

Paper VIII

PALLADIUM RECOVERY FROM AUTOMOTION CATALYST CONVERTERS USING IMPREGNATED RESINS IN A FLUIDIZED BED COLUMN

Miquel Rovira, Luisa Hurtado, José Luis Cortina,
Nuria Miralles, Ana Sastre and Josep Arnaldos.

Chemical Engineering Department. Universitat Politècnica de Catalunya.
Diagonal 647. 08028-Barcelona (Spain).

ABSTRACT

In this work a new hydrometallurgy process to recovery palladium (II) from aqueous solutions obtained during the leaching steps of automotive catalytic converters is presented. The extraction of palladium from chloride medium with impregnated resins prepared by direct adsorption of different extractants onto Amberlite XAD-2 using fluidized bed technology is studied. Impregnated resins with Alamine 336 showed the best performance on Pd (II) extraction. Solid-liquid mass transfer coefficients at different flow rates and initial Pd (II) concentrations have been determined.

INTRODUCTION

Motor vehicles are responsible for a significant proportion of the hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides (NO_x) emitted to the atmosphere.

The use of three way conversion catalysts in engine exhaust to control these emissions has been adopted by automotive manufacturers in all developed countries. The popularity of this catalyst is based on its ability to assist both oxidation and reduction reaction within the same catalyst matrix. These catalysts employ three precious metals, platinum, palladium and rhodium, in different combinations depending on the application, the emission regulations and the quality of the fuel. Pt and Pd oxidize HC and CO to CO₂ and H₂O and Rh reduce NO_x to N₂ and O₂ (Hagelüken, 1995b; Mooney 1995c).

The average composition of catalyst is 0.08% platinum, 0.04% palladium and 0.005% rhodium (Hoffmann, 1988a). These quantities of platinum-group metals (PGM) in catalysts are significant because these concentrations are in general, higher than those of the richest ore bodies.

The value of PGM from automotion catalyst converters make recycling economically viable and precious metals may be re-used in the production of new catalysts. Recycling processes can be broadly divided into three categories hydrometallurgical processes, gas-phase volatilization processes and pyrometallurgical processes.

When an hydrometallurgical alternative is used, in general the catalyst is leached in HCl solutions containing one or more oxidants. Then PGM dissolution from the ceramic matrix containing the metals is treated by extraction and separation steps of PGM using different metal extraction technology. Although processes based on ion exchange and solvent extraction have been published or patented, the research for specific PGM strategies for separation and recovery based in this technologies is needed (Mishra, 1989b).

In this context the extraction of palladium from chloride medium with solvent impregnated resins (SIR) using fluidized bed technology is studied. The combination of impregnated resins and fluidization can improve the recovery of metals with respect to present technologies such as fixed bed of ion-exchange resins, microfiltration with membranes, and liquid-liquid extraction systems. This is due to different reasons, as better selectivity of SIR than with ion-exchange resins, SIR have not unstability problems and fluidization technology can work with flow rates higher than those found in microfiltration processes, there are no extractant losses, neither difficulties in the phases separation, and volumes are much lower than those used in liquid-liquid extraction.

SIR were introduced in hydrometallurgical applications by Warshawsky et al. (1981) using the specificity of the metal extractants used in liquid-liquid extraction systems and to avoid the chemical functionalization of the polymeric supports. Recently several authors have studied the recovery of different metals using commercial extractants homogeneously dispersed in different Amberlite resins (Cortina et al., 1995a; Villaescusa et al., 1993). The results obtained with SIR showed the same specificity found with liquid-liquid extraction, and high recovery efficiency.

In this work the extraction of Pd(II) from chloride solution with DEHTPA di-(2-ethylhexyl) monothiophosphoric acid, and Alamine 336, mixture of tri C8-C10-alkylamines, impregnated in XAD2 is studied. XAD2-Alamine 336 system showed better performance and were applied in a fluidized bed. Solid-liquid mass transfer coefficients were studied.

