

Platinum leaching from automotive catalytic converters with aqua regia

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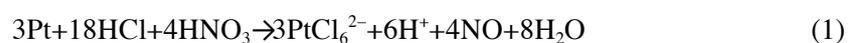
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Abstract. Herein, kinetics extraction of platinum from spent auto catalysts, using nitric acid as an oxidant in hydrochloric acid solution, was investigated. The parameters such as temperature, hydrochloric and nitric acid concentrations, stirring speed, particle size and liquid/solid ratio, were analysed. The kinetic data were analysed using the shrinking core model. A variant of this model fits the kinetic data more appropriately. At a temperature of 90°C, the values of R² in surface chemical reactions and diffusion were 0.819 and 0.937, respectively. With the alternative model, however, 0.991 was obtained. The activation energy for the dissolution was 35.75kJ/mol.

1. Introduction

Several investigations have been reported concerning the extraction of platinum from spent catalysts through pyro or hydrometallurgical processes [1]. Pyrometallurgical processes require high energy consumption, making the process less attractive to the industry. Instead, hydrometallurgy has emerged as the most suitable processing method for the recovery of a variety of metals. In the case of platinum, dissolution process has been frequently studied in the presence of chloride ions, Cl⁻ [2], and has been claimed that chloride is the only cost-effective medium to platinum dissolution [3-6]. In the commonly applied hydrometallurgical processes, platinum from used auto catalytic converters is leached in aqua regia, a simple 1:3v/v mixture of concentrated hydrochloric and nitric acids.

Aqua regia produces strong oxidizing agents: nitrosyl chloride, NOCl, and chlorine gas, Cl₂ [7]. The nitrosyl chloride further hydrolyses to nitrous acid, HNO₂, and chloride. Nitrous acid undergoes decomposition by a disproportionation reaction, producing nitrogen dioxide, NO₂, and nitric oxide, ·NO. The latter is an unstable radical, which can disproportionate into nitrogen dioxide and nitrous oxide. The simultaneous presence of several oxidizing agents makes the aqua regia very reactive, at the same time making complicated the mechanism of platinum dissolution. Thus, for instance, it has been suggested that HNO₂ in HNO₃ activates passive metals [8-10]. Therefore, in an overall form, Pt dissolution can be described by the following reaction (Equation 1).



In the present study, kinetics of auto catalyst dissolution by aqua regia has been studied. The influence of stirring speed, particle size, sulfuric and nitric acid concentrations, temperature and liquid/solid ratio was investigated.

2. Experimental

A ceramic-honeycomb-type automobile catalytic converter was crushed, dried and sieved to four size fractions. Both, chemical analysis of sample and a complete description of the leaching experiments can be consulted in another paper in this same volume. The leaching was performed for four hours. At specified time intervals, 10mL of the solution was taken from the leach solution and diluted using ultra-pure water (resistivity 18.2M Ω). All analyses of platinum were done using an atomic absorption spectrophotometer. The experimental conditions are shown in Table 1. Keeping the other parameters constant, the effect of each parameter on the dissolution rate was evaluated.

Table 1. Parameter values used for the leaching of platinum.

Parameter	Value
Temperature ($^{\circ}$ C)	40, 60, 80, 90, 100
[HCl] (M)	6.0, 8.5, 10.0, 12.0, 13.0
[HNO ₃] (M)	5.0, 7.5, 8.5, 9.5, 11.0
Particle size (μ m)	-53, -75+53, -106+75
Liquid to solid ratio (mL/g)	10, 20, 40
Stirring speed (rpm)	200, 400, 600

3. Results and discussion

3.1. Factor affecting Pt extraction with aqua regia

The effect of the solid/liquid ratio on platinum dissolution was studied for (10, 20 and 40) mL/g at 80 $^{\circ}$ C in a solution containing 12.0M HCl and 9.5M HNO₃. The stirring speed and the particle size were kept constant at 400rpm and -53+45 μ m, respectively. Platinum extraction increased with a decrease in the amount of solid (data not shown); this was caused by the increase of acid available per unit of solid. No significant difference in Pt extraction ~91% was obtained between the ratio of 10 and 20mL/g. Hence, to study the other leaching parameters, a 20mL/g solid/liquid ratio was chosen.

