

INFLUENCE OF H₂O₂ AND O₃ ON PGM EXTRACTION FROM USED CAR CATALYSTS

Catalytic converters contain the catalytic substance in their structure, which is a mixture of Platinum Group Metals (PGMs). The prices of these metals and a growing demand for them in the market, make it necessary to recycle spent catalytic converters and recovery of PGMs. In the study, the effect of ozone and hydrogen peroxide application on the possibility of extracting PGM from used car catalysts was investigated. The catalytic carrier was milled, sieved and then the fractions with the desired grain size were treated with the appropriate HCl mixture and 3%, 5%, 10%, 15% and 30% H₂O₂, respectively, and the tests were also carried out at temperature 333 K. Ozone tests were conducted with the O₃ flow in the range of 1,3,5 g/h. Samples for analysis were collected after 30 min, 1 h, 2 h, 3 h and after 4 h, respectively. The residue after the experiments and filtration process was also analysed. The obtained results confirmed the assumption that PGMs can be extracted using hydrochloric acid with the addition of H₂O₂ or ozone as oxidants. It allows to significantly intensify the carried out reactions and to improve the rate of PGMs transfer to the solution.

Keywords: spent catalytic converters, PGM metals, hydrometallurgy, O₃, H₂O₂

1. Introduction

Platinum Group Metals (PGMs), including platinum (Pt), palladium (Pd) and rhodium (Rh) are widely used in automotive industries due to their properties such as catalytic activity, chemical inertness and also resistance for corrosion [1]. However, application of PGMs as catalytic converters has also some disadvantages such as the high price, the non-renewability of these metals and high environmental impact caused in their extraction [2]. Additionally, the natural resources of these metals are limited and mainly found in Russia, North America, Canada and South Africa [3].

It was reported by Johnson Matthey that in 2017, demands for Pt, Pd and Rh in the field of automotive catalysts accounted respectively for Pt 41.5%, Pd 81.1% and Rh 81.7% of gross demand. The comparison of total supply and demand of PGMs in 2017 is presented in Table 1.

TABLE 1

The total supply and demand of PGMs in tonnes in 2017 [4]

	Pt	Pd	Rh
Total supply	186.9	206.2	23.4
Gross demand	236.5	315.0	31.1
Total recycling	-59.0	-84.2	-9.0
Total net demand	177.5	238.7	21.8
Movements in stocks	-9.4	-24.6	1.6

Automotive catalysts are an important group of waste because they are a source of valuable metals such as platinum, palladium and rhodium; which are not only rare, but also expensive. These metals play a catalytic function and they are almost impossible to be replaced by other cheaper metals. The use of automobile catalysts can greatly reduce the amount of hazardous chemicals released into the air, i.e. nitrogen oxides (NO_x), hydrocarbons (HC) and carbon monoxide (CO).

For automotive catalytic converters, ceramic or metallic carriers are frequently used. Currently, the majority of automotive catalysts is produced with a ceramic carrier (approx. 96%), but the percentage of new generation metal catalysts (MSC-Metal Substrate Converters) on the market is still growing [5].

Currently, the hydrometallurgical or pyrometallurgical and mixed methods for processing of spent catalysts are used all over the world [2,6]. It is necessary to use a number of intermediate steps to obtain pure metal in those technologies. Hydrometallurgical technologies are a preferred solution with regard to the processes, as they allow selective separation of metal ions from aqueous solutions [5]. In hydrometallurgical methods, due to a low chemical reactivity of platinum or ceramic carriers, it is necessary to use a large quantity of concentrated acids and strong oxidizing agents; additionally, it generates a large amount of waste solutions containing heavy metals and derivatives of strong acids. The pyrometallurgical methods – on the other hand – often require the aggregates to reach very high temperature, in some methods – even 2300 K [7]. Furnaces able to reach such