EXPERIMENTAL

Reagents and solutions

The extractants DEHTPA and Alamine 336, were supplied by Bayer AG and Henkel respectively, and were used without further purification, their purity was determined: 98.38 % for DEHTPA and 92.22 % for Alamine 336. Palladium (II) chloride (PdCl_2) (Aldrich, 99.999% of purity), hydrochloric acid and sodium chloride (Merck, AR grade), were used for the preparation of the Pd (II) solutions. Amberlite XAD-2 (Rohm and Hass), was adopted as a macromolecular adsorbent. To remove impurities, the resin was kept in contact during 12 hours with a 50% methanol-water solution containing 4 M HCl, then the polymer was washed with water until absence of the chloride ion and dried at 50°C.

Impregnation procedure

The impregnated resins were prepared mixing the dissolved extractants (DEHTPA in acetone and Alamine 336 in ethanol) with dry XAD2 until total evaporation of the diluent was reached. For the DEHTPA impregnated resins, the amount of extractant adsorbed on the resin was determined after washing a proper amount of resin with ethanol, which completely elutes the ligand, and

subsequent potentiometric titration by NaOH. In the case of Alamine 336 impregnated resins, the extractant content was evaluated using glacial acetic acid to elute the ligand that was titrated by HClO₄ in acetic acid medium (Blakeley et al., 1975).

Metal distribution with XAD2-DEHTPA and XAD2-Alamine 336

The extraction tests of Pd (II) were conducted with batch experiments at room temperature by shaking 0.05 g of impregnated resins, size 0.3 - 0.9 mm, with a 20 ml of a aqueous solution until equilibrium was achieved. The extractant concentrations (mmol/g) for the impregnated resins were: 0.508 (XAD2-DEHTPA) and 0.804 (XAD2-Alamine 336). To determine time to reach equilibrium, Pd(II) extraction for the different systems at constant pH as a function of time was studied contacting 0.2 g of impregnated resins with 20 ml of aqueous solution. As seen in Figure 2, Pd (II) is extracted very fast with both, XAD2-DEHTPA and XAD2-Alamine 336 impregnated resins. A time of 1 h was enough to reach equilibrium. In the case of the impregnated resins with DEHTPA, several hours after the extraction tests a precipitate appeared in the aqueous phase. Due to this reason this system was rejected for column operation.

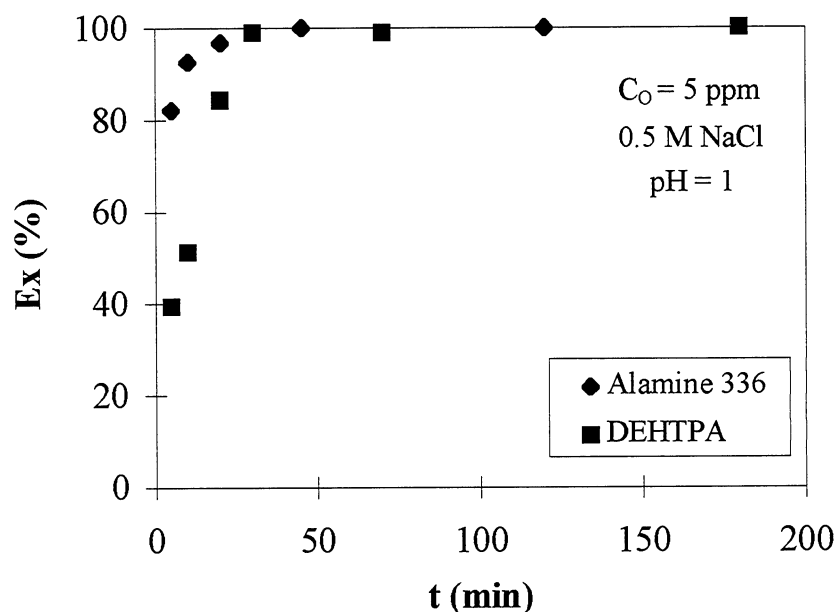


Figure 1. Variation in the extraction of Pd (II) as a function of time.

