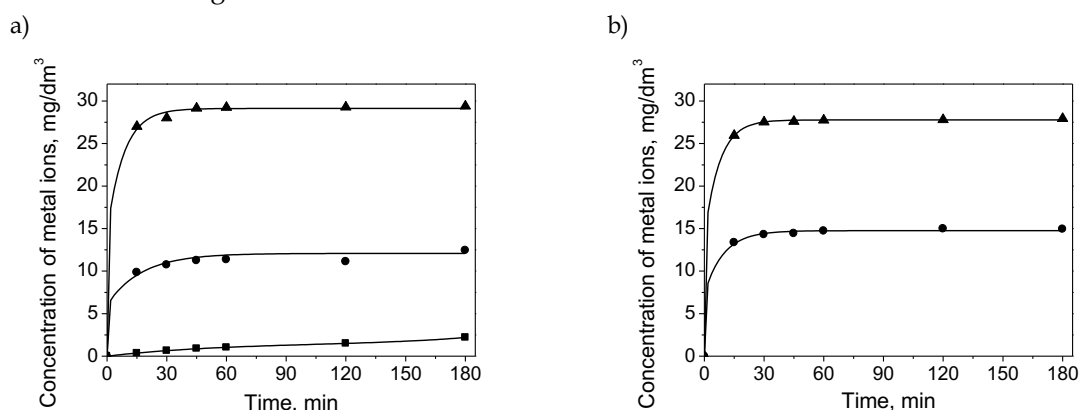


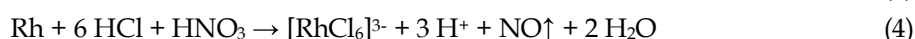
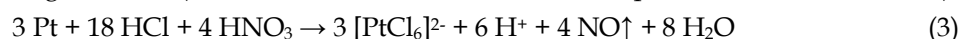
Fig. 4. Influence of time on leaching of metal ions from spent automotive converters (■) Fe(III), (●) Mg(II), (▲) Zn(II) (temperature: 40±2°C, leaching solutions: a) solution 3, b) solution 1

A comparison of two temperatures of leaching (40 and 70°C) indicates that leaching at the lower temperature (40°C) causes the inhibition of Fe(III) dissolution (Fig. 4). However, even at 70°C, only a small amount of iron(III) is leached (Fig. 3. b-d). Moreover, the elevated temperature does not significantly affect the amount of Zn(II) leached, the final concentration achieves 25-30 mg/dm³ in all the leaching systems (Figs. 3 and 4). On the contrary, Mg(II) leaching increases from 10-15 to 25 mg/dm³ at 40 and 70°C, respectively. However, Pt(IV) and Rh(III) in the solutions after leaching at 40°C were not observed. After 180 minutes of leaching at 70°C, some amounts of Pt(IV) and Rh(III) were obtained in the leaching solutions (as shown in Fig. 5).

3.2.3. The final compositions of the leaching solutions

As a summary of the leaching investigation, the final compositions of the leaching solutions (after 180 minutes) are presented in Fig. 5.

PGM leaching is difficult because of the high redox potential values of these noble metals, e.g. 1.188 and 0.987 V for Pt(IV) and Pd(II), respectively (Nogueira et al., 2014). This difficulty of PGM dissolution is visible in the results presented in Fig. 5. The biggest amounts of PGM ions, i.e. 20.84 mg/dm³ Pt(IV) and 5.45 mg/dm³ Rh(III); Fig. 5 a, are leached with freshly prepared aqua regia. This leaching runs according to the following reactions (Jimenez de Aberasturi et al., 2011; Pośpiech, 2012; Jha et al., 2013):



where HNO₃ is an oxidant, HCl provides an acidic reaction medium and is a Cl⁻ donor. On the one hand, aqua regia providing a high concentration of Cl⁻ facilitates PGM oxidation and dissolution because the redox potential of the ion/metal pairs strongly decreases in the presence of chlorides (Nogueira et al., 2014). Unfortunately, on the other hand, this leaching mixture is unfavorable for the environment due to the products formed as a result of the reaction of HCl and HNO₃ (e.g. NO, NOCl, Cl₂, HCl_(g)) (Jha et al., 2013):