* SILESIA UNIVERSITY OF TECHNOLOGY, FACULTY OF MATERIALS ENGINEERING AND METALLURGY, KATOWICE, POLAND

** CZESTOCHOWA UNIVERSITY OF TECHNOLOGY, FACULTY OF PRODUCTION ENGINEERING AND MATERIALS TECHNOLOGY, CZESTOCHOWA, POLAND

*** P.J. SAFARIK UNIVERSITY, FACULTY OF SCIENCE, KOSICE, SLOVAKIA

Corresponding author: Agnieszka.Fornalczyk@polsl.pl

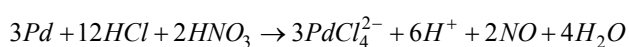
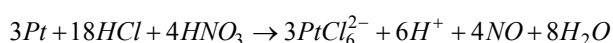
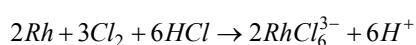
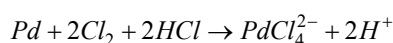
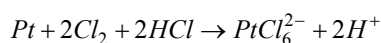
temperatures, and to provide the required working conditions, are costly, and the entire process is energy-intensive.

In hydrometallurgical techniques, metals are leached directly or after pre-treatment using suitable acidic and alkaline solutions in presence of oxygen, hydrogen peroxide, iodine, bromine, chlorine or ozone [3].

Leaching PGMs from spent catalysts has become widely used process due to simple technology. Many authors have studied PGM recovery from secondary materials such as spent automotive catalysts; there are also many reports about commercial-scale PGM production from these resources.

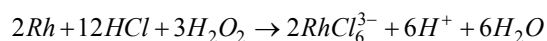
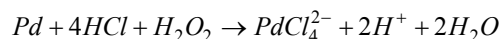
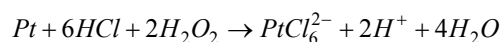
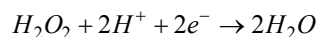
1.1. Leaching in aqua regia in solutions

PGMs in the spent catalyst are leached in hydrochloric acid medium with oxidizing agents HNO_3 . In the leaching system, the nascent chlorine provides high oxidation potential and high concentration of chloride ion [3]. As the result PGMs are mostly in the form of chloro-complex according to reactions [1]:



1.2. Leaching in the presence of hydrogen peroxide

PGMs in the spent catalyst can be also leached in hydrochloric acid medium with oxidizing agents, for example, H_2O_2 , Cl_2 , etc. [1]. With the H_2O_2 as an oxidizing platinum and palladium are completely dissolved according to its high oxidizing capacity. The reaction of PGM leaching in the presence of hydrogen peroxide takes place according to the following equations:

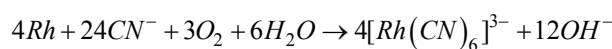
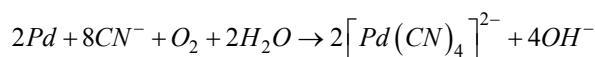
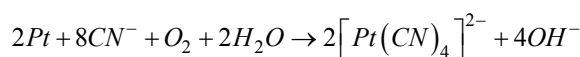


In the paper [2] the diagrams Eh-pH for these systems were presented, it confirmed (according to the thermodynamic requirements) the possible of Pt, Pd and Rh dissolution as a chloro-complexes in HNO_3/HCl and $\text{H}_2\text{O}_2/\text{HCl}$ media.

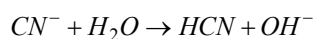
1.3. Leaching in the cyanide solution

In PGM recovery processes from spent auto catalysts, cyanide leaching methods are also successfully used.

Dissolution of PGMs occurs according to reactions:



Decomposition of cyanide:



In cyanide leaching process, the reaction rate has been controlled by a surface chemical reaction, similarly to gold cyanide reaction mechanism [1,8].

1.4. Leaching in the presence of chloride ions

In the world literature, there are also reports concerning the method of leaching of Pt from spent catalysts in the presence of AlCl_3 . Application of this salt allows reducing consumption of hydrochloric acid and generation of gases during the dissolution of platinum in aqua regia [3,9,10]. Also, [11] reported the possibility Pt recovery during leaching of industrial catalysts Pt-NiO/ Al_2O_3 in the presence of aluminium chloride solutions. Its allow to lower concentrations of nitric acid as an oxidant, instead of aqua regia.