Fluidization column extraction procedure

The experiments were carried out in the installation shown in Figure 2, consisting of a fluidization column 52 mm i.d., made in polymethylmethacrylate. The calming and the fluidization section have 24 cm and 51 cm respectively. A porous plate was used as a distributor. To impeller the liquid and to regulate the flow rate a peristaltic pump was employed. The flow rate was measured by using a rotameter.

In each experiment a volume of 5 l of palladium solution at pH 2 and 0.1M NaCl, optimum conditions for the metal extraction, were introduced into the stirred tank. Different tests were conducted at several initial palladium concentrations and flow rates. In all cases the resin mass

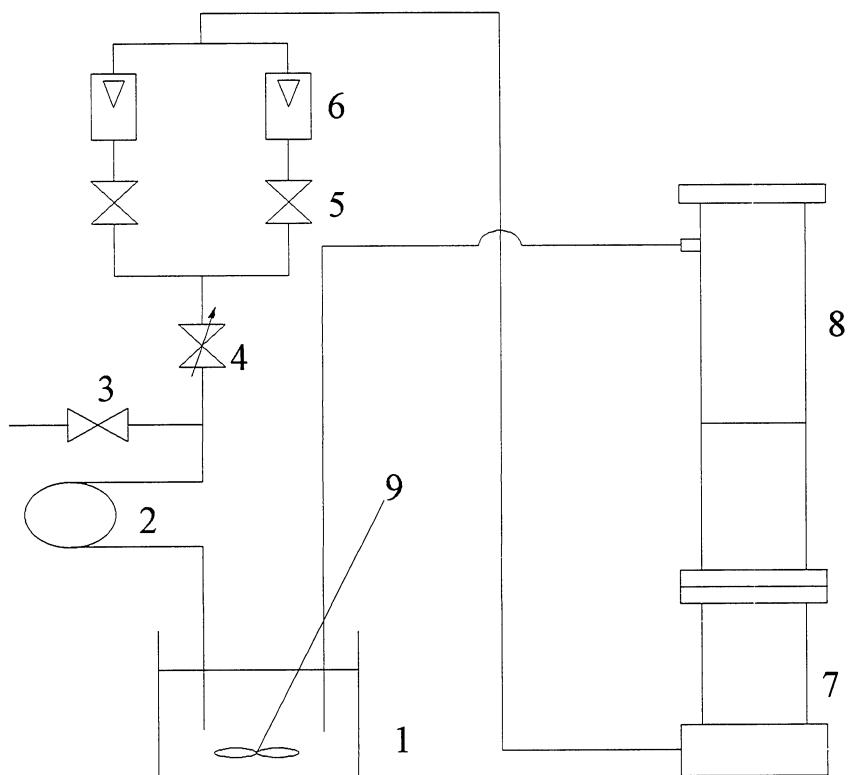


Figure 2. Fluidization column: 1 Stirred tank, 2 Pump, 3 Sampling, 4 Flow control valve, 5 Ball valve, 6 Rotameter, 7 Calming section, 8 Fluidization section and 9 Stirrer.

was constant and equal to 97g. The characteristics of the impregnated resins used were: Alamine 336 concentration 0.18 mmol/g, size 0.4-0.9 mm, average diameter 0.69 mm, shape factor 0.7, and particle surface area per unit volume, 12392 m⁻¹. A low Alamine 336 concentration on the resin was used in order to decrease its hydrophobicity and avoid flotation problems.

Metal analysis

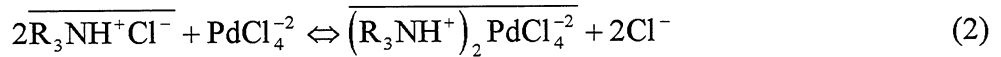
The palladium concentrations in the aqueous solutions were analyzed by atomic absorption spectrophotometry. A Perkin-Elmer 2380 AAS with air-acetylene flame was used.

