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Recovery of Palladium and Rhodium from Spent Automotive Catalytic Converters

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Platinum group metals recovery from spent automotive catalysts is new issue in Iran. Recovery of palladium and rhodium from spent automotive catalytic converters using HCl + NHO_3 as oxidising agents was investigated. Effects of temperature, leaching time and solid/liquid ratio were studied. Optimum conditioned were determined at temprature 90 ºC, time 4 h and solid content 100 g/L. Maximum palladium and rhodium extractions were 1.756 and 0.145 g/kg cat., respectively.

Key Words: Automative catalytic converters, Rhodium, Palladium.

INTRODUCTION

Automotive catalytic converters have been used increasingly since the mid-1970s to meet emission limits enforced by international legislation. The catalysts contain either platinum, platinum/palladium or palladium/rhodium combinations to convert carbon monoxide and hydrocarbons to carbon dioxide and moisture (H_2O). Platinum group metals are present in very small quantities in these class of catalysts and given their intrinsic value, it is worth recovering them from the spent exhaust systems. However, for such platinum group metal recovery processes to be cost-effective, well over 90 % of these precious metals must be recovered[1,2].

There are a range of hydrometallurgical or pyrometallurgical processes used in platinum group metals recovery[3]. Pyrometallurgical processes have the potential for high recovery rates as well as coping with the impurities found in catalysts.

The literature on the separation of the platinum group metals from spent catalysts can be classified into 3 different methods. These are the gas phase transport, support dissolution and the solution extraction methods. The gas phase transport involves the volatilization of the platinum group metals from the catalysts support. The support dissolution technique involves the dissolution of the catalysts support in non-oxidizing acid or base solutions leaving the platinum group metals undisturbed. The solution extraction involves the dissolution of the platinum group metals by an

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acid containing oxidant which leaves the catalysts support undissolved[4-6]. Chen and Huang[3] examined platinum group metals extraction from spent auto catalysts by cyanidation. However, at room temperature and pressure, the reaction between sodium cyanide and platinum group metals proceeds slowly due to poor kinetics. As a result, the cyanide leaching of platinum group metals must be performed at elevated temperatures and pressures. In addition to the high cost of operation at high temperatures and pressures, this process employs cyanide which is highly toxic. In fact, many major precious metals producers and research groups are actively developing alternate processes to replace the cyanide process.

Consumption of autocatalysts in Iran has increased sharply because of automotive industries developments which result in more automotive productions. Therefore, recovery of precious metals from spent catalysts is an important and of course new issue in Iran.

In this work, dissolution of palladium and rhodium from spent automotive catalytic converters Using HCl + NHO_3 as oxidizing agents was investigated. Effects of temperature, leaching time and solid/liquid ratio were also studied.

EXPERIMENTAL

The catalyst used in this investigation was a catalytic converter removed from a Peugeot 206, Iran Khodro. Phase identification of the catalysts was performed by powder X-ray diffraction (XRD) analysis. Aqua regia was freshly prepared by mixing concentrated hydrochloric acid (37 %) and concentrated nitric acid (65 %) (Merck Chemical Company) at different volume ratios.

Methods: The catalyst was ground through a rod mill. It was in the size range of -70 mesh. For each run, aqua regia was first charged into the reactor. Then, the system was quickly heated to the desired temperature under continuous stirring. When the temperature reached the pre-set value and remained stable, a certain amount of catalysts powder was added to the reactor. The reactor temperature was controlled with a precision of ± 2 ºC. Next, the mixture of the reactants was intensively stirred at 700 rpm under atmospheric pressure. Three milliliter samples of the leachate were taken at regular time intervals and then filtered. Palladium and rhodium concentrations of the liquid samples were analyzed by AAS and ICP, respectively.

RESULTS AND DISCUSSION

The XRD analysis showed that catalyst was in the form of a honeycomb and composed of magnesium cordierite, $2MgO\cdot 2Al_2O_3\cdot 5SiO_2$ (Fig. 1).

