

Towards environmentally safe recovery of platinum from scrap automotive catalytic converters

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Abstract

Dissolution of platinum that is incorporated in automotive catalytic converters is performed through chemical methods, which generate a large amount of secondary chemical waste that is hazardous to the environment. Therefore, there is a need to develop a cost-effective and environmentally friendly process for platinum dissolution. This paper summarizes research on the possibility of 10 HCl: 1 H₂O₂ solution to replace aqua regia for the mentioned task. Dissolution of platinum in this solvent was studied as functions of agitation rate, time, liquid/solid mass ratio, and the reaction temperature. A comparison of the solvent's efficiency with that of aqua regia was provided at every step. It was demonstrated that 95% dissolution of platinum in catalytic converters could be achieved with 10 HCl: 1 H₂O₂ solution under moderate experimental conditions, which are easy-to-adopt to industrial plants.

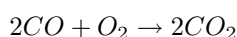
Key Words: Platinum, recovery, catalytic converter, aqua regia, HCl: H₂O₂ solution.

Introduction

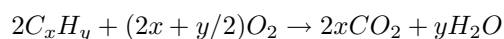
Platinum-based catalytic converters have been used increasingly in automotive exhausts since the mid-1970s in the USA, and more recently around the world to meet emission limits enforced by international legislation (Hennion, 1983).

A catalytic converter is a catalyst that provides an environment for a chemical reaction wherein toxic combustion by-products are converted to less-toxic substances. These chemical reactions can be grouped into 5 as below:

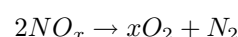
1. Oxidation of carbon monoxide to carbon dioxide:



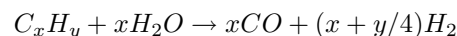
2. Oxidation of unburned hydrocarbons to carbon dioxide and water:



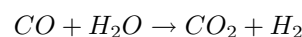
3. Reduction of nitric oxides to nitrogen and oxygen:



4. Steam Reforming:



5. Water – Gas Exchange:



Catalytic converters contain either platinum or platinum/palladium combinations to convert carbon monoxide and hydrocarbons to carbon dioxide and water. In recent catalysts, rhodium is employed for reduction of nitric oxides since it outperforms all other metals of the group in this task.

Platinum and platinum group metals are present in very small quantities (0.05% – 1.0 % by weight)

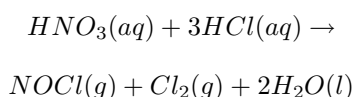
in catalytic converters. However, given their intrinsic value, it is worth recovering them from the spent exhaust systems (Kuczynski et al. 1995).

Platinum extraction from scrap catalytic converters is usually performed in a 2-step process. The first step is leaching the converter in a solution that dissolves Pt. In this way, Pt incorporated in the converter is transferred to an aqueous solution. The second step involves the recovery of pure Pt from this solution in metallic form.

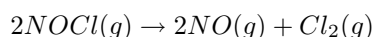
Unfortunately, both steps generate a large amount of secondary chemical waste, which poses environmental issues. In fact, commercially acceptable dissolution of Pt can be achieved only in highly toxic cyanides (Cheng and Huang, 2006) or in aqueous mixtures of strong oxidizers and acids, which are again highly hazardous and toxic.

One of the least hazardous solvents is the oldest one, the aqua regia, which is 3:1 (by volume) mixture of HCl and HNO₃ solutions. The fact that aqua regia dissolves platinum is well-known, and it has been successfully employed in Pt recovery from spent catalysts (Matjie et al., 2005 and Baghalha et al., 2008).

Yet, aqua regia is not totally safe to the environment. Even if it were to be disposed in line with the regulations, aqua regia causes toxic gas emissions. Such an emission occurs even in the absence of any dissolution process. This is because upon mixing hydrochloric acid and nitric acid, chemical reactions that yield toxic gases occur. The first of these gases is nitrosyl chloride, NOCl (*g*), which is formed along with chlorine gas according to the reaction below:

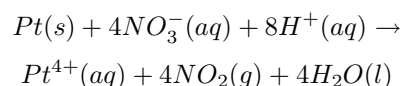
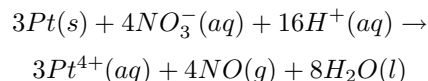


Nitrosyl chloride further decomposes into nitric oxide and chlorine. This dissociation is equilibrium-limited. Therefore, in addition to nitrosyl chloride and chlorine, the fumes over aqua regia contain nitric oxide.