RESULTS AND DISCUSSION

Palladium (II) extraction dependence with pH

The maximum extraction of Pd(II) was obtained at pH 2 as is can be seen in Figure 3. Taking into account that palladium exists as PdCl₄⁻² predominantly in HCl solution (Baes et al., 1977) and the mechanism for the adsorption of Pd(II) from HCl solutions with a macromolecular resin containing tri-n-octylamine (TOA) extractant very similar to Alamine 336 (Akita et al., 1993) the

extraction equilibrium of palladium with Alamine 336 may be expressed by a ion exchange reaction as follows:



where the overbar denotes the resin phase.

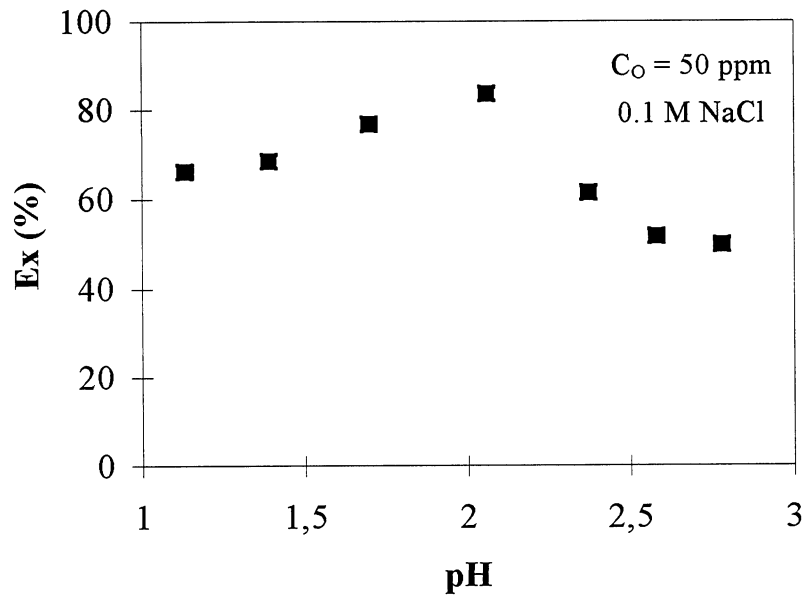


Figure 3. Variation in the distribution of Pd (II) as a function of pH.

Palladium (II) extraction with fluidization column

For the fluidized bed reactor used in this work it is reasonable to consider the next assumptions: a) idealized plug flow for the liquid, b) complete axial mixing of solid particles, c) the reservoir is a perfect back-mix system, d) the transport of the reactive ions in the reactor occurs under convective-diffusion control; for impregnated resins at low metal concentrations the rate-determining step of the metal extraction rate is the liquid film diffusion (Cortina et al., in press).

Accordingly, the mass transfer coefficient with respect to the diffusion-controlled reaction at the surface of the resin particles (K) is obtained by the following equation (Zarraf, 1992; Walker et al., 1977):

$$\ln \frac{C_0}{C} = \frac{t}{\tau} \left[1 - \exp\left(-\frac{KAaL}{Q}\right) \right] \quad (3)$$

Figures 4 and 5 show the dependence of $\ln C_0/C$ versus time at different flow rates and different initial Pd (II) concentrations respectively. By lineal regression analysis of these functions the mass transfer coefficients at different conditions are calculated and summarized in Table 1.

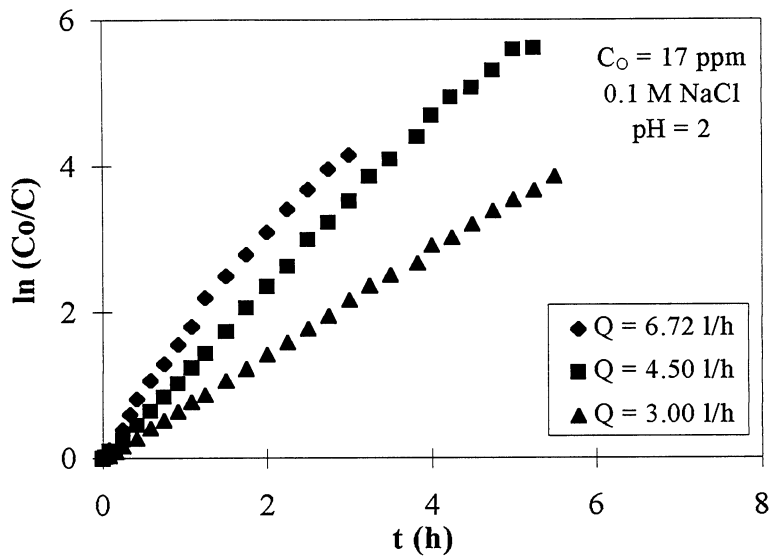


Figure 4. $\ln (C_o/C)$ versus time at constant initial Pd (II) concentration.