To investigate the influence of particle size on the dissolution rate, leaching experiments were carried out for different particle sizes (-106+75, -75+53, -53) μ m while other parameters were kept constant. Dissolution rate increased significantly with decreasing particle size, due to smaller particles providing larger contact surface area between solid and the leaching reagent (data not shown), thereby other leaching parameters were studied using the fraction of particle size less than 53 μ m.

The influence of stirring speed on auto catalyst leaching for platinum extraction was studied at (200, 400 and 600) rpm and 80 $^{\circ}$ C in solution containing 12.0M HCl and 9.5M HNO₃. The platinum recovered at 200rpm was almost 78%, whereas 91.1% and 93.0% when a stirring speed was maintained at 400rpm and 600rpm, respectively.

To determine the influence of temperature, leaching experiments were performed at five different temperatures: (60, 70, 80, 90 and 100) $^{\circ}$ C. The fixed laboratory parameters at this stage were: stirring speed 400rpm, 12.0M hydrochloric acid, 9.5M nitric acid, particle size -53 μ m and phase ratio 20ml/g. With an increase in temperature, the platinum dissolution rate increases. As can be seen in Figure 1, an increase of temperature increases the platinum extraction.

The effect of HCl concentration on platinum dissolution was studied for (6.0, 8.5, 10.0, 12.0, and 13.0) M HCl at 90 $^{\circ}$ C in solution containing 9.5M HNO₃. The results are shown in Figure 2. Platinum dissolution increased from 23% to 90.7% after 200min as the acid concentration was increased from 6.0 to 12.0M. With an increase in acid concentration to 13.0M, the dissolution rate increased to 92%.

The effect of HNO₃ concentration on platinum extraction is shown in Figure 3. Experiments were carried out at five different concentrations: (5.0, 7.5, 8.5, 9.5, and 11.0) M HNO₃. The results show that an increase in the oxidant concentrate accelerates platinum dissolution. At low concentrations of nitric acid, the platinum dissolution rate is very weak, confirming confirm the role of oxidant in oxidative dissolution of platinum.

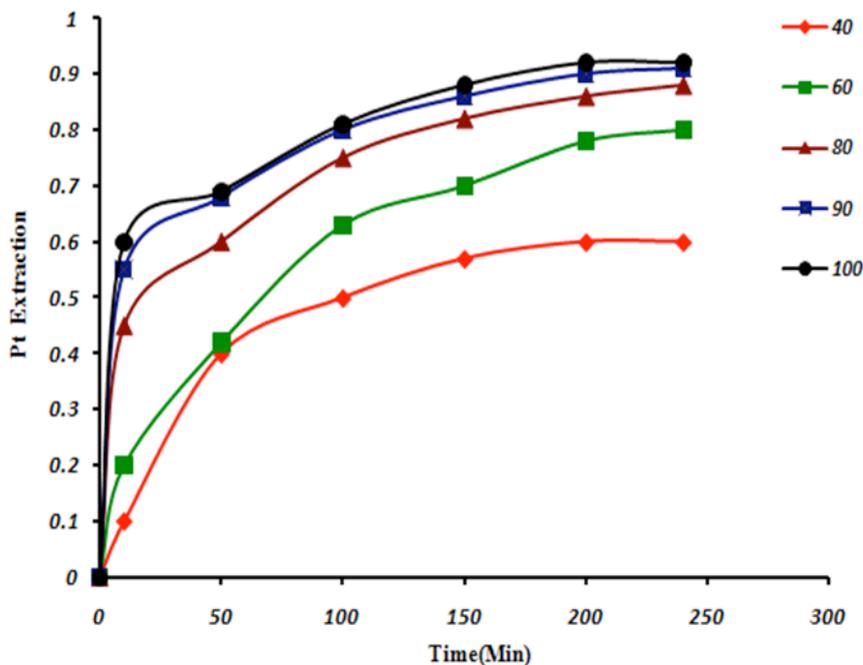


Figure 1. Effect of temperature on the platinum extraction.