It is believed that HNO_3 and HCl in aqua-regia undergo through the reactions (1) and (2) to some small extent[7]:

$$HNO_3 + 3HCl \rightleftharpoons NOCl + Cl_2 + 2H_2O \quad (1)$$

$$NOCl + H_2O \rightleftharpoons HNO_2 + HCl \quad (2)$$

Highly acidic chloride media are used in hydrometallurgical processes for the primary production and separation of platinum group metals; however, Fig. 2 predicts stability of palladium chlorocomplexes in near neutral solutions, the equilibrium pH with their respective oxides depending on the free chloride and dissolved metal activities[8].

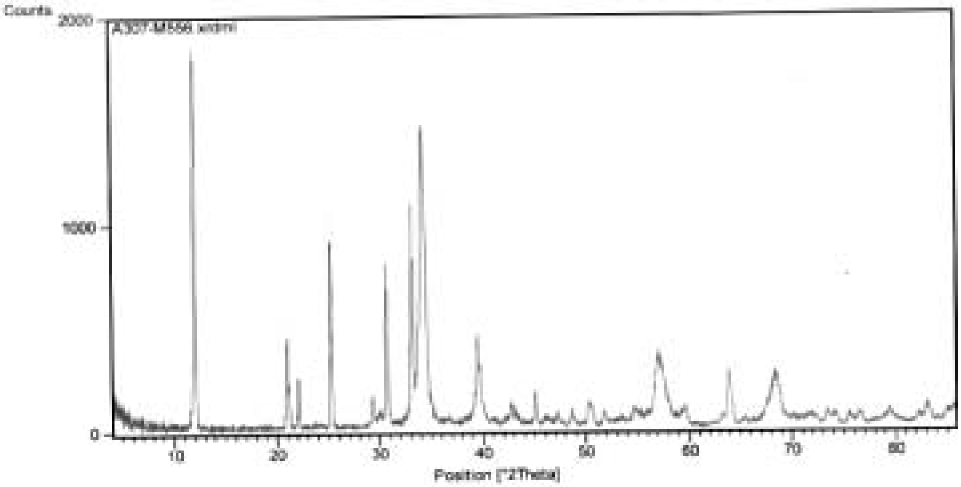


Fig. 1. XRD pattern of the catalyst

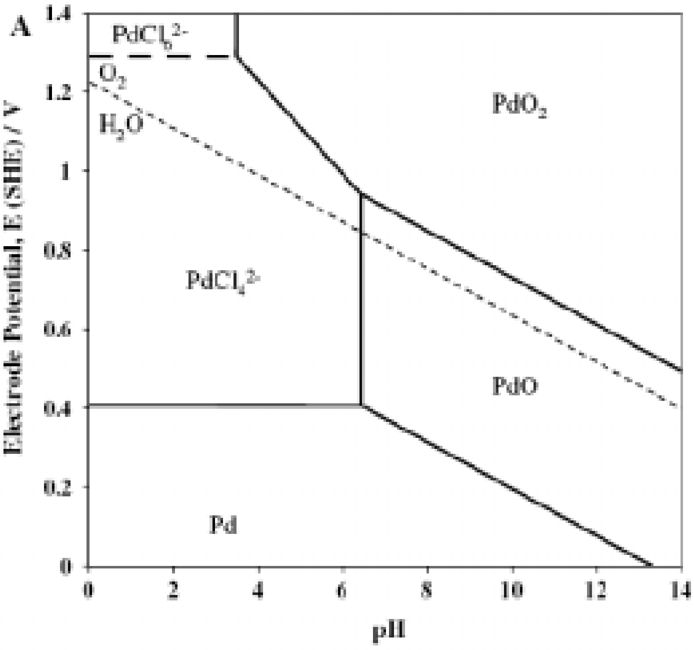


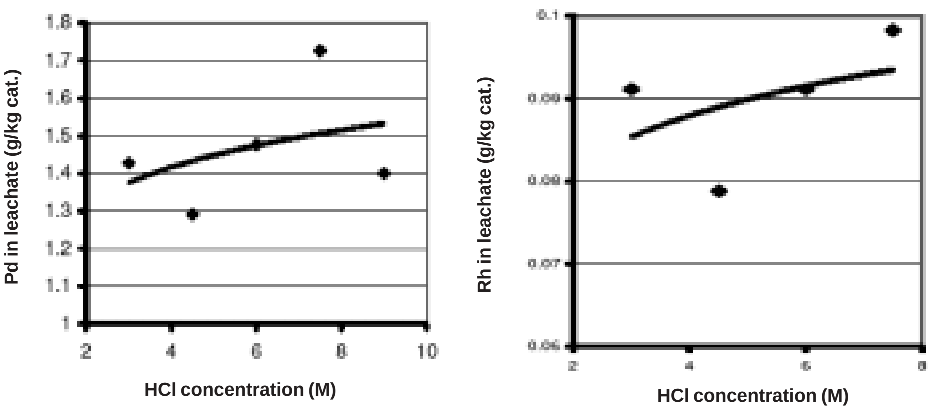
Fig. 2. Potential-pH diagrams for Pd-Cl-water system at 25 ºC, Cl activity 1 M, dissolved metal activities 10^{-5} [Ref. 8]

Palladium can be oxidized in the presence of a suitable oxidizing agent with a standard electrode potential value of 0.915 V. Palladium can form stable chloro-complexes such as $PdCl^+$, $PdCl_2$, $PdCl_3^-$ and $PdCl_4^{2-}$ in acidic chloride solutions. At about 0.1 M Cl^- and higher, the predominant species in solution is $PdCl_4^{2-}$. The formation of this complex in solution will enhance the dissolution of Pd from the containing materials[9]. Palladium can be oxidized with a standard electrode potential 0.62 V in the presence of chloride ions according to the reaction (3):

$$Pd + 4Cl^- = [PdCl_4^{2-}] + 2e^- \quad E^0 = 0.62\ V \qquad (3)$$

