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**DISSOLUTION OF CERAMIC MONOLITH OF SPENT CATALYTIC CONVERTERS BY USING HYDROMETALLURGICAL METHODS****ROZPUSZCZANIE MONOLITU CERAMICZNEGO ZUŻYTYCH KATALIZATORÓW NA DRODZE HYDROMETALURGICZNEJ**

Catalytic converters contain the catalytic substance in their structure, which is a mixture of Platinum Group Metals (PGMs): platinum, palladium and rhodium. 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. The ceramic monolith of catalytic converters is still a predominant material in its construction among of multitude of catalytic converters which are in circulation. In this work attempts were made to leach additional metals (excluding Pt) from comminuted ceramic monolith. Classic leachant oxidizing media 10M H<sub>2</sub>SO<sub>4</sub>, HCl and H<sub>3</sub>PO<sub>4</sub> were used considering the possibility of dissolution of the ceramic monolith.

*Keywords:* spent catalytic converters, PGMs, hydrometallurgy

Katalizatory samochodowe w swojej strukturze zawierają substancję katalityczną, będącą mieszaniną platynowców: platyny, palladu i rod. Ceny tych metali oraz rosnące zapotrzebowanie na nie, stanowią o konieczności recyklingu zużytych katalizatorów i odzysku z nich wspomnianych metali. Materiał ceramiczny, jako monolit katalizatora jest ciągle materiałem dominującym wśród katalizatorów dostępnych obecnie na rynku. W pracy podjęto próby rozpuszczenia ceramicznego monolitu z użyciem, jako czynnika ługującego klasycznych mediów utleniających 10M H<sub>2</sub>SO<sub>4</sub>, HCl i H<sub>3</sub>PO<sub>4</sub>.

**1. Introduction**

Catalytic converters contain the catalytic substance in their structure, which are a mixture of Platinum Group Metals (PGMs): platinum, palladium and rhodium. Platinum recovery process can be carried out by pyrometallurgical [1] or hydrometallurgical processes [2]. The choice of method depends on the type of catalytic converter with a ceramic or metal carrier. It is possible to combine both methods of pyro and hydrometallurgical, which allows for greater efficiency [3,4]. However the hydrometallurgical treatment has appeared to be the most economical alternative, low energy consumption, and the average platinum recovery efficiency of about 90% [5,6].

Hydrometallurgical process is selected to recovery PGMs through leaching process. PGMs extraction from catalytic converters is usually performed in a 2 step process. The first step is leaching spent converter in a solution in order to dissolve PGMs. In this way, metals contained in converter's carrier are transferred to an aqueous solution. Solution obtained in such way contains PGMs but their concentration is rather small, what become a major issue. Therefore the next stage is concentrating this solution, metals extraction and recovery of pure PGMs from solution in metallic form [7,8]. Pregnant solutions can be then treated by thermal hydrolysis,

electrowinning or zinc cementation [9]. Other processes for PGMs separation from the matrix are solvent extraction, ion exchange or chromatographic separation methods [10-12].

In general, PGMs dissolve in aqua regia and mineral acids, such as hydrochloric acid, nitric acid, sulphuric acid and cyanide, very often used in the presence of chlorine, bromates or hydrogen peroxide. PGMs go into the form of chloride complexes (MCl<sub>6</sub><sup>2-</sup>, MCl<sub>4</sub><sup>2-</sup>, where M – metal belongs to PGMs), cyanide complexes (M(CN)<sub>4</sub><sup>2-</sup>) as a consequence of dissolution these reagents [7, 13, 14]. The chemical resistance of the Platinum Group Metals to the selected acids is shown in Table 1.

Commercially dissolution of Pt can be achieved in highly toxic cyanides or in aqueous mixtures of strong oxidizers and acids. During all leaching processes many liquid wastes are generated which are the potential threat to the natural environment. Process generates toxic nitrogen oxide and chlorine gases as well [7,13].

The problem of platinum extraction form ceramic monolith to form of complexes in acids solutions is well documented, it also includes for example dissolving them in strong acids (HCl–H<sub>2</sub>O<sub>2</sub> and also NaClO–HCl, NaClO–HCl–H<sub>2</sub>O<sub>2</sub>) [13], in aqua regia [7] or using cyanide in recycling PGMs from automotive catalyt [15].

