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Leaching Kinetics of Platinum and Palladium from Spent Automotive Catalysts

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ABSTRACT

Empirical rate expressions for both platinum and palladium were obtained from mass balances and concentration-time data in a packed bed reactor using different (HCl):(HNO_3) leaching solution concentration ratios. The spent catalysts used in this study (-60+70 mesh to -120+140 mesh) were analyzed to be 3791 ppm platinum and 1306 ppm palladium. High initial rates for both platinum and palladium were obtained for the early stages of leaching and were followed by rapid decay up to about 110 minutes and 50 minutes respectively. Typical concentrations in the leached solution were about 40 ppm Pt and 20 ppm Pd after about 5 hours for the experimental conditions used. The extent of reaction for platinum was in the 90 percent range while that of the palladium was in the 70 percent range.

INTRODUCTION

Nearly all of the primary platinum group metal requirements of the United States are imported from South Africa (53%), Soviet Union (22%), and the United Kingdom (12%) (1-2). The domestic recycling of the platinum group metals (PGM) accounts for the balance of 13 percent (3).

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The secondary sources of the platinum group metals are mainly from spent catalysts. The 1981 statistics reported by the U.S. Bureau of Mines (4) on the quantity of the platinum group metals sold to consuming industries amounted to 949,078 troy oz, of which 607,283 troy oz were used by the automotive industry (64%), 230,560 troy oz were used by the chemical industry (24%), and 111,235 troy oz were used by the petroleum industry (12%). The U.S. Bureau of Mines estimates that about 16 pct of the sales to industry are recycled (1). On the average, the automobile catalytic converter contained 0.036 troy oz Pt and 0.14 troy oz Pd (5). New three-way catalysts introduced after the 1981 models contained 0.008 troy oz of Rh and as much as 0.077 troy oz of Pt (6).

General Motors and American Motors are using pellets of catalyst with alumina support (7). Ford and Chrysler (7) on the other hand, are using a honeycomb structured catalyst with a support made of corderite magnesium-alumina silicate. The pellet strucutre generally contains between 500 and 1200 ppm of platinum and between 0 and 300 ppm of palladium. The honeycomb type usually contains between 270 and 350 ppm of platinum and between 80 and 150 ppm of palladium.

The literature on the separation of the platinum group metals (PGM) from spent catalysts can be classified into three different methods. These are the gas phase transport (8-17), support dissolution (18-20), and the solution extraction methods (21-30). The gas phase transport involves the volatilization of the PGM from the catalysts support. The support dissolution technique involves the dissolution of the catalysts support in nonoxidizing acid or base solutions leaving the PGM undisturbed. The solution extraction involves the dissolution of the PGM by an acid containing oxidant which leaves the catalysts support undissolved.

D'Aniello (31) evaluated the above methods and concluded that the gas phase transport was not as efficient as either the support dissolution or the solution extraction methods and that the amount of energy needed to heat the catalyst is quite high. The support dissolution requires significant amount of reagents which may make downstream environmental compliance more difficult and is probably not economically feasible for the sparsely loaded automotive catalysts. D'Aniello concluded that the solution extraction method was "the best suited for noble metal recovery from spent automotive catalysts" and worked with aqua regia (HCl and HNO_3) as a leaching solution and found it to dissolve at an "appreciable" rate compared to HCl and other oxidizing agents.

The reactions of the chloride ion with palladium and platinum are as follows:

$$Pd + 4Cl^- \rightleftarrows PdCl_4^{2-} + 2e- \qquad E° = -0.62\ V \qquad (1)$$

$$Pt + 4Cl^- \rightleftarrows PtCl_4^{2-} + 2e- \qquad E° = -0.73\ V \qquad (2)$$

$$PtCl_4^{2-} + 2Cl^- \rightleftarrows PtCl_6^{2-} + 2e- \qquad E° = -0.74\ V \qquad (3)$$

The first two oxidation reactions are dissolution reactions, while the last one is a solution reaction. The corresponding reduction reactions are:

$$NO_3^- + 3H^+ + 2e^- \rightleftarrows HNO_2 + H_2O \qquad E° = 0.94\ V \qquad (4)$$

$$NO_3^- + 4H^+ + 3e^- \rightleftarrows NO + 2H_2O \qquad E° = 0.96\ V \qquad (5)$$

$$2NO_3^- + 4H^+ + 2e^- \rightleftarrows N_2O_2 + 2H_2O \qquad E° = 0.81\ V \qquad (6)$$