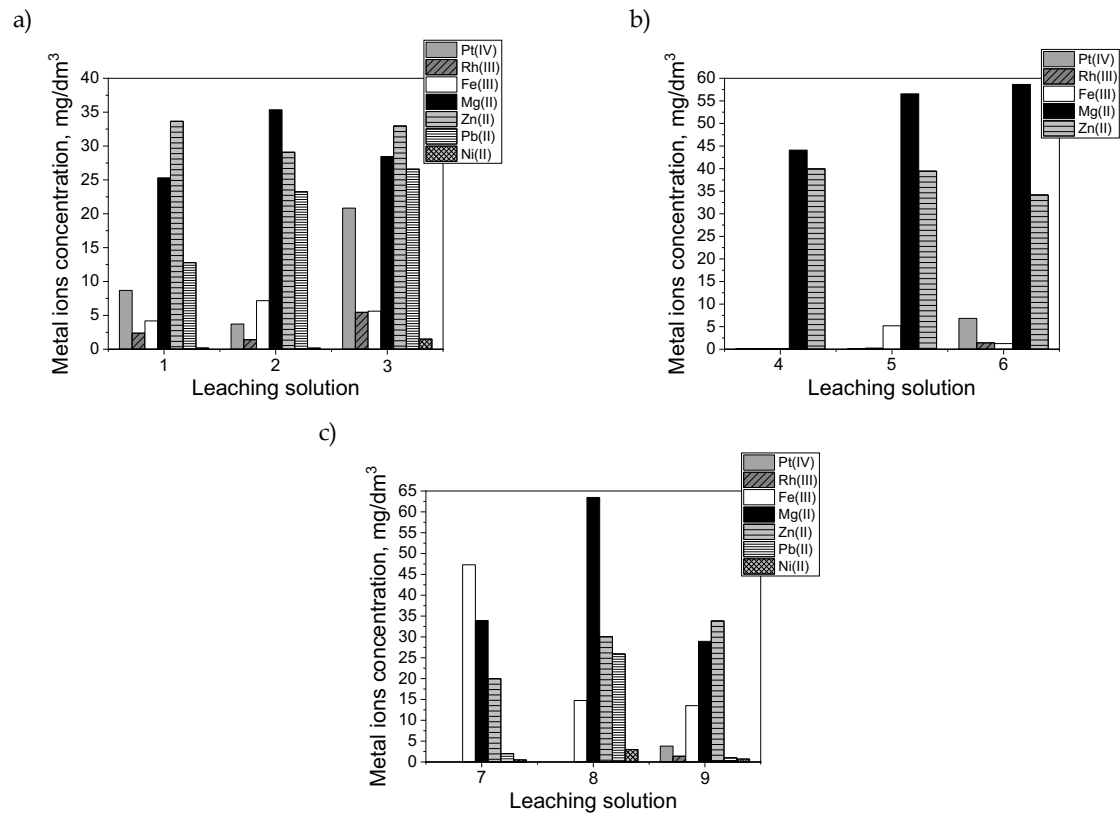
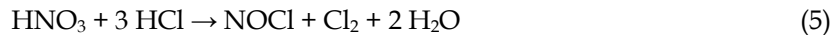


Fig. 5. The concentration of (■) Pt(IV), (▨) Rh(III), (□) Fe(III), (■) Mg(II), (≡) Zn(II), (≡) Pb(II) and (#) Ni(II) in the solutions after leaching at 70°C a) mixtures of acids and H₂O₂, b) solutions containing Cu(II) c) solutions containing Al(III)



Solution 1) can be an alternative to aqua regia. The addition of 98% H₂SO₄ increases the acidity of the solution, which leads to an increase in the amount of the leached Rh(III) in comparison to the HCl solution with the addition of 65% HNO₃ (Fig. 5 a) (Jha et al., 2013).