1.5. Leaching in the presence of ozone

Ozone is known as a strong oxidizing agent with a standard redox potential of 2.07 V. Therefore many of metals can be oxidized to the higher oxidation state in solution by ozonation. Advantages such as: relatively easy production, possibilities of using at very low aqueous concentration ($\sim 10^{-4}$ M) possibilities of direct injection to the aqueous solution cause that ozone may be a reasonable alternative oxidizing agent used in hydrometallurgical processes [12,13]. The use of ozone as oxidizing agent in leaching process to enhance the efficiency of metals recovery has been investigated by numerous researchers. These applications regard extraction of precious metals Au, Ag, Cu [14-16] and PGM [12] from ores (refractory gold ores, chalcopyrite, pyrrargyrite, tetraedrite, magnetite) or metallic scraps [13] but there is lack of publications concern ozone-leaching PGM from spent catalysts.

2. Experimental

2.1. Materials

Different types of catalysts were used in this study; all of them are ceramic honeycomb monolith. The scraps of ceramic supports were crushed and milled using a ball miller until a maximum particle size of 0.5 mm was achieved. The smallest fractions

were used for the research, as the initial analysis showed the highest PGM contents in them. The amount of catalysts used as a sample for each experiment was 30 g.

2.2. Analysis of PGMs contents

The content of platinum, palladium and rhodium in the sample was determined by the Microwave Plasma Atomic Emission Spectroscopy (MPAES) (Agilent MP-AES 4200). The composition was presented in Table 2.

Also residue found on the filter after the experiment and PGMs content in initial samples were analysed.

TABLE 2

The initial, average content with standard deviation of platinum, palladium and rhodium in the sample

	Pt, [%]	Pd, [%]	Rh, [%]
Content	0.2018	0.4130	0.0092
Standard deviation	±0.0223	±0.0183	±0.0014

2.3. Procedure

The presented research focused on leaching in the presence of an oxidizing agent in the form of H_2O_2 and O_3 . The results of these tests were compared with the leaching tests in the presence of aqua regia. Therefore, the presented studies consisted of three groups of studies:

- tests using 270 ml 3M HCl and 30 ml H_2O_2 (at 3%, 5%, 10%, 15% and 30% respectively), these tests were carried out at room temperature and for 333 K,
- tests with the use of 300 ml 3M HCl and with the O_3 flow (respectively with the flow of O_3 in the range of 1,3,5 g/h),
- research using 300 ml aqua regia.

Samples for analysis were collected after 0,5 h, 1 h, 2 h, 3 h and after 4 h, respectively. Solid samples – residue after the process was leached in hot aqua regia.

Ozone was generated using a Korona L 20 SPALAB generator, which produced ozone by the quiet corona discharges method. Ozone aeration experiments were carried out in the room temperature 293 K using flow rate range of 1-5 g O_3 /h for 4 h. Ozone was introduced directly in milled pulp without any mechanical agitation.

The steps applied in experimental procedure were shown in Fig. 1.

3. Results and discussion

3.1. Tests with hydrogen peroxide

The influence of hydrogen peroxide concentration and peroxide concentration at the temperature 333 K on the dissolution of Pd, Rh and Pt in the leaching solution was shown, respectively,