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Most materials from which recovered platinum may be dissolved in oxidizing acids, wherein the dissolution process can be conducted under normal and elevated pressure, as well as at elevated temperatures. Apart from the possibility of platinum extraction from spent catalyst, dissolution experiments (at elevated temperature) only ceramic carriers in acids have been also carried out. However, the number of papers in this fields against the recovery of PGMs by hydrometallurgical methods is greatly limited [16].

TABLE 1

Solubility of selected PGM in acids [14]

Type of reagent	Concentration	Temperature, °C	Solubility, mg·cm <sup>-2</sup> ·h <sup>-1</sup>		
			Pt	Pd	Rh
Aqua regia	-	20	10	10	-
		100	10	10	-
		150	10	10	0
HCl+Br <sub>2</sub>	-	20	0.1	10	0.1
		100	0.1	10	0
HCl+Cl <sub>2</sub>	-	20	0,1	1	-
		80	10	10	0
		100	1	1	0.1
HCl	36%	20	-	-	-
		100	-	0.1	-
HF	40%	20	-	-	-
		100	0,1	0.1	-
HI	57%	20	-	10	-
		100	10	10	-
HBr	60%	20	0.1	10	0.1
		100	0.1	10	1
H <sub>2</sub> SO <sub>4</sub>	96%	20	-	-	-
		100	-	0.1	0.1
HNO <sub>3</sub>	65%	20	0	10	-
		100	0	10	-

This paper attempts to dissolve ceramic carrier of the spent catalytic converter on the basis of alumina. The objective of this study was to extract metals forming ceramic carrier (in particular Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> but excluding Pt) in preliminary laboratory scale leaching experiments using basic acids as lixiviant: hydrochloric acid, sulphuric acid and phosphoric acid.

## 2. Materials and methods

The spent autocatalytic converter procured from Polish auto market was used after grinding to grain size < 0.4 mm. Dominant was fraction < 0,125 mm – 87%. The content of basic metals was determined by the atomic adsorption spectrometry (Solar M6.). Content of platinum and other metals found in catalytic converter is shown in Table 2. Metals such as Fe, and Zn are from the operation and degradation of the engine and automobile exhaust system. A small amount of Pb was also found, which inadvertently is present in unleaded gasoline

[17].

Leaching was conducted with 10 M H<sub>2</sub>SO<sub>4</sub>, HCl and H<sub>3</sub>PO<sub>4</sub> inside a 500 ml flask. Heating and stirring were provided by a hot plate and variable speed stirrer motor, respectively. Sample of spent catalyst was placed inside flask in quantity of 50 g. Ratio of liquid to state phase was 5:1. The content of flask was heated to temperature interval 90-95°C for 1-4 hours and stirred.

TABLE 2

Content of basic metals in analysed catalytic converter

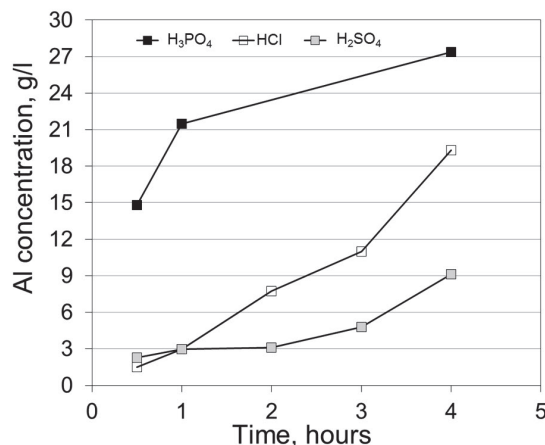
Metal	Zn	Pb	Fe	Pt	Rest (mainly alumina and silicon oxide)
Content, %	0,17	0,12	0,89	0,14	98.68

Samples of 5 ml were taken every 1 hour to analyse concentration of metals. After leaching, residue was washed with distilled water, dried in 60°C during 24 hours, weighted and analysed for metals content. The residue after leaching was analysed by using a scanning electron microscope (SEM), equipped with a Hitachi S 4200. Microanalysis of the chemical composition was performed by EDS method (Energy Dispersive Spectrum).