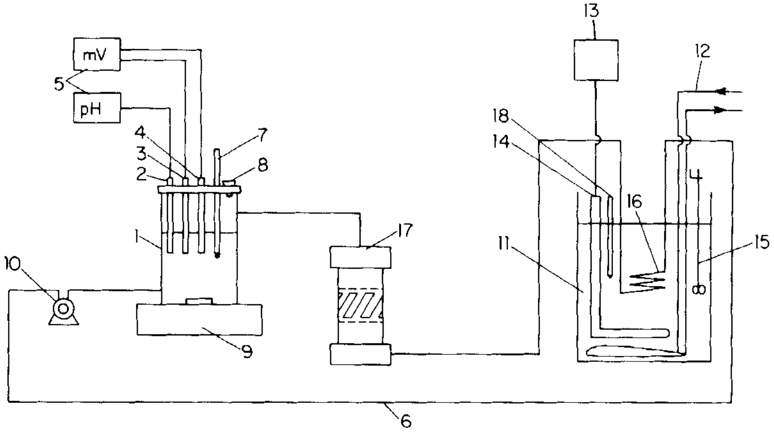
The potentials of these reduction reactions are high enough to allow the oxidation reactions to take place. During a leaching run, there are equilibrium reactions occurring between the different ionic species in solution. D'Aniello also suggested that platinum and palladium complexes $PtCl_6^{2-}$ and $PdCl_4^{2-}$ may hydrolyze, creating hydroxo complexes. In order to suppress this, a high chloride concentration and a pH<1 must be maintained. Platinum and palladium can also occur as oxides on a catalyst. Prereducing the catalysts with either 5% H_2/N_2 for 2 hours at 300°C, hydrazine in 0.1 M NaOH for 1 hour at 100°C, or ammonium formate in 0.1 M NaOH for 1 hour at 100°C prior to leaching should convert the oxides into the metals. D'Aniello found that there existed no true benefit in using prereduction where HCl and HNO_3 are used as the leaching solution.

EXPERIMENTAL

Equipment

A schematic diagram of the equipment used in the leaching at atmospheric pressure is shown in Fig. 1. The experimental apparatus consisted of a packed bed reactor, a constant stirred tank reactor (CSTR), a temperature control system, a pump, a nitrate electrode, a pH electrode, a reference electrode, and two pH meters. The catalyst was held between two filter disks in the cylindrical packed bed reactor. The dissolution reactions took place in this chamber.

The chamber had a 3.4 cm inside diameter and a length of 2.8 cm, while the filter disks were 4 cm in diameter and approximately 3 mm thick. The CSTR was a teflon container with a screw-on lid. There were holes in the lid which allowed for insertion of a nitrate electrode, a double junctioned pH electrode, a reference electrode, a thermometer, and a sampling port. The CSTR was 7 inches long and had an inside diameter of 3.5 inches. The temperature control system consisted of a coiled glass tube in a constant temperature water bath. A heating unit was in this bath, and temperature of the bath was controlled by regulating the flow of cold water through cooling coils. The flow of the leaching solution through the system was controlled by a model no. 7013-2 Cole Palmer peristaltic pump.



1. CSTR (CONTINUOUS STIRRED TANK REACTOR)
2. pH ELECTRODE
3. NITRATE ELECTRODE
4. REFERENCE ELECTRODE
5. DIGITAL pH METERS
6. TYGON TUBING
7. THERMOMETER
8. SAMPLING PORT
9. MAGNETIC STIRRER
10. PERISTALTIC PUMP
11. TEMPERATURE BATH
12. COOLING COILS
13. TEMPERATURE BATH CONTROLLER
14. ELECTRIC HEATER
15. MECHANICAL STIRRER
16. GLASS COIL
17. PACKED BED REACTOR
18. CONTACT THERMOMETER

Figure 1. Schematic diagram of the leaching equipment.