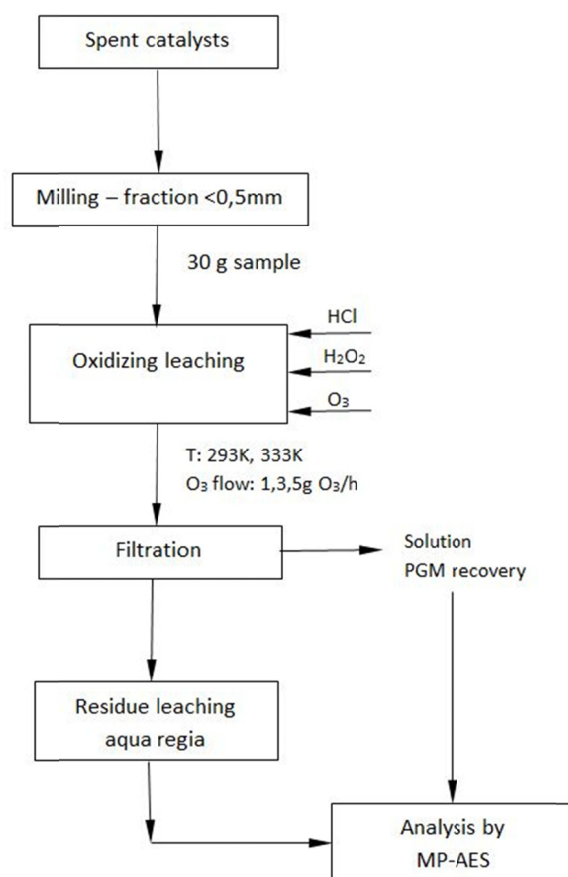


Fig. 1. The experimental procedure of PGM leaching from spent auto catalysts

in Figs. 2-9. All results were compared with the leaching tests in the presence of aqua regia.

Dissolution of each PGM increases with increasing leaching time.

In the case of Platinum extraction:

- the rate of Pt dissolution is much smaller than for conditions treated as reference conditions, i.e. for aqua regia – respectively the best result was obtained for application of 30 ml 3% H_2O_2 24.6 mg/dm³ where for aqua regia was 226.6 mg/dm³,
- raising the temperature of the process significantly improved the situation, the best results were obtained for application of 30 ml 5% H_2O_2 – 192.1 mg/dm³, similar results for experiments using lower concentrations, i.e. in the 3-15% range, the worst result was observed for application of 30 ml 30% H_2O_2 concentration 65.4 mg/dm³ (for aqua regia 226.6 mg/dm³).

In the case of Palladium extraction tests:

- the results of Pd leaching obtained in the application 270 ml of 3M HCl leaching test with hydrogen peroxide were better than the results obtained in the reference conditions, i.e. aqua regia – respectively the best result for 5% H_2O_2 was 176.1 mg/dm³ where for aqua regia was 147.1 mg/dm³,
- the above results remained at a similar level regardless of whether the process was carried out at temperature 333 K or not.

In the case of Rhodium extraction:

- the results were similar to platinum, much worse than in the case of aqua regia – respectively the best result for application of 30 ml of 15% H₂O₂ was 2.2 mg/dm³ where for aqua regia was 7 mg/dm³.
- the application of 333K temperature improved the results and it allowed to dissolve up to 6 mg/dm³.

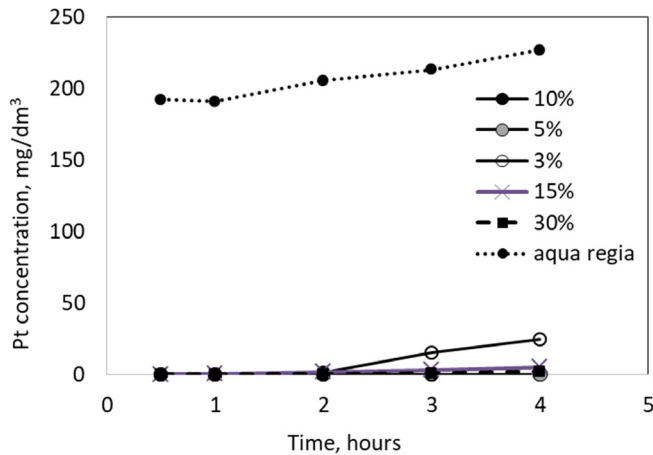


Fig. 2. Relationship of platinum concentration on time in the leaching process with addition hydrogen peroxide

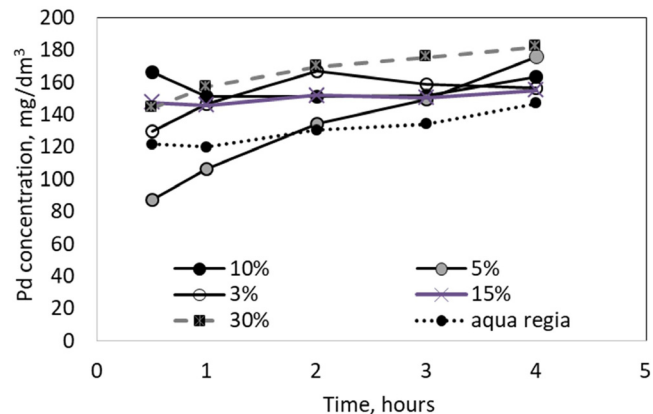


Fig. 3. Relationship of palladium concentration on time in the leaching process with added hydrogen peroxide