Thus, less aggressive, but having oxidizing properties, leaching media, i.e. CuCl₂ and AlCl₃ in 8 M HCl were applied in this investigation to leach metal ions from spent catalysts. The chloride salts were used as additional resources of chloride ions in the system (apart from these derived from HCl). Leaching in the presence of chloride ions reduces the consumption of HCl and the formation of by-products, e.g. during leaching with aqua regia at 70°C, large amounts of NO and HCl vapor are released. For this reason, HCl can be replaced in the leaching mixtures by chloride salts, the most commonly by AlCl₃ as it provides as many as 3 chloride ions, opposite to other chloride salts (e.g. NaCl). Moreover, the presence of Al(III) ions in a leaching solution reduces the rate of the substrate dissolution (does not dissolve the entire alumina washcoat). Also, Al(III) in leaching solution has not affect on the efficiency of Pt leaching (Boliński, 1991; Angelidis and Skouraki, 1996).

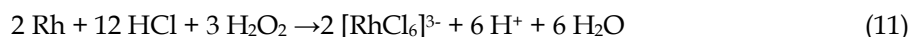
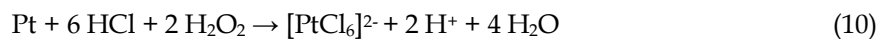
Regardless of the concentration of CuCl₂ or AlCl₃ used (without the addition of H₂O₂), no PGM ions are leached from the spent catalyst (Fig. 5 b and c). The additional function of copper(II) in CuCl₂ leaching solution was not only Cl⁻ donation but also being an oxidant (Cu²⁺), as proposed by Nogueira et al. (2014):



Despite the presence of copper ions (an oxidizing agent) the amounts of Pt(IV) and Rh(III) after leaching with such solutions were very low, below 1 mg/dm³ (Fig. 5 b). It means that CuCl₂, in the

applied concentration range, as an oxidant is not strong enough to dissolve PGMs. However, the presence of the copper(II) salt significantly enhances the leaching of non-valuable metals (even up to 55 and 40 mg/dm³ of Mg(II) and Zn(II), respectively).

Leaching of chemically resistant PGM involves not only precursors (AlCl₃ or CuCl₂) but also oxidants such as H₂O₂ (Jimenez de Aberasturi et al., 2011; Jha et al., 2013; Fornalczyk et al., 2016). Eventually, the addition of H₂O₂ as an oxidant to the leaching solutions containing CuCl₂ or AlCl₃ in HCl caused leaching of a small amount of Pt(IV) and Rh(III) (Fig. 5 b and c) according to the following reactions:



However, still, the concentration of PGMs leached with acidic salt solutions is lower than that leached with aqua regia. It should be indicated that the AlCl₃ acidic solution leached the largest amount of Fe(III) (Fig. 5 c). Pb(II) is not leached with the solutions containing CuCl₂ (Fig. 5 b), and in all the cases, Ni(II) was hardly leached.

3.3. Extraction of metal ions from solutions after leaching

The compositions of the solutions after leaching are presented in Table 3. The obtained results were compared with the results reported by other authors. The differences in the concentrations of Pt(IV) result from the amount of sample taken for research.

Table 3. The compositions of the solutions after leaching

Material	Leaching solutions and conditions	Composition of the solution after leaching	Ref.
Spent automotive catalyst (15 g of sample)	100 cm ³ of concentrated HCl, 70°C, 50 cm ³ of a 10% NaClO ₃ solution (adding dropwise)	520 mg/dm³ Pt(IV), 5.5 mg/dm³ Pd(II), 1.3 mg/dm³ Rh(III) , 204 mg/dm ³ Fe(III), 2 mg/dm ³ Cu(II), 3.4 mg/dm ³ Ni(II), 0.2 mg/dm ³ Co(II)	Malik and Paiva, 2010
Spent automotive catalyst	15% HCl and 0.33% AlCl ₃ , 90 min, 90°C	19.4 mg/dm³ Pt(IV), 10.8 mg/dm³ Pd(II), 3.3 mg/dm³ Rh(III)	Yin et al., 2013
	8 M HCl, ambient temperature, 30 min, next distillation at 110°C	625 mg/dm³ Pt(IV), 104 mg/dm³ Rh(III)	Jaree and Khunphakdee, 2011
Spent automotive catalyst (1 g of sample)	10.3 M HCl, 1 M H ₂ SO ₄ , 0.55 M H ₂ O ₂ , 70°C, 3 h	19.5 mg/dm³ Pt(IV), 4.3 mg/dm³ Rh(III) , 2.1 mg/dm ³ Fe(III), 17.8 mg/dm ³ Mg(II), 31.5 mg/dm ³ Zn(II), 27.6 mg/dm ³ Pb(II), 0.9 mg/dm ³ Cu(II), 1.1 mg/dm ³ Ni(II)	own research
	aqua regia, 70°C, 3 h	33.3 mg/dm³ Pt(IV), 7.9 mg/dm³ Rh(III) , 3.6 mg/dm ³ Fe(III), 21.2 mg/dm ³ Mg(II), 30.8 mg/dm ³ Zn(II), 30.6 mg/dm ³ Pb(II), 0.9 mg/dm ³ Cu(II), 1.3 mg/dm ³ Ni(II)	own research