## 3. Results and discussion

The results of metals leaching from the spent catalyst in the presence of 10 M H<sub>2</sub>SO<sub>4</sub>, HCl and H<sub>3</sub>PO<sub>4</sub> are shown on Fig. 1 and Fig. 2. Fe and Zn were leached in the amount of 2,4 g/l and 0.5 g/l respectively, when HCl was used (Fig. 1). Also Pb and Cr were best extracted during 4 hours in HCl as lixiviant. The effect of reaction time on dissolution rate of Al was slowest for sulphuric acid and next to the chloric and phosphoric acid. Al was dissolved in the range of 27.3 g/l after the reaction for 4 hours using H<sub>3</sub>PO<sub>4</sub>.

Only 26.8% of leached grounded spent catalytic converter was dissolved after the reaction for 4 h for 10M H<sub>3</sub>PO<sub>4</sub> (Fig. 2). Results for HCl and H<sub>3</sub>PO<sub>4</sub> were even poorer - 18%.



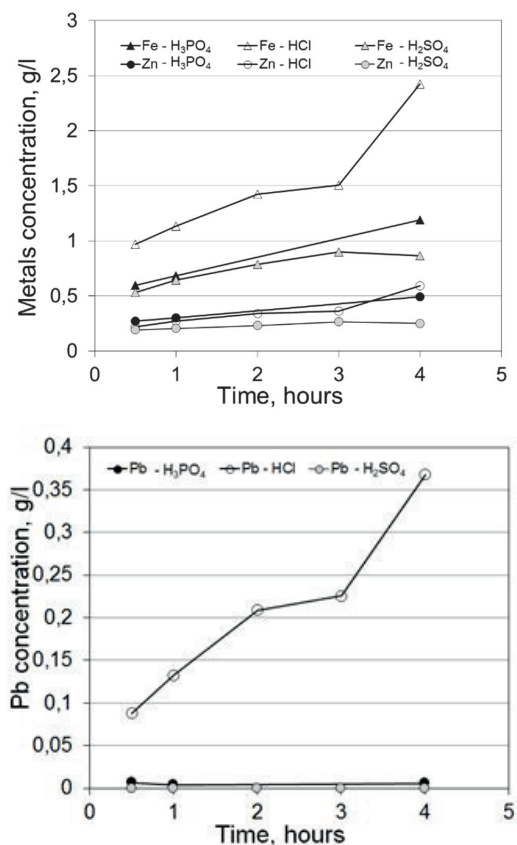


Fig. 1. Metals concentration (Al, Fe, Zn, Pb) in solutions after leaching in acids

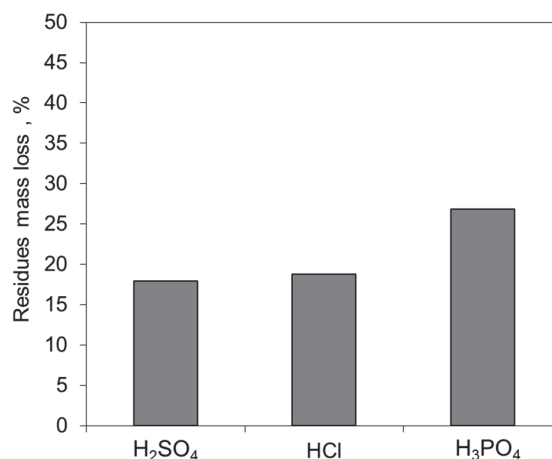


Fig. 2. Residues mass loss after 4 hours leaching in acids

The pictures of the surface of raw spent catalytic converter and converter after the process of leaching in the different acids solutions have been presented in Fig. 3 and in Table 2. The corresponding EDX spectra analysis show that particles of raw spent catalytic converter are mainly composed of Al and Si oxides (Table 3). Al is 15.90 at. % and Si is 7.24 at. % from raw converter whereas the corresponding values are 4.29 at. % and 16.97 at. % from spent catalytic converter leached in H<sub>3</sub>PO<sub>4</sub>. Proportion of Al and Si was changed correspondingly, indicates that Al was dissolved during leaching whereas Si was rather insoluble fraction.