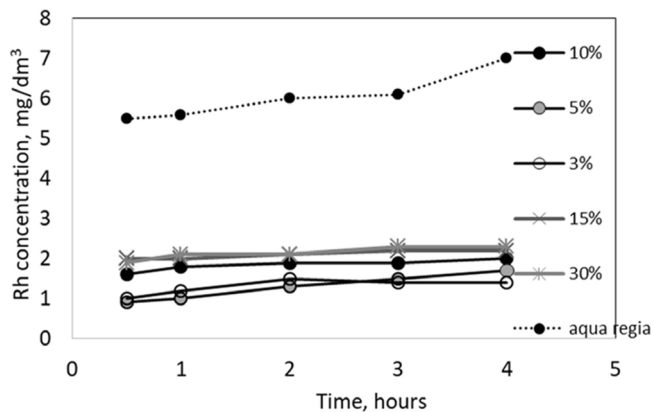


Fig. 4. Relationship of rhodium concentration on time in the leaching process with added hydrogen peroxide

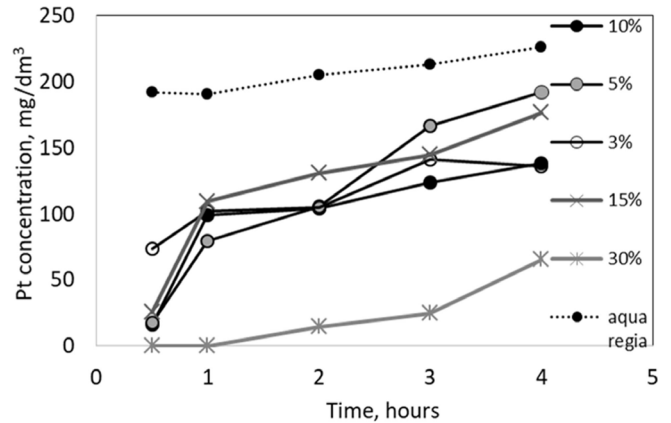


Fig. 5. Relationship of platinum concentration on time in the leaching process with added hydrogen peroxide at temperature 333K

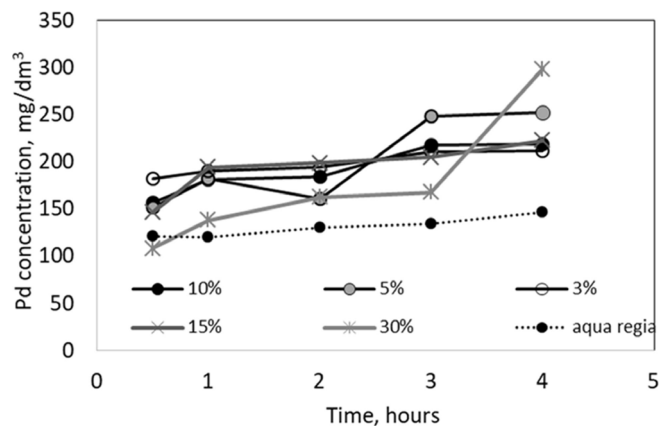


Fig. 6. Relationship of palladium concentration on time in the leaching process with added hydrogen peroxide at temperature 333K

Figs. 8-9 shows influence of hydrogen peroxide concentration on PGM extraction. The applied research allows concluding that only for palladium, satisfactory results were obtained. The results remained at a high level, regardless of hydrogen peroxide concentration. Increasing the temperature at which the process is carried out improved the results also for platinum and rhodium. The most favorable results were obtained for the