Procedure

The CSTR was filled with distilled water prior to each run, and the water was pumped through the system to clean it out. THE CSTR was then filled with 900 ml of leaching solution consisting of 3.65 M HCl and 0.35 M HNO_3. A specified weight of catalysts filled the packed bed to a known height. The packed bed did not need to be totally filled since the leaching solution flow rates were low enough to leave the bed undisturbed. Prior to each start-up, the electrodes were calibrated for various levels of nitrate and hydrogen ion concentrations. These concentrations were set near values that the actual run would experience. The pumps were then turned on, and the leaching solution was piped through tygon tubings. The solution passed through the constant temperature bath at 25°C, passed through the packed bed reactor, and then completed the loop back to the CSTR. At various times, both the electrode readings were recorded and 5 ml samples were removed. After the runs were completed, the samples were prepared to remove the NO_3^- ions. The platinum and palladium analyses were carried out using a Perkin-Elmer 5000 Atomic Absorption Spectrophotometer and platinum and palladium standards at near extreme concentrations for the linear working range.

Material

The catalyst used in this investigation was a catalytic converter removed from a 1976 Ford with approximately 10,000 miles. The catalyst was in the form of a honeycomb and was ground through a ball mill. The catalyst sample used was in the size range of 60 to 140 mesh. The specific surface area of the catalyst was determined using the B.E.T. method, and the average value came out to be 6.354 m^2/g. Upon analysis of the catalyst, it was determined that the amount of platinum was 3790.8 ppm and the amount of palladium was 1305.7 ppm. Other metals which may be present in various small amounts on the catalyst are lead, phosphorus, sulfur, zinc, calcium, and iron. This method of determination was developed by Hill and Potter (33).

Mathematical Model

The experimental data of interest are the platinum and palladium concentrations of the solution in the CSTR at various times. These concentrations are also the concentration of the outlet stream of the CSTR. There are two mass balances that can be used. The first mass balance represents what is going on in the CSTR and is given by:

$$v_o C_{Ai} = v_o C_{Ao} + V dC_{Ao}/dt \qquad (7)$$

where C_{Ai} is the platinum or palladium concentration in the inlet stream, C_{Ao} is the platinum or palladium concentration in the outlet stream, v_o is the volumetric flowrate, V is the accumulation in the CSTR, and t is time. The second mass balance represents what is going on in the packed bed reactor and is given by:

$$v_o dC'_A = r_A dW \qquad (8)$$

where C'_A is platinum or palladium concentration in the packed bed reactor, v_o is the volumetric flowrate, W is the weight of the catalyst material, and r_A is the rate of reaction of platinum or palladium in the packed bed reactor based on weight. The experimental data which were collected consisted of C_{Pdo} and C_{Pto} versus time. In order to find C_{Pdi} and C_{Pti}, information concerning dC_{Pdo}/dt and dC_{Pto}/dt had to be sought out. Since the time parameter was not varied in increments of equal time, the method used to find the derivatives involved searching for an empirical relationship between C_{Pdo} and t and C_{Pto} and t. In this instance, t=0 refers to the point in time when the liquid entering the CSTR initially contains platinum and/or palladium. A curve fitting program was employed to determine C_{Ao} as a function of time, which now allowed access to derivative values. Since the derivatives were readily determined, the values of C_{Ao} and dC_{Ao}/dt were then substituted into Eq. (7) to find C_{Ai}. Note that the value of V was not constant during a run and decreased with each data reading by 5 ml. In order to correct for this, the value of V decreased by 5 ml for each data point calculation of C_{Ai}. When Eq. (8) is rearranged and a linear relationship between C_A' and W is assumed, the following expression is obtained:

$$r_A = \frac{v_o dC'_A}{dW} = \frac{v_o(C'_{Ao}|_{t-t_a} - C'_{Ai}|_{t-(ta+tPB)})}{W} \tag{9}$$