Nitric oxide is one of the gases against which catalytic converters in automobile exhausts are employed. It is toxic and is an actor in ozone layer depletion (Dessler, 2000). In the atmosphere, it may further convert to nitric acid, an important contributor of acid rains (Kennedy, 1992).

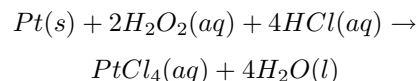
A further emission of NO takes place when platinum is dissolved in aqua regia. During this dissolution, NO₂, another element of air pollution, may accompany NO. The following chemical reactions depict how these hazardous gases are formed during the dissolution of platinum:



Accordingly, a cleaner alternative to aqua regia has been sought for a long time. As it is estimated that platinum recovery from spent catalytic converters will lead to a large business opportunity, it is imperative to find environmentally friendly solvents for this task. However, to date, research, like that of Pinheiro et al. (2004), to find less hazardous alternatives has not offered efficient solvents for Pt in catalytic converters.

When researching for an alternative to aqua regia, which is safer to the environment, a considerable amount of work is focused on binary mixtures of hydrochloric acid, HCl. This is because among the strong inorganic acids, which are commonly utilized in industry, hydrochloric acid is one of the least hazardous ones. Furthermore, intermediate strength hydrochloric acid solutions are quite stable upon storage, maintaining their concentrations over time.

In this study, for the dissolution of the Pt, a HCl-H₂O₂ mixture has been worked on as an alternative to aqua regia. HNO₃ of aqua regia is replaced by hydrogen peroxide, H₂O₂, in this combination, and Pt dissolution now takes place in line with the reaction below:



This change is appealing from an environmental point of view since mixing HCl and H₂O₂ or dissolution of Pt in this solution yields less hazardous gases.

The dissolution process was studied with an optimization with respect to 3 parameters: agitation rate, solid/liquid mass ratio (wt/wt), and the reaction temperature. Time progression of the dissolution was also examined as it is an important parameter determining the cost of the process. Any dissolution experiment conducted with the HCl-H₂O₂

mixture has also been tried with aqua regia, and a comparison of the efficiency of the 2 solvents was provided at each step.

Experimental Work

The catalytic converter used in the study was obtained from a disposed exhaust of a Citroen-make automobile. It was a monometallic, Pt/Al₂O₃ catalyst in the form of a ceramic honeycomb. First, outer shell surrounding the converter was removed and the honeycomb structure inside the shell was taken out. This structure was crushed, ground, and sieved to 250-355 µm using ASTM standard sieves (-45 +60 mesh). Then this catalytic converter powder was mixed in a 3-dimensional mixer to achieve homogenization. All analyses and leaching experiments were performed on samples taken from this homogenized powder.

Chemical analysis of the catalytic converter powder was carried out by X-ray fluorescence analysis and spectrometric methods, and results obtained from the chemical analysis are given in Table 1.

Long duration leaching of powder samples in aqua regia at high temperatures, and subsequent elemental analyses by inductively coupled plasma optical emission spectrometry revealed the platinum content of the converter to be 0.084% by weight.

High purity hydrochloric acid (37%, Merck), concentrated nitric acid (65%, Merck), and hydrogen peroxide, H₂O₂ (36%) were employed in dissolution experiments. A fresh solution was prepared for each

experiment. The HCl-H₂O₂ mixture was prepared in a volume ratio of 10 HCl: 1 H₂O₂. Distilled water was used for all purposes, namely wet chemical analyses, dilution, and filtration.

Each experiment was performed with a 1000 mg sample of catalyst powder in a cylindrical glass beaker, with a 50 mL of volume and 6 cm of diameter, under magnetic agitation. For the sake of consistency, beakers and magnets of the same kinds were employed at each run.

This work investigated the effects of 4 different parameters: agitation rate, dissolution time, the liquid/solid mass ratio, and the solution temperature. Experimentation was carried out by varying one parameter at a time. A series of experiments were conducted to see the effect of each parameter.

When temperature was not the parameter under the study, all experiments were conducted at room temperature.

Following each run, solid/liquid separation was carried out by centrifugation using a NUVE NF 415 centrifuge. The concentration of the platinum ion remaining in the solution was measured with an inductively coupled plasma-optical emission spectrometer (ICP-OES) (Perkin Elmer, Optima 2100 DV). X-ray fluorescence (XRF) analyses of powder samples were performed before and after leaching as a second means to monitor the change of Pt content. The XRF spectrometer used for this purpose was a Thermo Fisher model NITON XL3t, which was operated at 40 kV and 0.005 mA settings using Cu K-α radiation.

