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PLATINUM RECOVERY FROM USED AUTO CATALYSTS: DISSOLUTION AND PRECIPITATION STUDIES

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ABSTRACT. Noble metals are used in a plethora of applications, from electronic and communication equipments, to aerospacial engines, mobile phones and catalytic convertors. Currently, there is a continuous interest in the recovery of noble metals from waste, as their natural reserves are limited. Herein, the paper presents studies on the recovery of platinum from spent automotive catalysts. The process involves two steps - dissolving of platinum, followed by its precipitation into a hexacloroplatinum complex. The optimum reaction conditions for dissolving Pt from the spent automotive catalyst use a mixture of H_2O_2 + HCl (1:5.5 molar ratio) at 30°C, for 8 h. For the full recovery of platinum from the solution, the volumetric ratio of 4:1 between the platinum solution and the precipitating ammonium chloride solution is optimum. In addition, studies regarding the precipitation time and temperature have also been performed. All the obtained precipitates were analyzed by X-ray powder diffraction and showed the structure of the hexachloroplatinic $(NH_4)_2[PtCl_6]$ complex, with high purity. Upscaling of the processes for technological transfer show promising results in the recovery of platinum from spent automotive catalysts.

Key words. *Spent automotive catalyst, Pt recovery, (HCl + H_2O_2) leaching, precipitation.*

INTRODUCTION

Protecting the environment against the polluting emissions of internal combustion engines, especially diesel ones, led the automotive industry to create catalytic systems containing metals from the platinum group. Catalytic converters are part of the exhaust system in modern vehicles that help to reduce the dangerous gases produced by cars, such as CO, unburned hydrocarbons, and NO_x (Venkateswarlu et al., 2019) The continuous increase in emission standards has led manufacturing companies to improve their automotive catalytic converter to comply with government regulations. The introduction of catalytic converters on the car market in 1975 generates an enormous amount of waste every year, consisting in used, inactive catalysts contained in spent convertors. Also, the very high growth of the automobile industry in the last decade has led to a further increase in this waste (Kovalcik et al., 2021).

To carry out the reduction reactions, automotive catalytic converters mainly use platinum, palladium and rhodium known as platinum group metals (PGM). Spent catalysts are one of the most important secondary resources of PGMs. It is estimated that spent automotive catalytic converters deliver more than 57% of PGMs' European supply, being considered a crucial resource for PGM recovery (Yakoumis et al., 2021). In 2020, the automotive catalyst industry uses about 32% of total Pt, 85% of total Pd, and 90% of total Rh. The quantity of platinum, palladium and rhodium in auto catalysts depends mainly on the vehicle type, manufacturer, country, production year or other additional factors. In two ways converters platinum is the main catalytic metal, the ratio of Pt/Rh being 5 to 1, and the ratio of Pd/Rh 7 to 1, with actual concentration of platinum in a large range (from tens to thousands of ppm depending on the above-mentioned factors) (Fornalczyk et al., 2009).

Recovering PGM from the spent automotive catalysts can be realized by two methods: the pyrometallurgical and hydrometallurgical methods. The pyrometallurgical methods use high temperature (over 1600°C) generated by plasma or by electric arc furnace to melt the PGMs (Peng et al., 2017; Dong et al., 2015; Devyatykh et al. 2018). The second type of methods (hydrometallurgy) are more eco-friendly and offer several advantages: lower process temperature, lower energy consumption, higher purification yield, process control and economically profitability (Saguru et al, 2018; Rzelewska-Piekut and Regel-Rosocka, 2018; Asadzadeh and Sajadi, 2018).

The hydrometallurgical processes are based on the dissolution of PGMs using strong oxidizing media, followed by the metal recovery from solution by selective precipitation and calcination. Among the three PGM metals, platinum is found in the largest quantities in used car catalytic converters and therefore is suitable for recovery by hydrometallurgical methods. Different leaching processes can be used for the dissolution of PGMs, all being combinations of hydrochloric acid and strong oxidizing agents (HNO_3, Cl_2, NaClO, $NaClO_3$, H_2O_2, etc.) (Grumett, 2003; Marinho et al., 2011; Sun and Lee, 2011).