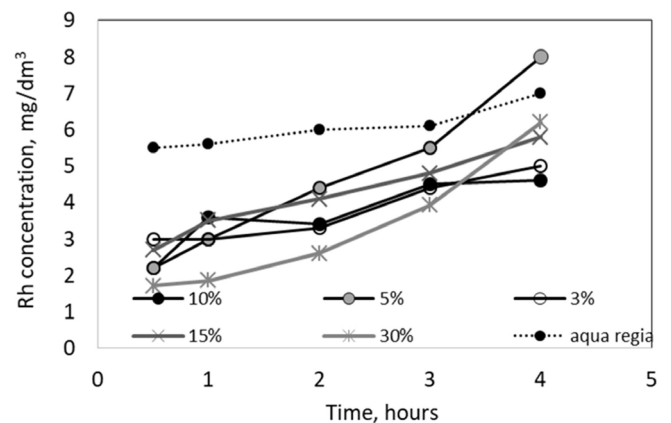


Fig. 7. Relationship of rhodium concentration on time in the leaching process with added hydrogen peroxide at temperature 333 K

hydrogen peroxide concentration range of 5-15%, which is additionally beneficial due to lower harmfulness for the natural environment. The obtained results can be a good basis for the separation processes of Pt, Pd, and Rh from this type of waste because for each of these metals different process conditions are more favorable.

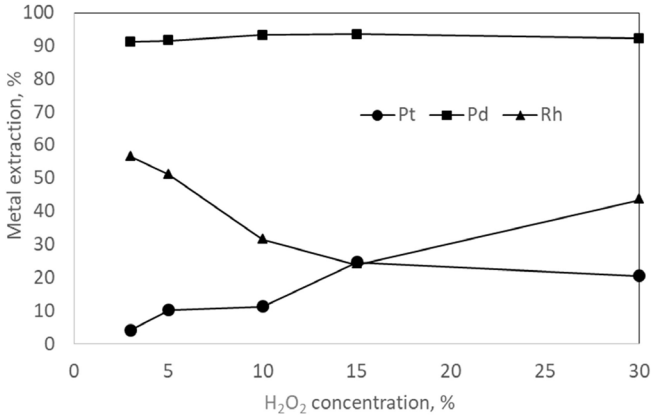


Fig. 8. Relationship of metal extraction on H₂O₂ concentration

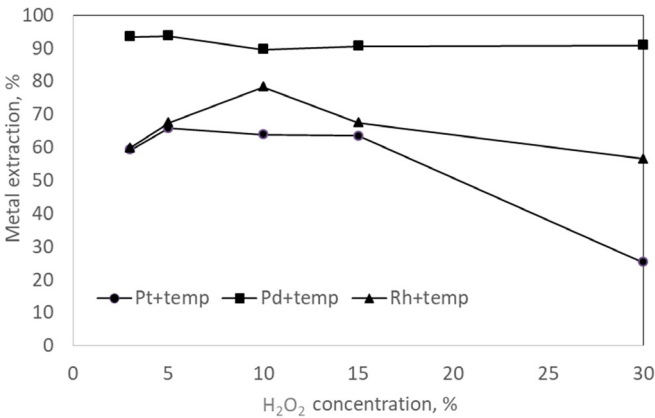


Fig. 9. Relationship of metal extraction on H₂O₂ concentration at temperature 333K

3.2. Tests with ozone flow

The effects of ozone on the dissolution of Pd, Rh and Pt in the leaching solution was shown, respectively, in Figs. 10-12. Dissolution of each PGM increases with increasing leaching time. The extraction of Pd and Rh in the HCl-O₃ system was relatively fast during first 2 hours, then slightly increased from 1.8-2.2 mg/dm³ to the level of 2.36 mg/dm³ for Rh and from 153-167 mg/dm³ to the level of 166.5-173.9 mg/dm³ for Pd. The character of the Pt dissolution process was slightly different with a visible constant increase in the concentration of platinum in the solution. Concentration of Pt 36.2 mg Pt/dm³ was obtained in solution using ozone flow 3 g/h within 4 hours.

Fig. 13 shows the influence of ozone flow on PGM extraction. In the case of Pd and Rh, increase in ozone mass flow rate had no beneficial impact on the amount of these metals extraction. Therefore it is postulated that excess of ozone is not neces-

sary. During 4 hours 91,6% of Pd and 29,3% of Rh was extracted using ozone flow rate of 1g/h. It was noticed that platinum was influenced by the flow of ozone in the system. 21.1% of Pt was dissolved using 1 g O₃/h and 22.6% using a flow rate of ozone 5 g/h, while 47.8% when O₃ flow rate was 3 g/h.