where C'_{Ao} is the concentration of Pd or Pt in the outlet stream to the packed bed reactor, C'_{Ai} is the concentration of Pd and Pt in the inlet stream to the packed bed reactor, t_a is the amount of time required for the outgoing fluid from the packed bed to travel and reach the CSTR, and t_{PB} is the amount of time required for the incoming fluid to the packed bed to travel through the packed bed. The time required for a 'plug front' of liquid (assuming no axial mixing) to leave the CSTR and then go through the loop and to reenter the CSTR is represented by t'. Dimensionless time can then be represented by z = t/t'. For $0 \le z \le 1$, the concentration of Pd and Pt in the inlet stream to the packed bed reactor, C_{Ai}', will be equal to zero as fresh leaching feed solution is continually added. Thus, Eq. (9) becomes:

$$r_A = \frac{(v_o C'_{Ao}|_{z-t_a/t'})}{W} \qquad 0 \le z \le 1 \tag{10}$$

The relationship between the packed bed concentration and the CSTR concentration for $0 \le z \le 1$ is $C'_{Ao}|_{z-ta/t'} = C_{Ai}|_z$. Thus, Eq. (10) now becomes:

$$r_A = \frac{v_o C_{Ai}|_z}{W} \qquad 0 \le z \le 1 \tag{11}$$

For z > 1, the rate expression becomes:

$$r_A = (v_o/W)[C'_{Ao}|_{z-ta/t'} - C'_{Ai}|_{z-(t_a/t' + t_{PB}/t')}] \tag{12}$$

The relationships between concentrations in the packed bed reactor and the CSTR need to be developed. As before, $C'_{Ao}|_{z-t_a/t'} = C_{Ai}|_z$

for all z's and $C'_{Ai}|_{z-(t_a/t' + t_{PB}/t')} = C_{Ao}|_{z-t'/t'} = C_{Ao}|_{(z-1)}$. Here $t' = t_a + t_{PB} + t_b$ and t_b is the amount of time required for fluid to travel from the exit of the CSTR to the entrance of the packed bed reactor. Thus, Eq. (12) can now be expressed in terms of the CSTR concentration and now becomes:

$$r_A = (v_o/W)[C_{Ai}|_z - C_{Ao}|_{(z-1)}] \qquad z > 1 \tag{13}$$

The entire rate expression can be defined as:

$$r_A = \frac{(v_o C_{Ai}|_z)}{W} \qquad 0 \le z \le 1 \tag{14a}$$

$$r_A = (v_o/W)[C_{Ai}|_z - C_{Ao}|_{(z-1)}] \qquad z > 1 \qquad [14b]$$

In order to make use of Eq. (14), an empirical relationship between C_{Ao} and time was used. Expressions for C_{Ao} and dC_{Ao}/dt with respect to time were then substituted into Eq. (7) to obtain $C_{Ai} = f(z)$. The resulting expressions for $C_{Ai}(z)$ and $C_{Ao}(z)$ could then be substituted into Eq. (13) to obtain an empirical rate expression based on the data collected in this investigation.

RESULTS AND DISCUSSION

The results of the experimental runs made at varying conditions are given in Table 1. The data were taken from the CSTR and analyzed on an atomic absorption spectrophotometer unit for platinum and palladium concentrations. The results obtained in this work include empirical rate expressions for the dissolution reactions and the characterization of the influence of other parameters upon the extent of reaction.

Empirical Rate Expression

The data obtained for each run were C_{Ao} and t. Different analytical expressions were tried to find the best expression for the relationship between C_{Ao} and t. The best fit was obtained with the expression:

$$C_{Ao} = A \ln(1 + Bt) \tag{15}$$

where A and B are empirical constants. This equation appeared to fit the general shape of the experimental points containing rapidly rising concentrations at early times, and a gradual leveling out of

Table 1. Experimental data on the leaching of spent auto catalyst initially containing 3790.8 ppm Pt and 1305.7 ppm Pd.