In this study, spent catalysts from unknown producers were used to develop a more eco-friendly and low energy consuming method for platinum recovery than the usual patented methods. For the solubilization of the platinum from waste catalysts, HCl and H_2O_2 as oxidizing agents are used, avoiding thus the usage of nitric and sulfuric acids, which generate harmful gaseous and liquid wastes. The reduction potential of the H_2O_2 shows that it is capable to solubilize platinum, providing favorable reaction kinetics (Barakat et al., 2006). The reaction of dissolution undergone by platinum is described by the following equation:

$$Pt_{(s)} + 2H_2O_{2(aq)} + 6HCl_{(aq)} \leftrightarrow [PtCl_6]^{2-}_{(aq)} + 2H^+_{(aq)} + 4H_2O \qquad (1)$$

where subscript aq and s represent aqueous and solid, respectively.

This step is followed by filtration and selective reduction of the formed platinum complexes ($PtCl_6^{2-}$) by NH_4Cl (Burkin, 2001).

$$[PtCl_6]^{2-}_{(aq)} + NH_4Cl_{(aq)} \leftrightarrow (NH_4)_2[PtCl_6]_{(s)} \qquad (2)$$

The reaction needs saturated ammonium chloride solution which was added to the hexachloroplatinic acid solution in order to precipitate diammonium hexachloroplatinate complex (Barakat and Mahmoud, 2004)

EXPERIMENTAL

Materials and Chemicals

Spent automotive catalysts with a honeycomb structure were ground and sieved to a particle size fraction lower than 1 mm. Chemicals used for the leaching procedure were hydrochloric acid (HCl, 37%) and hydrogen peroxide (H_2O_2, 30%, w/w) solutions from Honeywell-Fluka, used as purchased. Ammonium chloride (NH_4Cl) employed for the precipitation procedure was used as received from VWR Chemicals. Double distilled water was used throughout the experimental procedures.

Instruments

Inductively coupled plasma quadrupole mass spectrometry (ICP-MS, ELAN DRC-e, Perkin Elmer) was used for elemental analysis and concentration measurements. X-ray powder diffraction (XRD) measurements were made using a Bruker D8 Advanced Diffractometer with Cu Kα1 radiation, 40 kV operating voltage and 40 mA current.

RESULTS AND DISCUSSIONS

Leaching of Platinum from the spent automotive catalysts

The choice of leaching procedure of platinum from spent automotive catalysts was motivated, besides the Pt recovery efficiency, by safety and environmental reasons if employed in a dedicated facility, and not in a specialized laboratory. Thus, although several Pt leaching procedures proved their efficiency, for the purpose of this work, a mixture of H_2O_2 and HCl in a molar ratio of 1:5.5 was used. By means of this mixture, leaching of Pt from the spent automotive catalysts undergoes as described in Introduction.

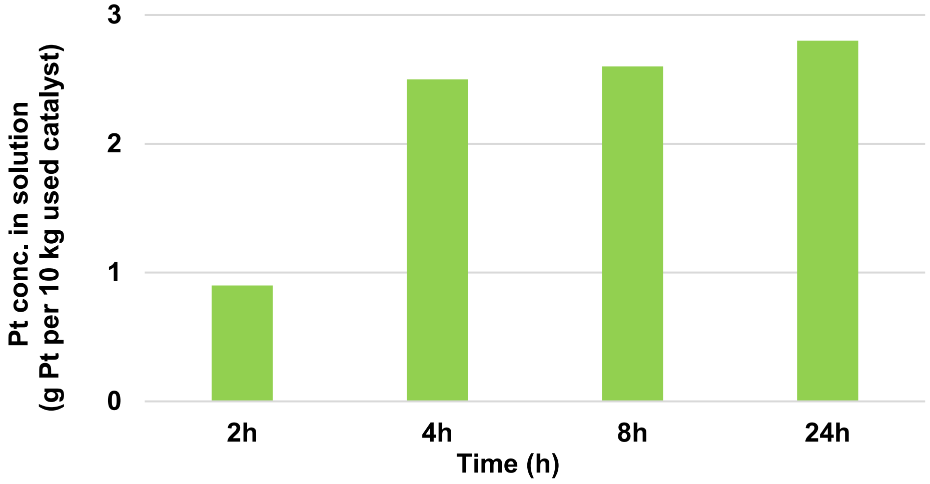

Fig. 1. *The influence of dissolving time on the Pt concentration in the leached solution (conditions: 0.5 g used catalyst; 0.68 ml H_2O_2 (conc) + 3.13 ml HCl (conc); molar ratio = 1: 5.5, 30°C).*