Table 1. Chemical composition of catalytic converter powder as determined by XRF and ICP-OES measurements.

Components	Wt /wt, % determined by XRF	wt, % determined by ICP-OES
Al ₂ O ₃	93.2 %	-
S	0.93 %	-
SiO ₂	0.85 %	-
CaO	0.49 %	-
Fe ₂ O ₃	0.19 %	-
Cl	0.19 %	-
Ti	3560 ppm	1790 ppm
Zn	103 ppm	82 ppm
Zr	152 ppm	217 ppm
Pd	< D.L.	14 ppm
Co	< D. L.	36 ppm
Ag	< D.L.	9.6 ppm

Results and Discussions

The following results outline the effects of aforementioned parameters on the dissolution of platinum content of a catalytic converter in aqua regia and 10 HCl- 1H₂O₂ solutions.

Effect of agitation rate

The first experimental series was performed to study the effect of agitation rate on the dissolution efficiency. For leaching platinum in 1000 mg catalytic converter powder, 10 mL of aqua regia and HCl-H₂O₂ solutions were employed. Four different agitation rates, increasing from 200 rpm to 500 rpm in steps of 100 rpm, were tested. After 60 min of dissolution, the solution was filtered and the platinum content was measured by ICP- OES. The percentages of dissolved platinum were calculated after these concentration measurements and are displayed in Figure 1.

Several conclusions can be drawn from the 2 curves in the Figure. First, HCl-H₂O₂ solution performs better dissolution than aqua regia at room temperature. This is rather promising when it is considered to replace aqua regia; however, the attained dissolution percentages are too low to be a part of a cost-effective recovery process. As Benson et al. (2000) describes a cost-effective Pt recovery process as the one that provides more than 95% recovery of the whole Pt content, other parameters need to be optimized.

The second important point about the curves is a significant increase in the dissolution efficiency as the agitation rate increases from 200 to 300 rpm. This increase is followed by a rather flat line through the rest of the curves. The identity of this pattern for both curves suggests the manifestation of a kinetic factor. It is well-known that solid leaching processes require fast agitation to suspend solid particles and to preferentially eliminate the external mass-transfer resistances, which are required to achieve fast kinetics, especially in small-sized reactors. In the present experimental setting, the agitation rate of 300 rpm corresponds to the agitation that provides a complete suspension of the solid particles, and thus beyond that value there is no significant increase in the dissolution efficiency.

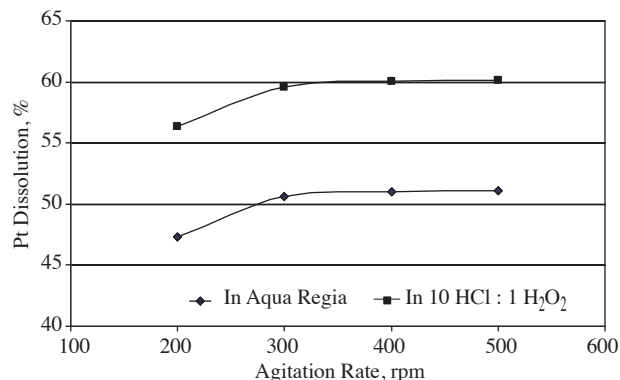


Figure 1. Platinum dissolution efficiency as a function of agitation rate. Solid/liquid mass ratio = 1/10, T = room temperature, and agitation time = 60 min.

Time progression of platinum dissolution

In this experimental series, the time progression of the platinum dissolution process was studied. In line with the findings from the previous subsection, agitation rate was fixed at 300 rpm while other experimental parameters were kept the same. Five experiments, whose durations varied from 30 min to 4 h, were conducted to find out the time progress of dissolution in each of the solvents.

Figure 2 shows the platinum dissolution progressions for the 2 solvents as a function of time. In the HCl-H₂O₂ solution, 67% of platinum was dissolved after 4 h while in aqua regia solution this value could reach %52 at the end of the same period. More than 75% of the total dissolution was completed within 30 min for both solvents. This was followed by a slowing of the dissolution rate and only less than 2% of the whole dissolved amount was dissolved in the last 2 h for both solutions.