Effect of HCl concentration: Although the fixed 1/3 volume ratio of HNO_3-to-HCl is often applied in commercial laboratories for total dissolution of metals and minerals, it has been reported that the dissolution power of aqua-regia, in fact, depends on three factors *i.e.*, the metal being dissolved, aging of the prepared solution and the ratio of HNO_3 to HCl[10].

Effect of various HCl concentrations on palladium and rhodium dissolution was studied in the range of 3 to 9 M. Fig. 3 shows the results.



(a) (b)

Fig. 3. Effect of HCl concentration on (a) Palladium and (b) Rhodium dissolution (Temperature = 80 ºC, time = 3 h, solid/liquid = 200 g/L, $\frac{M_{HCl}}{M_{HNO_3}} = 3$)

According to Fig. 3, HCl concentration increasing leads to increased palladium and rhodium recovery and the best results were obtained when 7.5 mol L^{-1} HCl is used, 1.726 and 0.098 g/kg cat. for palladium and rhodium, respectively. Theses results indicate that better palladium and rhodium removal occur when more concentrated hydrochloric acid is utilized as hydrochloric acid concentration plays a major role in palladium and rhodium removal. More increasing in HCl concentration than 7.5 mol L^{-1} resulted in palladium removal decreasing. These results may related to variation in solution potential according to reactions (1) and (2). Further investigation on solution potential must be done.

Effect of temperature: Effect of temperature was studied at 50-90 ºC during 3 h. Every 1 h a sample was taken and analyzed for Pd and Rh. Figs. 4 and 5 show the results.