In order to optimize the leaching procedure by means of H_2O_2+HCl, the influence of dissolving time was evaluated. Thus, several reaction mixtures using the same amounts of grounded spent catalyst and H_2O_2 and HCl solutions were stirred in round bottom flasks at 30°C for different time ranges. For a better understanding, the amount of Pt leached from the spent automotive catalyst was expressed as grams of Pt per 10 kg of catalyst. Figure 1 illustrates the variation of dissolved Pt from the spent catalyst as a function of time. It may be observed that the longer the reaction time, the greater the amount of Pt recovered from the spent catalyst. However, the amount of dissolved Pt from the solid catalyst increases to a very low extent if the reaction time increases from 4 to 24 h. It may be concluded that the optimum reaction time for dissolving Pt from the spent automotive catalyst with a mixture of H_2O_2 + HCl (1:5.5 molar ratio) at 30°C is 8 h.

Precipitation of Platinum from the leached solutions

Platinum can be separated from the acidic leached solution by precipitation with ammonium chloride, as described in Introduction. In this precipitation reaction, the molar ratio of the reactants and temperature are among the most important variables. These parameters can be varied in a wide range, from 1:5 to 1:40 (Nguyen et al., 2022) and 25-80°C (Nagai et al., 2017), respectively, and the outcome of the precipitation reaction depends on the initial platinum content of the solution. It should be accounted that the solubility of the hexachloroplatinic complex is rather high, therefore finding the right conditions to precipitate the Pt complex without its further dissolving, in order to maximize the recovered amount of Pt, is of utmost importance.

Thus, optimization of the precipitation procedure was pursued by investigating the influence of several parameters such as: (a) volume of saturated NH_4Cl solution; (b) temperature; (c) reaction time. Upscaling of the precipitation procedure was also pursued by investigating the amount of platinum solution which can be efficiently treated. Each precipitation experiment was performed using an initial leached acidic Pt solution with a concentration of 155 mg Pt/L and a saturated solution of NH_4Cl (45 g NH_4Cl to 100 mL H_2O, dissolved at 40°C).

(a) Influence of saturated NH_4Cl solution volume

The addition of supplementary NH_4Cl precipitating agent is accompanied by the presence of extra water in the system, which highly affects the precipitation – dissolution process due to the very low concentration of Pt in the initial leaching solution (figure 2). It was established that, for the platinum solution used in this study, the volumetric ratio of 4:1 between the platinum solution and the precipitating solution is optimum. The rest of the parameters were optimized using this ratio between the reagents.

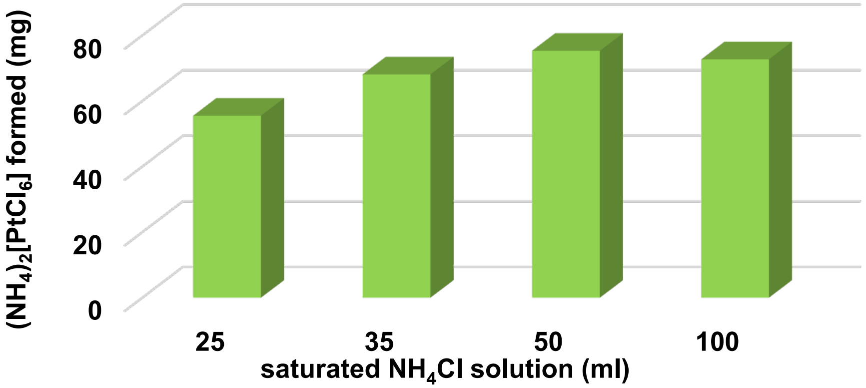

Fig. 2. *The influence of NH_4Cl quantity on the formation of the platinum precipitate (conditions: 200 ml platinum solution; 15 minutes reaction time; 40°C).*

(b)Influence of temperature

Three temperature values were tested for the precipitation of 200 ml leached Pt solution with the determined optimum volume of saturated NH_4Cl solution of 50 ml. As illustrated by the results presented in figure 3, it may be observed that the amount of formed platinum precipitate increases to a very low extent with increasing reaction temperature. If at 40°C 73 mg of $(NH_4)_2[PtCl_6]$ is formed, by doubling the temperature only a benefit of 3 mg of precipitate is obtained (an enhancement of 5.5 %), which does not economically justify the extra amount of employed energy. Thus, it may be concluded that the optimum precipitation temperature is 40°C.