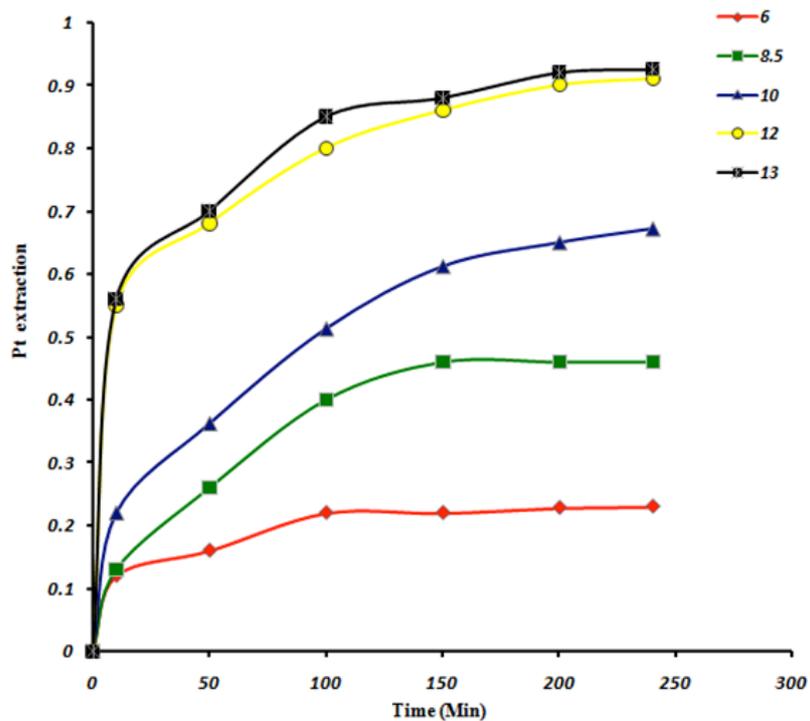


Figure 2. Effect of HCl concentration on the platinum extraction.

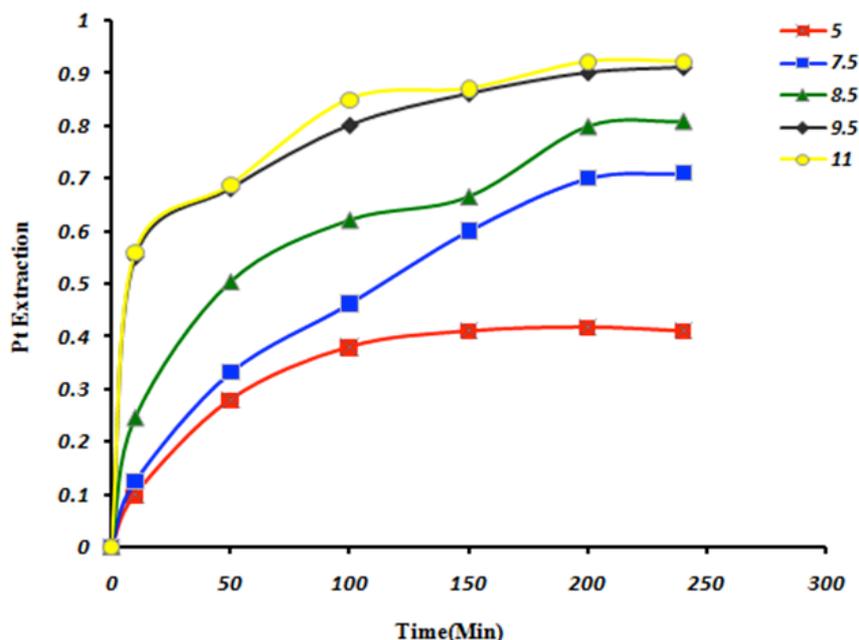


Figure 3. Effect of HNO₃ concentration on the platinum extraction.

