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LEACHING PROCESS OF PLATINUM METALS FROM SPENT AUTOCATALYSTS

Mišić Ljubiša, Kovačević Renata
Gardić Vojka, Marković Radmila, Petrović Jelena
Mining and Metallurgy Institute Bor
Zeleni bulevar 35, 19210 Bor, Serbia
E-mail: ljubisa.misic@irmbor.co.rs

ABSTRACT
The basis of each autocatalyst is a ceramic monolith with deposited valuable platinum metals. The spent autocatalysts are solid waste and also the rich raw material for recovery of platinum metals. The aim of this paper is a separation of present platinum metals from spent autocatalysts. Samples of spent autocatalysts were used for laboratory experimental researches with the following average content of platinum metals: 0.2% Pt, 0.03% Pd and 0.005% Rh. A series of laboratory experiments was carried out with the aim to examine the main parameters of translation process the platinum metals into ionic form. The tests were focused on selecting the most suitable solvent, process time, temperature and ratio of solid: liquid. The highest degree of transformation the platinum metals into ionic form was achieved during the following conditions of the leaching process: reagent of hydrochloric acid in the presence of oxidant, process temperature 95^oC, time 1 h and the S:L ratio of 1:3. The obtained results indicate a high degree of extraction the platinum metals >95 % from spent catalysts for the automotive industry.
Keywords: autocatalyst, platinum, palladium, rhodium, leaching

1. INTRODUCTION
By many of his activities including the use of vehicles, a person violates the ecological balance on the Earth. In production, exploitation and disposal of old vehicles in the form of various waste, degradation of the environment, soil, water and air is developed. In the mid of 80's of the last century, the use of catalysts has started which were aimed to reduction of emission the harmful gases into the atmosphere, generated by the fuel burning in the vehicle engine. Catalysts are an inevitable part of every new vehicle in the last ten years. This is due to the prescribed environmental standards by the European regulations on the composition of exhaust gases that vehicles must meet [1].
The largest demand for platinum, palladium and rhodium is in the automobile industry. These three metals are used in the automobile catalyst converters for the conversion of toxic exhaust gases from automobiles into non-polluting gases. A study of various acid combinations on the spent autocatalyst samples was performed to explore the possibility of improving the recoveries of Pt , Pd and Rh [2,3]. The content of active noble metal catalysts with a metal is 0.5-2% [4].

2. EXPERIMENTS
2.1. Characterization of the spent catalysts samples for automotive industry
Table 1 gives the chemical characterization of 12 samples of catalysts for automotive industry originated from different manufacturers and with different degrees of exploitation. Chemical characterization of samples was carried out using the X-ray fluorescent analysis - XRFA on apparatus NITON XL3t-900 according to the program Mining mode - AutoCat file.

Table 1. Chemical characterization of different catalyst simples

Simple No.	ELEMENT, %														
	Pt	**Pd**	**Rh**	**Si**	**Al**	**Sr**	**Zr**	**Cr**	**Pb**	**Fe**	**V**	**Zn**	**Ce**	**Ca**	**Ti**
1	0.18			36.15	2.05	3.40						1.24			
2	0.79			5.05	15.19		1.96			0.23					0.14
4		0.45	0.01	2.26	7.44		1.65		1.04	0.44	3.03		6.92		
5	0.13		0.02	6.41	18.20		2.32	1.27	0.12	0.41					
6	0.43			37.76	2.23	2.63	0.55					0.55			
7	0.21			10.65	10.65				0.11	0.76					
8	0.25			6.01	11.57		1.95			0.47	0.41			0.24	0.15
9		0.08	0.06	3.74	8.12		2.09	0.97		0.40	1.28	0.04	4.47	0.21	
10	0.54	0.002		12.41	8.86					0.35					
11	0.004	0.35	0.004	4.60	14.77			0.09	0.97	0.68	0.19	0.31		0.95	0.32
12	0.2			14.71	11.98			0.03	0.06	0.60		0.05		0.27	0.44

A composite sample, made after grinding in ball mill of the 12 samples and obtaining the grain size of 100% - 300 μm, was used for experimental testing. The grain-size distribution of composite sample is given in Table 2.
Chemical analysis of composite sample, used for experimental research, is presented in Table 3.

Table 2. The grain-size distribution of spent catalyst composite sample

Klass, mm	**M, %**	**Σ M, %↓**	**Σ M, %↑**
-0.300 + 0.212	3.5	3.5	100.0
-0.212 + 0.106	12.0	15.5	96.5
-0.106 + 0.075	6.0	21.5	84.5
-0.075 + 0.053	9.5	31.0	78.5
-0.053 + 0.038	12.0	43.0	69.0
-0.038 + 0.000	57.0	100.0	57.0

Table 3. Chemical analysis of the composite sample

Element	**Pt**	**Pd**	**Rh**	**Al**	**Si**	**Ca**
Content, %	**0.2187**	**0.0261**	**0.0049**	5.15	28.87	0.24

2.2. Description of laboratory leaching experiments of spent catalysts for automotive industry

A series of laboratory experiments was carried out aimed to examine the basic parameters of translation process the platinum metals into ionic form. The tests were focused on selection the most suitable solvent, process time, temperature and ratio of solid: liquid.
All laboratory experiments were conducted with 100 g composite sample, using the magnetic stirrer with automatic temperature control and mixing speed. After each experiment, chemical analysis of the concentration of platinum metals in the solution after leaching (analytical method: ICP-AES atomic emission spectrometry with inductively coupled plasma, according to the Standard VMK Gg 5:2007) and chemical analysis of solid residue (X-ray fluorescent analysis - XRFA on apparatus NITON XL3t-900 according to the program Mining mode - AutoCat file) were carried out.