TABLE 3

Chemical composition of the raw spent catalytic converter and residues after leaching in different acids by EDS method (points marked on Fig. 3)

Raw spent catalytic converter (Fig. 3)										
Analysis, No.	Atom, %									
	C	O	Mg	Al	Si	P	S	Ca	Zr	Ti
pt1	-	69.85	4.83	12.57	12.30	-	-	-	0.44	-
pt2	-	70.38	0.43	23.25	2.77	-	-	0.37	2.80	-
pt3	3.38	69.76	2.12	15.90	7.24	0.82	0.32	0.19	-	-
Residue after leaching in H <sub>2</sub> SO <sub>4</sub>										
pt1	3.04	65.55	1.60	16.05	11.69	-	0.56	-	1.15	0.35
pt2	-	65.00	1.43	18.57	13.57	1.42	-	-	-	-
pt3	1.74	67.91	3.80	13.37	12.71	-	0.18	-	0.30	-
Residue after leaching in HCl										
pt1	2.24	68.66	0.33	17.76	8.09	1.94	0.13	-	-	0.84
pt2	-	71.07	1.50	9.33	17.37	0.72	-	-	-	-
pt3	3.76	69.62	1.79	9.35	14.38	0.56	0.17	-	-	0.08
Residue after leaching in H <sub>3</sub> PO <sub>4</sub>										
pt1	-	71.78	0.23	4.40	17.73	5.85	-	-	-	-
pt2	0.88	73.41	1.03	2.61	14.23	7.19	0.20	-	-	0.45
pt3	1.86	69.84	1.22	4.29	16.97	4.94	0.35	-	-	0.33

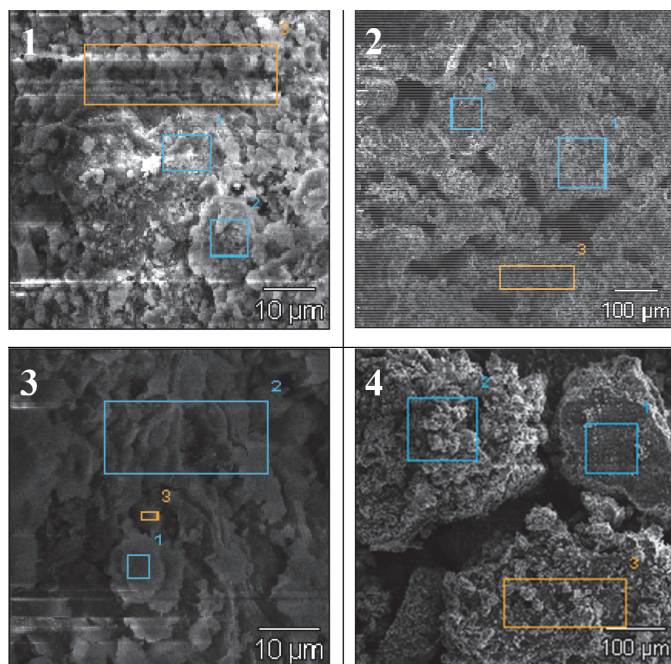


Fig. 3. SEM images of leached surface of spent catalytic converter after 4 hours in different acids: 1 – raw spent catalytic converter; 2 – 10M H<sub>2</sub>SO<sub>4</sub>; 3 – 10M HCl; 4 – 10M H<sub>3</sub>PO<sub>4</sub>.

#### 4. Conclusion

During preliminary test work in which basic 10M acids as lixiviant were used (H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, HCl) for dissolution ceramic carrier of the spent catalytic converter, it was found that 10M H<sub>3</sub>PO<sub>4</sub> was best leaching reagent – 26 % of waste was dissolved. Sulfuric and chloric acid are poorer leachent then phosphoric acid. Al was dissolved partly, whereas Si was rather insoluble fraction. Generally as a whole, the results are rather poor. Possible change within the experiment parameters (e.g. acid concentration, temperature, time, additional oxidants), could get better results especially if phosphoric acid would be used.

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