The obtained results indicate the possibility of PGM recovery in the presence of HCl-O₃ system in a selective manner.

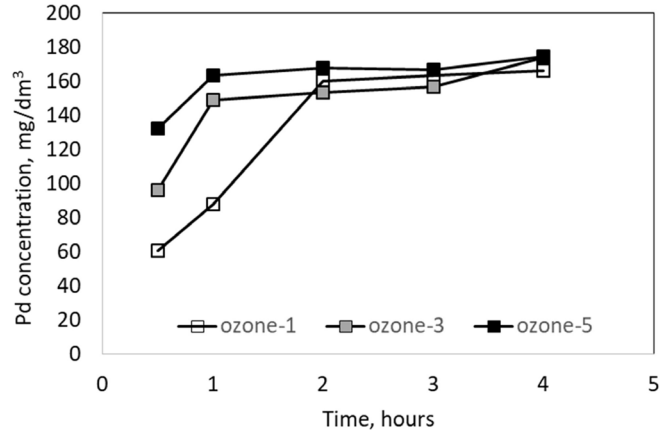


Fig. 10. Palladium concentration in HCl-O₃ system with ozone mass flow in the range 1-5 g/h

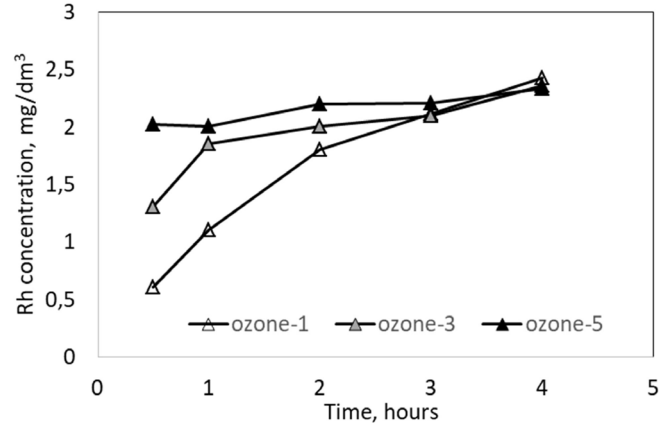


Fig. 11. Rhodium concentration in HCl-O₃ system with ozone mass flow in the range 1-5 g/h

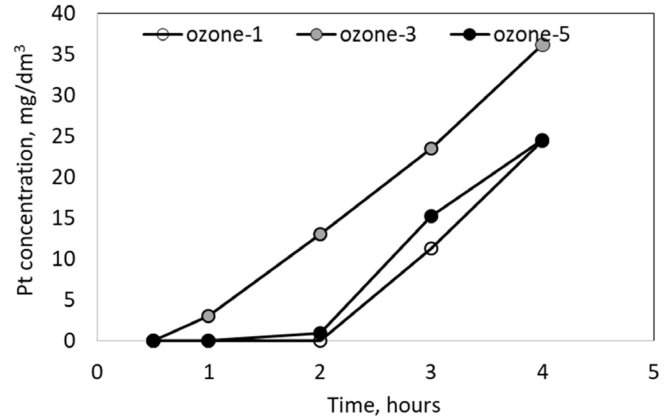


Fig. 12. Platinum concentration in HCl-O₃ system with ozone mass flow in the range 1-5 g/h

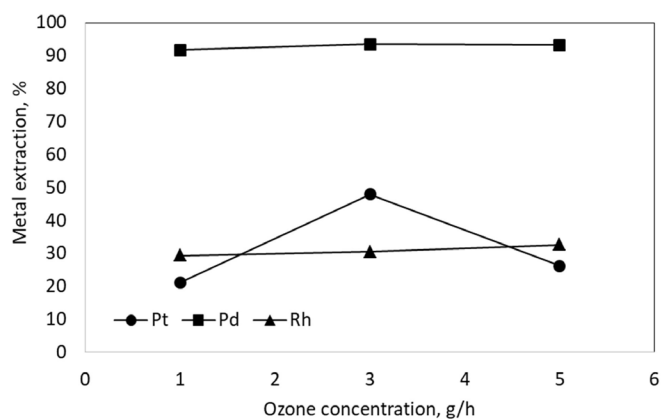


Fig. 13. Influence of ozone flow on PGM extraction; conditions: 4 h, 3MHCl

Using the flow rate of ozone at the level of 1 g/h, it seems to be possible to separate palladium from platinum and rhodium in solution. In this way during first 2 hours, there was no platinum in the system HCl-O₃, Rh concentration was 1.8 mg/dm³, while a large majority of palladium (160.0 mg/dm³) was dissolved in solution (see Figs. 10-12).