3. RESULTS AND DISCUSSION

3.1. Solvent effects on the platinum metals leaching from spent catalysts for automotive industry

In order to select the most suitable solvent for the leaching platinum metals from spent catalyst samples for automotive industry, several solvent were used: aqua regia, mixtures of mineral acids in the presence of oxidant and hydrochloric acid in the presence of chlorine as an oxidant.
Experiments were carried out at temperature of 95 °C, the ratio of S/L = 1/5 and time - 4 h. The achieved degree of leaching of platinum metals, depending on the type of solvent, is given in Table 4.

Table 4. Leaching degree of platinum metals by using different solvents

Element	Leaching degree, %		
	$HCl + Cl_2$	Mixtures of mineral acids	Aqua regia
Pt	92.18	75.14	86.42
Pd	99.31	75.86	98.08
Rh	88.16	40.81	73.47

The highest degree of transition of platinum metals in ionic form was achieved by using hydrochloric acid in the presence of oxidants and all experimental testing were carried out using this solvent in order to define the optimum parameters of leaching of the catalyst.

3.2. Effect of time on the platinum metals leaching from spent catalysts for automotive industry

In order to determine the optimum time for platinum metals leaching from spent catalysts, a series of experiments was carried out with the following conditions: solvent - HCl in the presence of Cl_2, the ratio of S/L = 1/5, the process temperature of 95 ^oC. The percentage of leaching of the platinum metals, depending on the leaching time is shown in Figure 1.

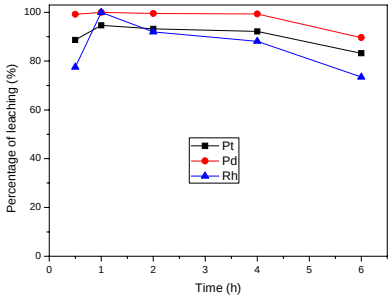

Figure 1. Leaching degree of the platinum metals depending on the time

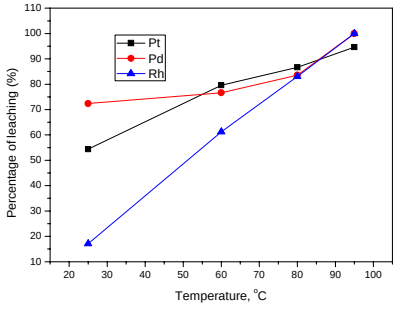

Figure 2. Leaching degree of the platinum metals depending on the temperature

Based on the results shown in Figure 1, it can be concluded that the highest level of transition of the platinum metal was achieved during the leaching time of 1 h. With increasing leaching time, the lower degree of leaching the platinum metals was observed.

3.3. Effect of temperature on the platinum metals leaching from spent catalysts for automotive industry

Experiments were carried out at 25, 60, 80 and 95^oC in the following leaching conditions: solvent - HCl in the presence of Cl_2, the ratio of S/L = 1/5, time - 1 hour. The achieved degree of leaching the platinum metals is shown in Figure 2.
The best achieved leaching degree of all present platinum metals was obtained at temperature of 95^oC, as shown in Figure 2.

3.4. Effects of ratio solid:liquid on the platinum metals leaching from spent catalysts for automotive industry

In order to determine the optimal ratio of solid: liquid in the process of the platinum metals leaching from spent catalysts, a series of experiment was carried out with the following conditions: solvent – HCl in the presence of Cl_2, time of process - 1 h, temperature - 95 ^oC. The percentage of the platinum metals leaching, depending on the ratio of S/L is shown in Figure 3.

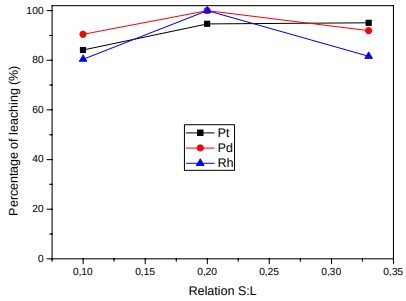

Figure 3. Leaching degree of the platinum metals depending on the ratio solid:liqued

Based on the realized testing of the platinum metals leaching process at the ratio of S/L = 0.1 (1/10), 0.2 (1/5), 0.3 (1/3), the highest level of leaching is achieved at the ratio of S/L = 1/5, shown in Figure 3.

4. CONCLUSIONS

Based on the results of experimental research at the laboratory level, it can be concluded that the highest level of transition the platinum metal into ionic form was achieved in the following conditions of development the leaching process: reagent hydrochloric acid in the presence of chlorine, the process temperature 95^oC, time 1 h and the ratio of S/L = 1/5. The obtained results point out the high degree of extraction the platinum metals > 95% from the spent catalyst for automotive industry. Further research should be aimed to the investigation the influence of partical size of ground catalysts to the leaching process as well as development of methodes for the platinum metal recovery from solution obtained after leaching process.

5. ACKNOWLEDGEMENTS

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