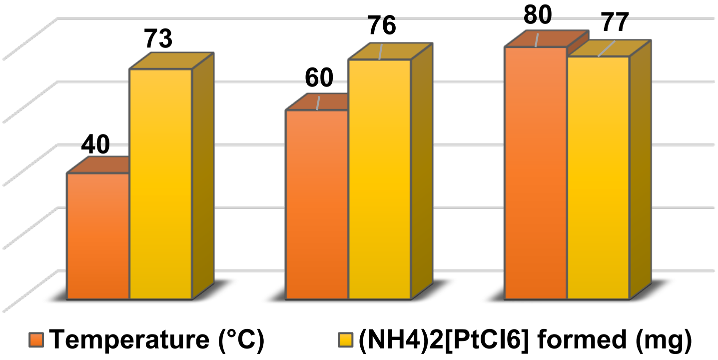

Fig. 3. *The influence of temperature on the formation of the platinum precipitate (conditions: 200 ml platinum solution; 50 ml saturated NH_4Cl solution; 15 minutes reaction time).*

(c) Influence of reaction time

Considering the rather high solubility of the Pt complex, this should be removed from the solution in order to avoid its further dissolving. However, the precipitate does not form immediately after the saturated NH_4Cl solution is added to the leached Pt solution, but slowly starts to form under the stirring conditions. Therefore, in order to find the optimum reaction time for the formation of the platinum precipitate, six precipitation experiments were performed using 200 ml Pt solution and 50 ml saturated NH_4Cl solution at 40°C, in the time range 5 – 120 min. Results presented in figure 4 show that the highest amount of $(NH_4)_2[PtCl_6]$ precipitate is obtained after only 5 min of reaction, while any other increase in the reaction time leads to a decrease in the obtained amount of precipitate as a consequence of its partial dissolving in the solution. It can be observed that after 15 minutes, the equilibrium between precipitation and dissolution is reached. It may be concluded that a 5 min reaction time is the necessary required time to precipitate the largest amount of $(NH_4)_2[PtCl_6]$. This reaction time was further used for the upscaling experiments.

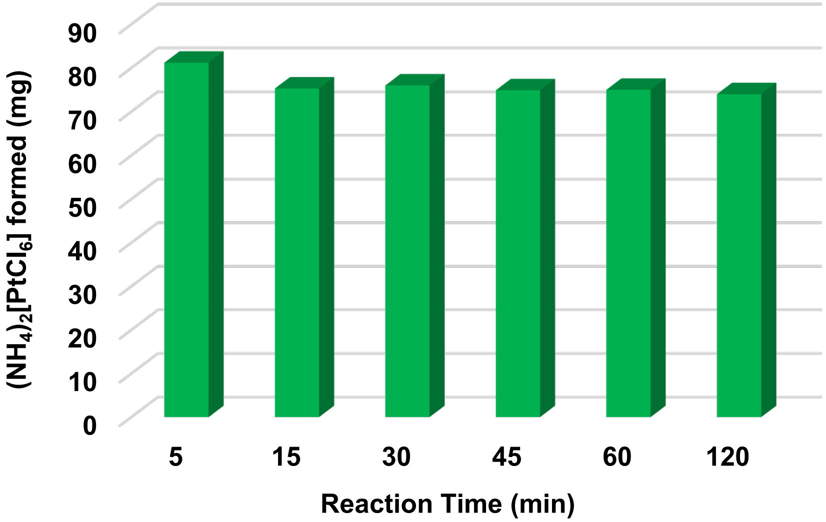

Fig. 4. *The influence of reaction time on the formation of the platinum precipitate (conditions: 200 ml platinum solution; 50 ml saturated NH_4Cl solution; 40°C).*

(d) Structural analysis of $(NH_4)_2[PtCl_6]$ complex and precipitation degree analysis

In order to confirm the formation of the hexacloroplatinic complex, and also to check its purity, the obtained precipitates were analyzed by powder X-ray diffraction (XRD). The measured diffractograms were identical for all the above experiments and proved the reproductibility of the precipitation and separation of $(NH_4)_2[PtCl_6]$. The comparison of the experimental pattern with the one from XRD database proved the identity of amonium hexachloroplatinate complex (figure 5). No other additional diffraction peaks were identified.