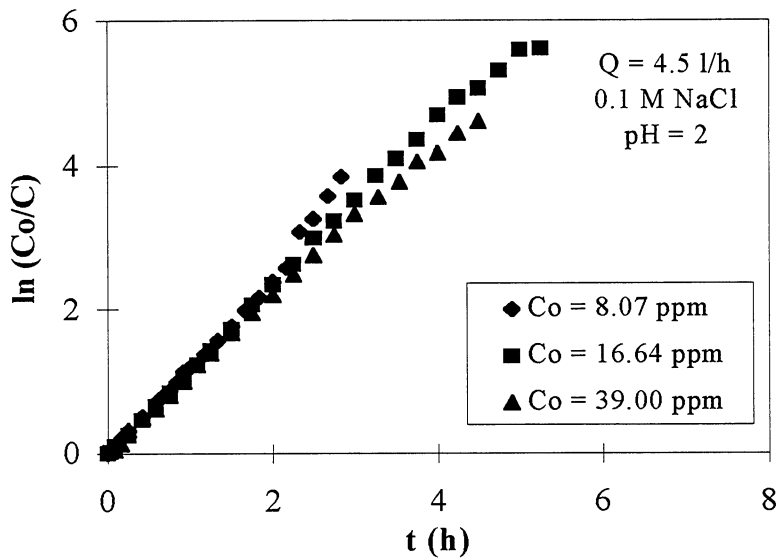


Figure 5. $\ln (C_o/C)$ versus time at constant flow rate.

Table 1. Conditions for the different experiments and mass transfer coefficients obtained.

Test	C_o (ppm)	Q (l/h)	τ (h)	K (m/s)
1	16.56	3.00	1.23	6.43×10^{-7}
2	16.64	4.50	0.82	1.53×10^{-6}
3	17.68	6.73	0.55	9.87×10^{-7}
4	8.07	4.57	0.81	1.90×10^{-6}
5	39.00	4.57	0.81	1.08×10^{-6}

The dependence of the mass transfer coefficient with the superficial velocity, reaches a maximum value as can be seen in Figure 6. Firstly, the coefficient increases according to the hydrodynamic boundary layer theory, since the thickness of the diffusion layer is related to that of the

hydrodynamic boundary layer, it follows that the thickness of the diffusion layer at the surface of the resin particles decreases with increasing hydrodynamic flow rate which, in turn, enhances the rate of mass transfer (Zarraf, 1992), but from a certain superficial velocity even increasing the flow rate the diffusion layer has no reduction of its thickness (Villaescusa et al., 1994) and due to the high flow rate and consequently the important amount of Pd (II) supplied to the resin, probably the diffusion problems in the matrix resin reduce the mass transfer coefficient.