Effect of solid/liquid ratio

The solid to liquid mass ratio (wt/wt) was another major parameter that was investigated. Five levels - 1/5, 1/10, 1/15, 1/20, and 1/25- of solid/liquid ratios were examined. All solutions were prepared using 1000 mg of powder, and the temperature of all these tests was kept at room temperature. The obtained platinum extraction results for these experiments are presented in Figure 3. For both solvents, the extraction kinetics becomes faster as the solid/liquid ratio increases.

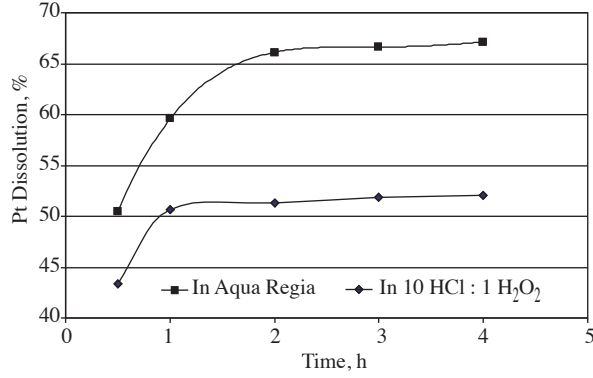


Figure 2. Platinum dissolution efficiency as a function of time. Solid/liquid mass ratio = 1/10, T = room temperature, and agitation rate = 300 rpm.

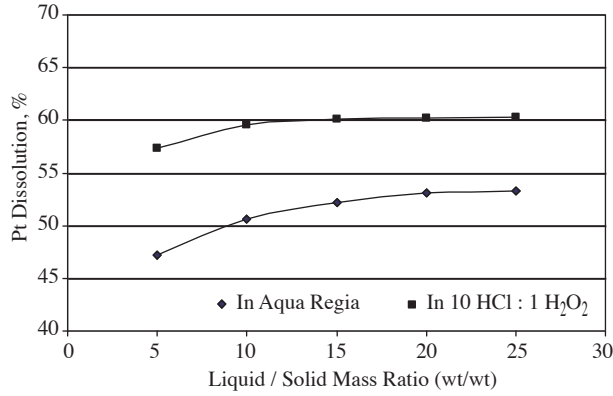


Figure 3. Platinum dissolution efficiency as a function of liquid/solid mass ratio. Agitation rate = 300 rpm, T = 25 °C and duration = 60 min.

Effect of temperature

The Pt dissolution kinetics was finally studied at 5 temperature levels from 25 to 80 °C. For leaching platinum in 1000 mg of catalytic converter powder, 20 mL of aqua regia and HCl-H₂O₂ solutions were employed. Each dissolution experiment was conducted for 2 h at an agitation rate of 300 rpm.

The results of these experiments for the extraction of Pt are presented in Figure 4. The figure clearly shows that increasing temperature greatly enhances the extraction kinetics of Pt dissolution for both solvents. This large temperature impact suggests high activation energies for the dissolution reactions.

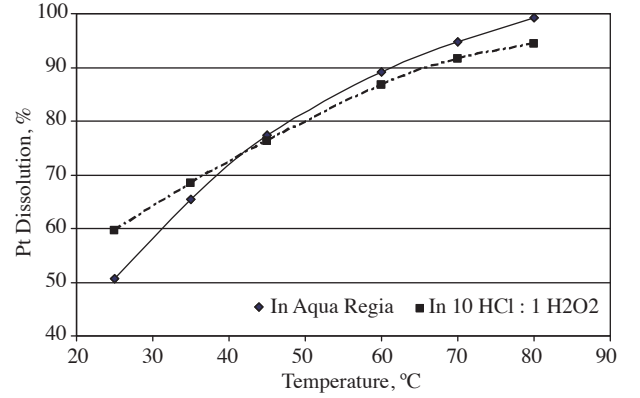


Figure 4. Platinum dissolution efficiency as a function of temperature. Agitation rate = 300 rpm, liquid/solid mass ratio = 20, and duration = 2 h.

The sharp increase is more significant for aqua regia whose efficiency surpasses that of 10 HCl: 1 H₂O₂ solution after a temperature of 45 °C. While a 95% dissolution efficiency was attained at 70 °C with aqua regia, the 10 HCl: 1 H₂O₂ solution had to be heated to 80 °C to achieve the same level of efficiency.