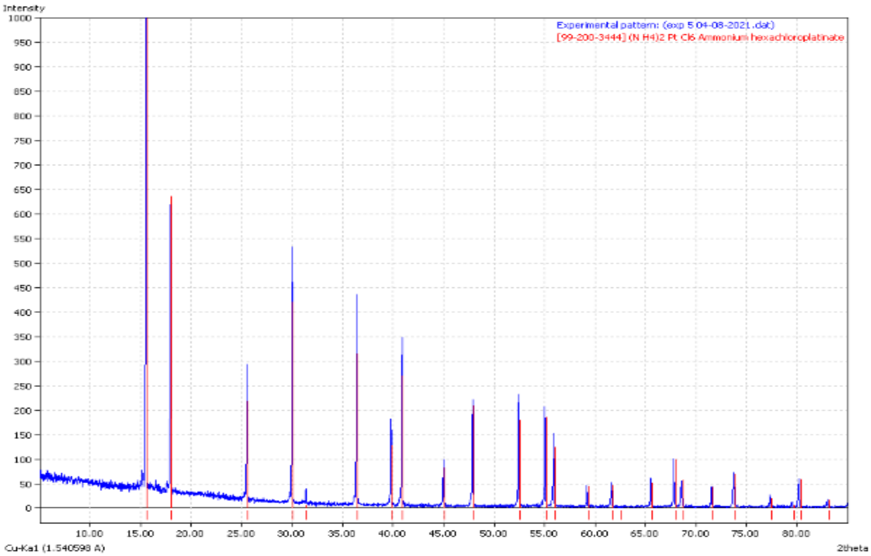

Fig. 5. *XRD pattern of the platinum precipitate.*

The balance of the platinum element has been calculated. The initial solution (200 ml) contains 32 mg of platinum while the precipitate (81 mg) incorporates 33 mg of platinum element. This is indicative for a total recovery of platinum from the solution, by using the optimized reaction conditions.

(e) Upscaling of the precipitation procedure

Scale up batches were performed in order to demonstrate the feasibility of the precipitation process to be later transferred to a pilot technology. The volume of initial solution has been doubled step-by-step up to 800 ml, while the quantity of the formed precipitate increased linearly, with the same increment (figure 6). The quality of the platinum precipitate was measured for each experiment. The results showed that high purity amonium hexachloroplatinate was formed every time. This shows the real potential of this process to be transferred into production.

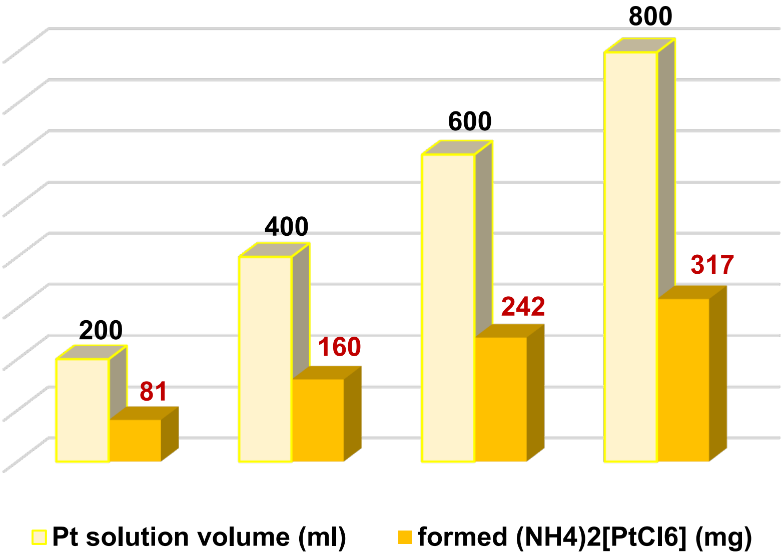

Fig. 6. *Upscaling of the platinum precipitation process; (conditions: 40°C; 5 minutes reaction time).*

CONCLUSIONS

An optimized method for platinum recovery from real spent auto catalysts was developed. The method comprises two steps: platinum dissolution from catalysts and platinum recovery from acid leaching solutions as amonium hexachloroplatinate. The optimum parameters of recovery metod are: (i) dissolution in $HCl+H_2O_2$ solution (molar ratio = 1 : 5.5), at 30°C for 8h; (ii) the volumetric ratio of leached platinum solution and the saturated NH_4Cl solution is 4:1; (iii) precipitation temperature 40°C; (iv) precipitation time 5 minutes.

High purity amonium hexachloroplatinate is obtained from platinum acid solution using the optimised parameters.

The precipitation method was scaled up to 800 mL platinum solution proving its potential to be further transfered and adapted for higher scale (pilot scale).

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