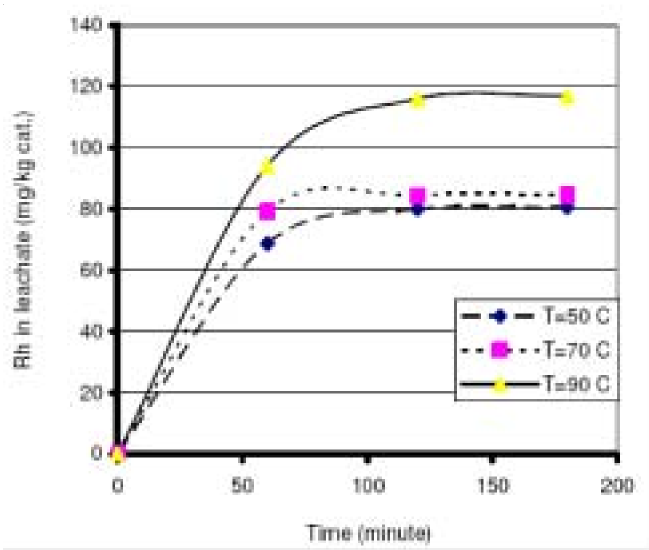


Fig. 4. Effect of temperature on Pd dissolution.
[HCl] = 3 M , time = 3 h, solid/liquid = 200 g/L, $\frac{M_{HCl}}{M_{HNO_3}} = 3$

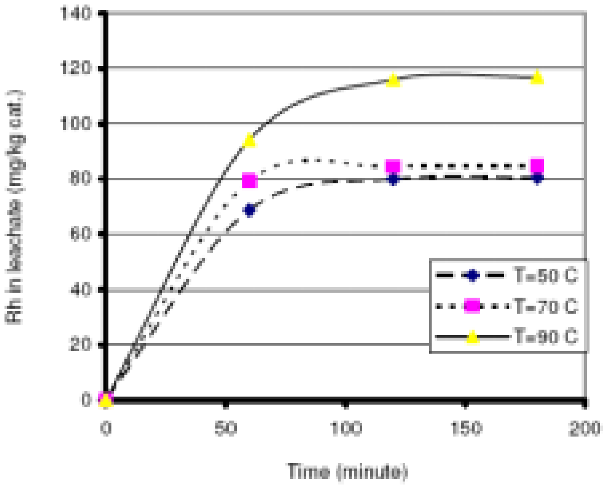


Fig. 5. Effect of temperature on Rh dissolution.
[HCl] = 3 M , time = 3 h, solid/liquid = 200 g/L, $\frac{M_{HCl}}{M_{HNO_3}} = 3$

According to the results temperature increasing resulted in higher palladium and rhodium dissolution. During 3 h, when temperature increases from 50 to 90 ºC, palladium extraction increases from 1.167 to 1.41 g/kg cat. and kinetic of dissolution increases. This is more atractive specialy when increasing from 70 to 90 ºC. In case of rhodium, extraction of 117 mg/kg cat. was obtained at 90 ºC after 3 h. Temprature increasing from 50 to 90 ºC was more effective on rhodium dissolution.

These observations clearly show that increasing temperature greatly enhances the extraction kinetics and maximum recovery of both palladium and rhodium. This large temperature impact must be due to relatively high activation energies for the extraction reactions.

Effect of time: In order to study effect of time, the experiment was repeated at 90 ºC during 6 h. Fig. 6. shows the results. Extraction of palladium and rhodium after 6 h were 1.544 and 0.128 g/kg cat., respectively.

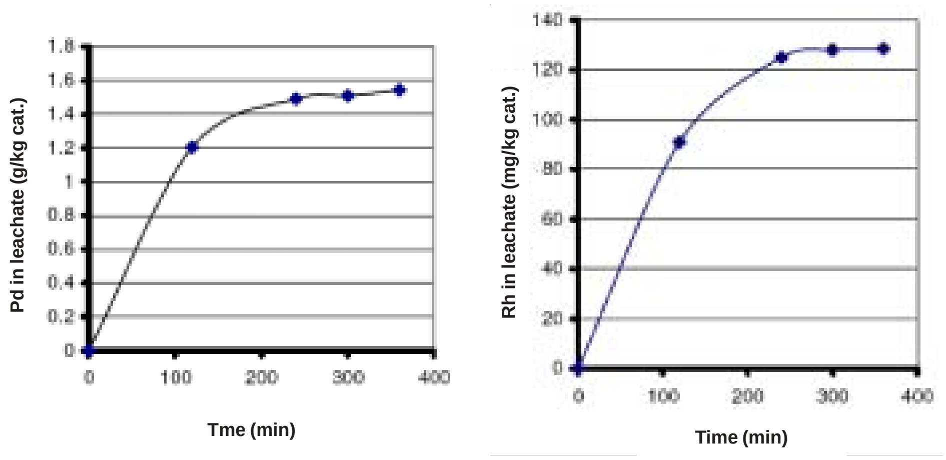


Fig. 6. Effect of time on (a) Palladium and (b) Rhodium dissolution.