Thus, for the next step (solvent extraction), two solutions after leaching with aqua regia and a mixture of HCl, H₂SO₄, and H₂O₂ were selected, due to the largest content of Pt(IV) and Rh(III). The results of solvent extraction are presented in Table 4.

The extraction of metal ions was carried out at a volume ratio of A/O = 1 or 2. Regardless of the A/O and the feed solution composition, Fe(III) was quantitatively extracted with 0.005 M Cyphos IL 101. Quantitative extraction of Pt(IV) and Zn(II) was noted only from feed solutions after leaching with a mixture of HCl, H₂SO₄, and H₂O₂. Rh(III) in all cases remained in the raffinate. The extraction efficiency of Mg(II) was poor, below 10%.

Obviously, the extraction of PGM from real solutions runs differently compared to the extraction from model mixtures (Rzelewska-Piekut and Regel-Rosocka, 2019), mainly due to the presence of significant amounts of non-precious metal ions (e.g. Zn(II), Fe(III), Pb(II)), which are first extracted with trihexyl(tetradecyl)phosphonium chloride.

On the one hand, extraction of metal ions from the solution after leaching with a mixture of HCl, H₂SO₄, and H₂O₂ is more favorable than extraction with aqua regia, because platinum can be separated from rhodium. On the other hand, after leaching with aqua regia, non-precious metals are extracted and platinum and rhodium stay in the raffinate. In this case, the additional extraction step must be applied to separate Pt and Rh.

In the last step, metal ions were stripped with 1 M HNO₃ from the loaded organic phases after extraction. The results are presented in Table 5.

Table 4. The extraction efficiency of Pt(IV), Rh(III), Fe(III), Mg(II), Zn(II) and Pb(II) from two solutions after leaching with a mixture of HCl, H₂SO₄, and H₂O₂ or aqua regia

Feed solution	A/O	Extraction efficiency, %					
		Pt(IV)	Rh(III)	Fe(III)	Mg(II)	Zn(II)	Pb(II)
Solution after leaching with a mixture of HCl, H ₂ SO ₄ , and H ₂ O ₂	1	100	0.0	100	3.2	100	46.7
	2	100	0.0	100	4.8	97.5	31.5
Solution after leaching with aqua regia	1	8.9	0.0	100	8.7	0.0	4.6
	2	1.3	0.0	100	8.2	0.0	1.0

Table 5. The stripping efficiency of Pt(IV), Rh(III), Fe(III), Mg(II), Zn(II) and Pb(II) with 1 M HNO₃ from the loaded organic phases after extraction (A/O = 2) from leaching solutions 1 or 3

Loaded organic phase	Stripping efficiency, %					
	Pt(IV)	Rh(III)	Fe(III)	Mg(II)	Zn(II)	Pb(II)
After extraction of metal ions from leaching solution containing HCl, H ₂ SO ₄ , and H ₂ O ₂ (solution 1)	18.6	0.0	100	32.7	44.2	67.5
After extraction of metal ions from leaching solution containing aqua regia (solution 3)	0.0	0.0	55.2	33.6	2.5	0.0

The nitric acid solution is an efficient strippant for non-precious metal ions. The efficiency of Pt(IV) stripping is poor. Thus, in this step ions of base metals can be separated from precious Pt(IV). Further investigation of the second step of stripping to recover Pt(IV) from the loaded organic phase and enrich the stripping solution in Pt(IV) will be carried to improve the whole process.