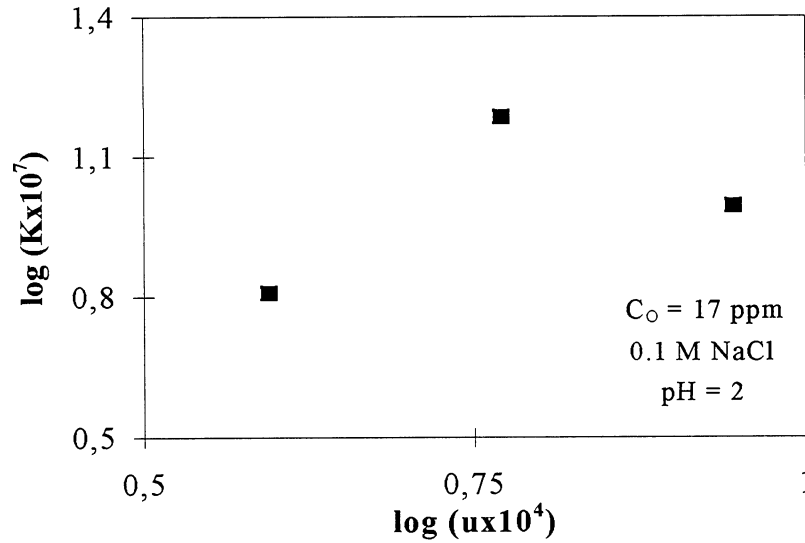


Figure 6. Effect of superficial liquid velocity on the mass transfer coefficient at constant initial palladium concentration.

Figure 7 shows that the mass transfer coefficient decreases when initial palladium concentration increases. The variation observed may be explained for the fact that in concentrated solutions, ions are more rapidly supplied to the resin surface and the slower diffusion in the resin then decreases the mass transfer.

From Table 1 is concluded that in the working conditions range of this study the effect of the flow rate on the mass transfer coefficient is more important than that of the Pd (II) concentration, and the rate-determining step for the studied process, is a combination of the liquid film diffusion and the diffusion in the resin porous which takes more significance as the Pd (II) concentration increases.

CONCLUSIONS

Based on the results obtained in this work, several conclusions may be drawn. The XAD2-DEHTPA impregnated resins extract Pd (II) but column operation is not possible due to precipitate formation. Impregnated resins XAD2-Alamine 336 show a high performance for Pd (II) extraction in the experimental conditions of this study. Concerning the Pd (II) extraction using fluidized bed, the model used describes the experimental data satisfactorily. The mass transfer coefficient exhibits a maximum when optimum flow rate is used and increases reducing initial palladium concentration.

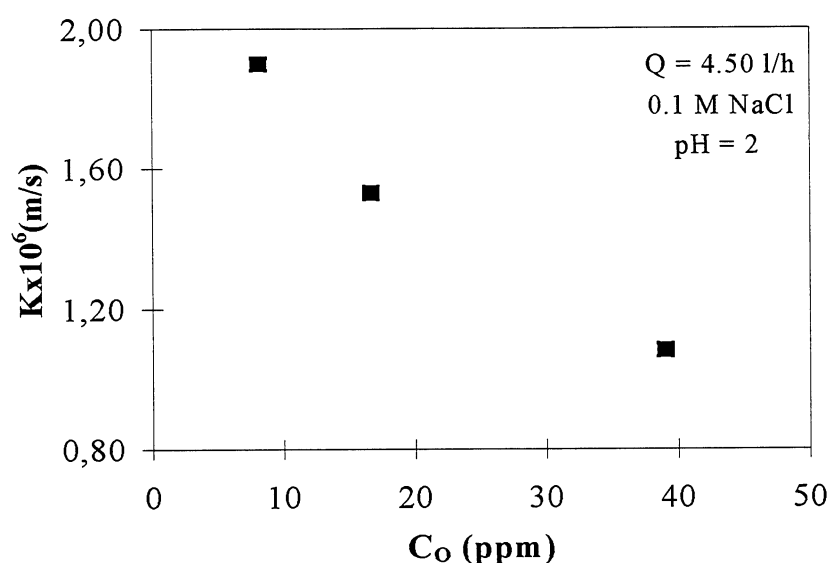


Figure 7. Effect of initial palladium concentration on the mass transfer coefficient at constant flow rate.

NOMENCLATURE

A	Cross sectional area of column (m^2)
a	Particle surface area per unit volume (m^{-1})
C	Palladium concentration at time t (ppm)
C_o	Initial palladium concentration (ppm)
Ex	Extraction efficiency (%)
K	Mass transfer coefficient (m/s)
L	Bed height (m)
Q	Volumetric flow rate (m^3/s)
t	Time (s)
u	Superficial velocity (m/s)
τ	Residence time (s)

ACKNOWLEDGMENTS

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