3.2. Kinetics of leaching process

A variant of the shrinking core model proposed by Dickinson and Heal [11] is a more complete type of diffusion-control model, where both solid and acid concentrations have a role in controlling the reaction rate, and diffusion occurs in two directions. An equation of this model is given as follows.

$$\frac{1}{3} \ln(1-X) + \left[(1-X)^{-\frac{1}{3}} - 1 \right] = K_m t \quad (2)$$

where K_m is a kinetic constant. In Figure 4 was plotted versus time at different temperatures. The slope of this line is the specified kinetic constant.

Conventional shrinking core model [12] was compared to modified model (Equation 2). According to the results given in Table 2, the shrinking core model with diffusion through the product layer (compared to the chemical reaction-controlled model) showed a better fit to the data, but the alternative model of the shrinking core model proposed by Dickinson provided an even better fit.

Table 2. Correlation coefficients R^2 values for different temperature and models.

Temperature (°C)	Surface Reaction	Diffusion	Variant of SCM
40	0.824	0.940	0.967
60	0.819	0.937	0.991
80	0.938	0.931	0.995
90	0.862	0.988	0.985
100	0.839	0.962	0.946

The activation energy of platinum leaching in hydrochloric acid medium determined from Arrhenius equation [12] was 35.75kJ/mol, which can be considered as the mean value, in the above classifications between diffusion (usually of the order of 5kcal or less) and surface chemical activation

energy amounts [5,12]. Hence, considering the new model used in this research, according to which, the rate of leaching is both diffusion and chemical controlled, the amount of activation energy here obtained could be considered as a reflection of the intermediate model.

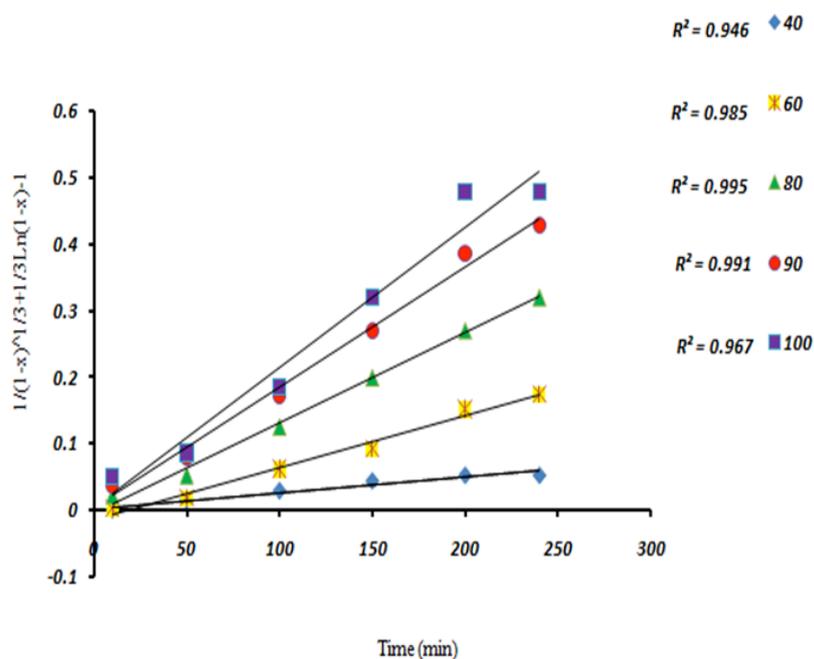


Figure 4. The variation in $\frac{1}{3} \ln(1-x) + \left[(1-x)^{-\frac{1}{3}} - 1 \right] = K_m t$ with time at various temperatures.

4. Conclusions

In the present study, the kinetics of platinum leaching from auto-catalyst in aqua regia was studied. The effect of experimental parameters such as temperature, hydrochloric and nitric acid concentrations, stirring speed, particle size and liquid/solid ratio were analysed. Acid concentration and temperature were the most important variables affecting the leaching process. The activation energy was calculated to be 35.75kJ/mol.

Acknowledgements

Authors are grateful to Tarbiat Modares and Tehran Universities for supporting this research. The Universidad Industrial de Santander (VIE-UIS project 1336) also supported this project.

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