[HCl] = 3 M, temprature = 90 ºC, solid/liquid = 200 g/L, $\frac{M_{HCl}}{M_{HNO_3}} = 3$

Effect of solid to liquid ratio: Solid to liquid ratios were studied at 100, 200 and 300 g catalyst per litre of solution. Figs. 7 and 8 show the resultes. These observations show that the maximum palladium and rhodium extractions (1.756 and 0.145 g/kg cat., respectively) was obtained when solid content was 100 g/L after 5 h. In both cases of palladium and rhodium, as the solid to liquid ratio decreases, the extraction kinetics becomes faster. As the liquid/solid ratio increases, [H^+] molarity also increases. H^+ ion is a major reactant for extraction reactions. As a result, it is expected that higher acidity due to higher liquid to solid ratio produces faster kinetics.

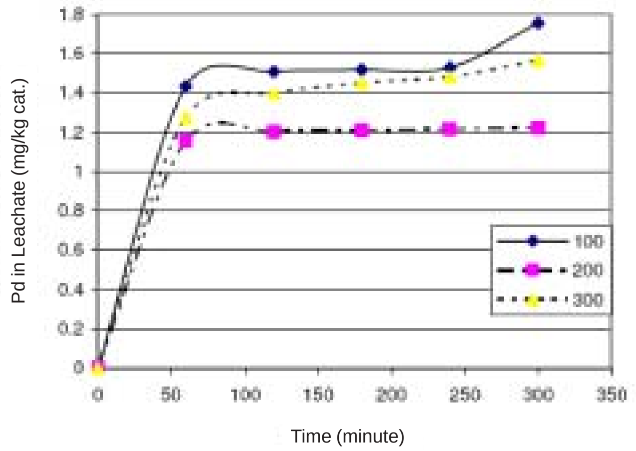


Fig. 7. Effect of solid to liquid ratio on palladium dissolution.

[HCl] = 3 M , temprature = 90 ºC, solid/liquid = 200 g/L, $\frac{M_{HCl}}{M_{HNO_3}} = 3$

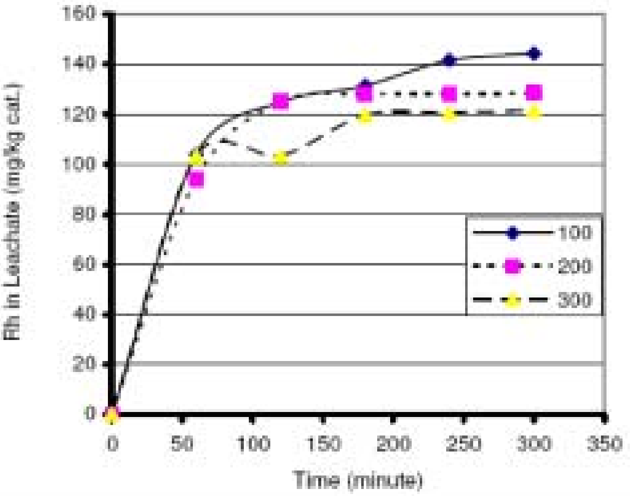


Fig. 8. Effect of solid to liquid ratio on rhodium dissolution.

[HCl] = 3 M, temprature = 90 ºC, solid/liquid = 200 g/L, $\frac{M_{HCl}}{M_{HNO_3}} = 3$

Conclusion

In this study, recovery of palladium and rhodium from spent automotive catalytic converters using HCl + HNO_3 as oxidizing agents was investigated. Experimental results showed that it is possible to recovery platinum group metals. Effects of temperature, leaching time and solid/liquid ratio were studied. Optimum conditioned were determined as temprature 90 ºC, time 4 h and solid to liquid ratio 100 g/kg cat. maximum palladium and rhodium extractions were 1.756 and 0.145 g/kg cat., respectively.

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