4. Conclusions

The XRD analysis confirmed the presence of cordierite (indialite) in the samples of the spent catalyst. The largest amounts of Pt(IV) and Rh(III) were leached with freshly prepared aqua regia and the mixture of HCl, H₂SO₄, and H₂O₂. Pt(IV) can be separated from Rh(III) using extraction with quaternary phosphonium ionic liquid (Cyphos IL 101) from solutions after leaching with the mixture of HCl, H₂SO₄, and H₂O₂. In the case of the solution after leaching with aqua regia, it is not possible to separate Pt(IV)

from Rh(III) selectively by extraction with Cyphos IL 101. It was also proved that temperature has a positive influence on the amount of the leached metal ions, except Zn(II).

Future research should focus on the efficient separation of Pt(VI) from the loaded organic phases using various stripping solutions. A proper O/A ratio should be chosen to enrich the stripping solution in the PGM recovered and increase the concentration of these metal ions compared to the feed.

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Appendix

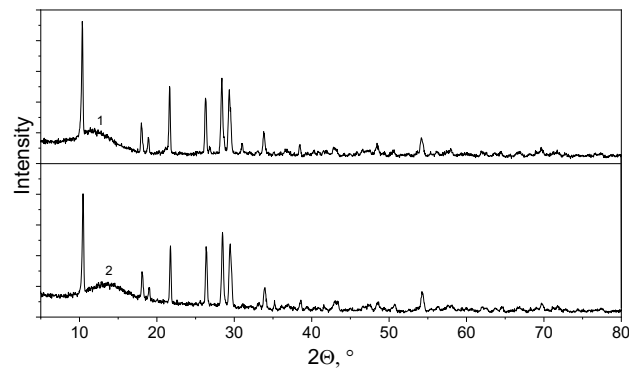


Fig. A1. X-ray diffraction pattern of a spent automotive converter (1) before leaching and (2) after leaching

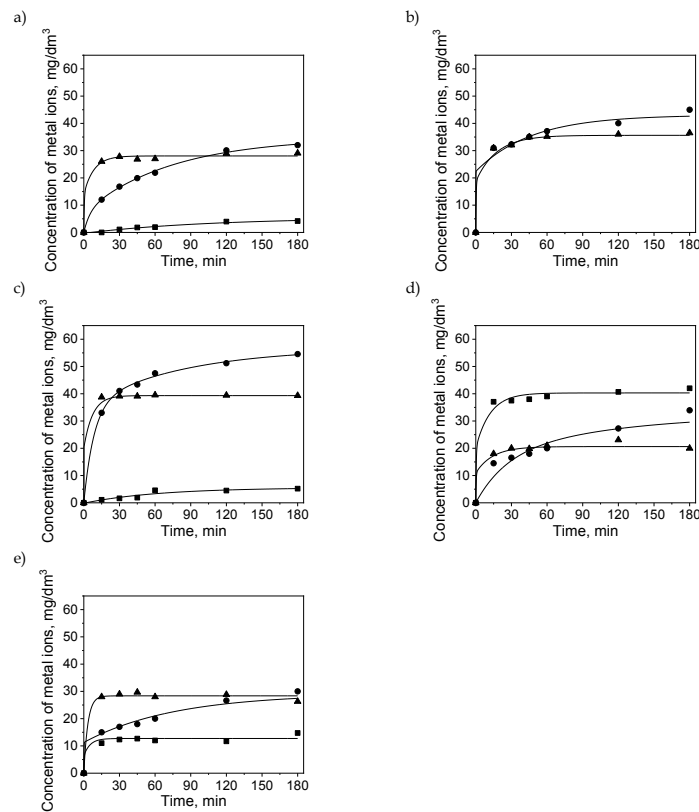


Fig. A2. Influence of time on leaching of non-precious metal ions from spent automotive converters (■) Fe(III), (●) Mg(II), (▲) Zn(II) (temperature: $70 \pm 2^\circ\text{C}$, leaching solutions: a) solution 2, b) solution 4, c) solution 5, d) solution 7, e) solution 8

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