Our findings are similar to those reported by Viñals et al. [12]. They applied ozone-leaching method for recovery precious metals from metallic scraps. At ambient temperature and low (~0.1 M) H⁺ and Cl⁻ concentrations of gold and palladium were recovered while rhodium and platinum remained stable.

4. Conclusion

The paper presents the results of dissolving spent automotive catalysts on ceramic carriers in acids. The effect of H₂O₂ concentration, ozone flow as well as the temperature on the degree of platinum, palladium and rhodium recovery from this kind of waste was examined. The results confirmed the assumption that PGMs can be extracted using hydrochloric acid with the addition of H₂O₂ or ozone as oxidants. This allows to significantly intensify the carried out reactions and to improve the rate of PGMs transfer to the solution. This method is also quite simple and not expensive to implement in industrial conditions.

Acknowledgements

This paper was created with the financial support of Polish Ministry for Science and Higher Education under internal grant BK111/RM0/2018 (11/990/BK18/0057) for Department of Extractive Metallurgy and Environmental Protection, Silesian University of Technology, Poland.

REFERENCES

- [1] H. Dong, J. Zao, J. Chen, Y. Wu, B. Li, *Int. J. of Mineral Processing* **145**, 108-113 (2015) <http://dx.doi.org/10.1016/j.minpro.2015.06.009>.
- [2] D. Jimenez de Aberasturi, *Minerals Engineering* **24**, 505-513 (2011).
- [3] M.K. Jha, J. Lee, M. Kim, J. Jeong, B. Kim, V. Kumar, *Hydrometallurgy* **133**, 23-32 (2013). <http://dx.doi.org/10.1016/j.hydromet.2012.11.012>
- [4] http://www.platinum.matthey.com/documents/new-item/pgm%20market%20reports/pgm_market_report_may_2017.pdf
- [5] M. Kucharski, *Recykling metali nieżelaznych*, Wydawnictwo AGH, Kraków 2010.
- [6] J.S.Yoo, *Catalyst Today* **44**, 27-46 (1998).
- [7] J. Willner, A. Fornalczyk, J. Cebulski, et al., *Archives Of Metallurgy And Materials* **59** (2), 801-804 (2014).
- [8] M.E. Wadsworth, X. Zhu, J.S. Thompson, C.J. Pereira, *Hydrometallurgy* **57**, 1-11 (2000).
- [9] M. Saternus, A. Fornalczyk, J. Willner, H. Kania, *Przemysł Chemiczny* **95** (1), 78-83 (2016)
- [10] F.K. Letowski, P.A. Distin, *International Precious Metals Institute*, Allen Town, 41-49 (1989).
- [11] T.N. Angelidis, E. Skouraki, *Appl. Catal. A Gen.* **142**, 387-395 (1996).
- [12] R. Torres, G.T. Lapidus, *Hydrometallurgy* **166**, 185-194 (2016).
- [13] J. Viñals, E. Juan, M. Ruiz, E. Ferrando, M. Cruells, A. Roca, J. Casado, *Hydrometallurgy* **81**, 142-151 (2006).
- [14] C. Rodríguez-Rodríguez, F. Nava-Alonso, A. Uribe-Salas, *Hydrometallurgy* **149**, 168-176 (2014).
- [15] M. Ukasik, T. Havlik, *Hydrometallurgy* **77**, 139-145 (2005).
- [16] C.F. Patiño, R.E. Salinas, P. Carrillo, F. Raul, A.M. Hernandez, B. Mendez, The use of ozone to improve cyanidation process for silver and gold extraction from a refractory ore. *Proc. 27th Conference, IPMI, Pensacola, FLA*, pp. 50-62, 2003.