Figure 5 shows the XRF energy spectra of the powder sample, which was leached in 10 HCl: 1 H₂O₂ solution at 80 °C for 2 h, before and after leaching. The spectrum obtained after leaching is drawn atop the other one by adding a constant value that does not alter the scale. The vertical lines, which cut both spectral curves, denote the points where XRF peaks of Pt should be situated. Pt peaks at 9.44 keV and 11.1 keV, which can be seen clearly

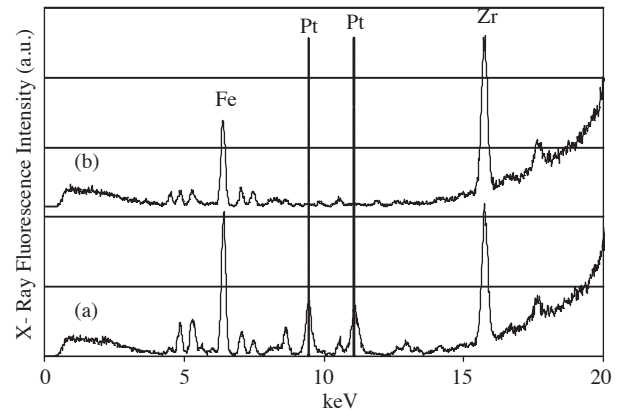


Figure 5. X-Ray Fluorescence Spectrum of powder sample a) before and b) after leaching in 10 HCl: 1 H₂O₂ solution.

in the lower spectrum, disappear in the upper one that belongs to sample after 94.78% of its Pt content being extracted. These XRF spectra have served as a verification of the results obtained by the ICP optical emission spectrometer.

Conclusions

This study explored the possibility of extracting the platinum content of spent catalytic converters using 10 HCl: 1 H₂O₂ solution as a solvent, which would be less hazardous to the environment than a commonly used one, aqua regia. The capability of this solution to dissolve platinum in powdered samples obtained from a scrap catalytic converter was examined in detail as functions of agitation rate, liquid/solid mass ratio, time, and temperature, all in comparison with aqua regia.

Temperature was found to be the most important parameter affecting the efficiency of platinum dissolution for both solutions. Commercially acceptable rates of dissolution could not be achieved at around room temperature with both solvents. The 10 HCl: 1 H₂O₂ solution which performed better than the aqua regia at room temperature fell behind it at temperatures higher than 45 °C. Yet, a cost-effective dissolution of 95% of the whole platinum content of the catalytic converter was achieved with this solution under moderate experimental conditions, which are easy-to-adopt to the industrial plants.

Nomenclature

ICP-OES	Inductively coupled plasma optical emission spectroscopy
XRF	X-Ray fluorescence
D. L.	Detection Limit

References

- Baghalha M., Khosravian H. and Mortaheb, "Kinetics of Platinum Extraction from Spent Reforming Catalysts in Aqua-Regia Solutions", *Hydrometallurgy*, (in press), doi:10.1016/j.hydromet.2008.06.003, 2008.
- Benson M., Bennett C.R., Harry J.E. and et al., "The Recovery Mechanism of Platinum Group Metals From Catalytic Converters in Spent Automotive Exhaust Systems", *Resources, Conservation and Recycling*, 31 1–7, 2000.
- Chen, J., and Huang, K., "A New Technique for Extraction of Platinum Group Metals by Pressure Cyanidation", *Hydrometallurgy*, 82, 164–171, 2006.
- Dessler, A.E., *The Chemistry and Physics of Stratospheric Ozone*, Academic Press, San Diego, 2000.
- Hennion F.J. "Availability of Precious Metals from Spent Catalysts. Platinum Group Metals — An In-depth View of the Industry", 1983 IPMI Seminar, Williamsburg, VA, 10–13, 61–81, 1983.
- Kuczynski R.J., Atkinson G.B. and Dolinar W.J., "Recovery of Platinum Group Metals from Automobile Catalysts — Pilot Plant Operation", In: *Third International Symposium on Recycling of Metals and Engineered Materials*. (ed. Queneau P.B. and Preston R.D.), The Minerals, Metals & Materials Society, Warrendale, Pennsylvania, 527–541, 1995.
- Kennedy, I. R., *Acid Soil and Acid Rain*, Research Studies Press, Tauton, 1992.
- Matjie R.H., Scurrel M.S. and Bunt J. "The Selective Dissolution of Alumina, Cobalt and Platinum from a Calcined Spent Catalyst Using Different Lixiviants", *Minerals Engineering* 18, 801–810, 2005.
- Pinheiro A.A., Lima, T.S., Campos P. C. and Afonso J.C., "Recovery of Platinum from Spent Catalysts in a Fluoride-Containing Medium", *Hydrometallurgy* 74, 77–84, 2004.