Run No.	Solution flow rate (ml/min)	Catalyst weight (g)	Bed height (cm)	Size fraction (mesh)	Leaching sol. composition (M)	Metal	Extent of Reaction
1	10.57	11.59	1.6	-70+80	3.65 M HCl 0.35 M HNO_3	Pt Pd	73.67 % 96.32 %
2	10.57	12.27	1.7	-100+120	3.65 M HCl 0.35 M HNO_3	Pt Pd	80.39 % 95.88 %
3	10.57	20.13	2.8	-60+70	3.65 M HCl 0.35 M HNO_3	Pt Pd	57.59 % 76.45 %
4	10.57	15.89	2.5	-80+100	3.0 M HCl 1.0 M HNO_3	Pt Pd	98.31 % 76.12 %
5	10.57	20.03	2.8	-70+80	3.0 M HCl 1.0 M HNO_3	Pt Pd	96.64 % 72.22 %
6	10.57	21.50	2.8	-100+120	3.0 M HCl 1.0 M HNO_3	Pt Pd	91.27 % 75.42 %
7	10.57	20.11	2.8	-120+140	3.0 M HCl 1.0 M HNO_3	Pt Pd	91.06 % 73.64 %

concentration values at longer times. This equation also satisfied two boundary conditions which were $C_{Ao} = 0$ at $t = 0$ and $dC_{Ao}/dt \rightarrow 0$ as $t \rightarrow \infty$. There were other equations that fitted the points better but did not satisfy the boundary conditions, and equations that satisfied the boundary condition but did not accurately fit the shape of the curve. The plot of C_{Pto} vs. t is shown in Fig. 2, and the plot of C_{Pdo} vs. t is shown in Fig. 3. Both figures represent data from run 3.

If the curve fit of $C_{Ao} = A \ln(1 + B'z)$ is employed (z is dimensionless time and $B' = Bt'$), a relationship of empirical nature between r_A and z can be obtained. First, there is: $C_{Ao} = A \ln(1 +$

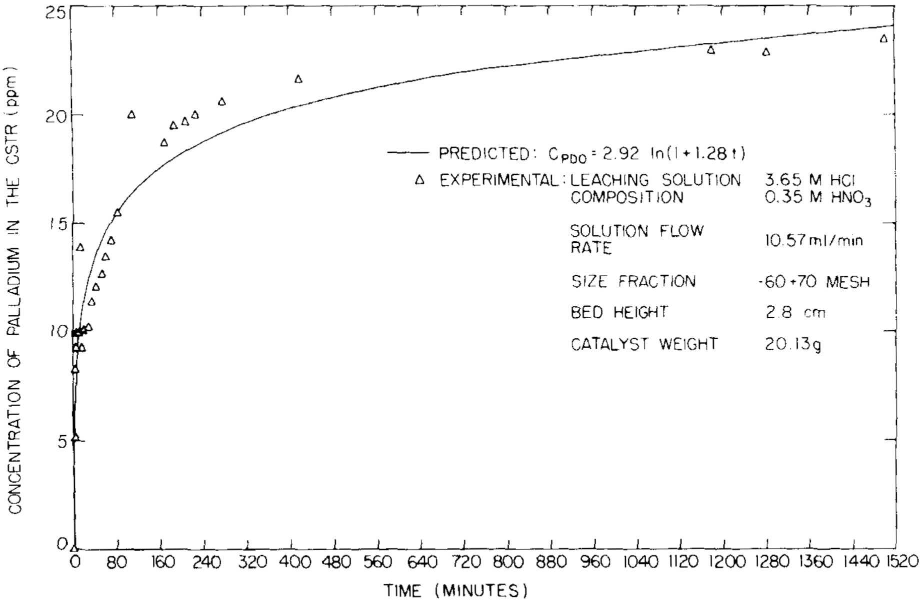


Figure 2. Concentration of platinum in the CSTR versus time for run 3.

B'z) and dC_{Ao}/dt = AB/(1 + B'z). These expressions are then substituted into Eq. (7), with j = 1, ... n where n is the number of samples, to obtain:

$$C_{Aij} = A \ln(1 + B'z) + (V_j/v_o)[AB/(1 + B'z)] \qquad (16)$$

When the forms for C_{Aij} and C_{Ao} are substituted into Eq. [13], the empirical rate expression becomes:

$$r_{Aj} = (v_o/W)[A \ln(1 + B'z) + (V_j/v_o)[AB/(1 + B'z)] \qquad 0 \leq z \leq 1$$

$$r_{Aj} = (v_o/W)[A \ln(1 + B'z) +$$

$$(V_j/v_o)[AB/(1 + B'z)] - A \ln(1 + B'(z-1)] \qquad z > 1$$

or

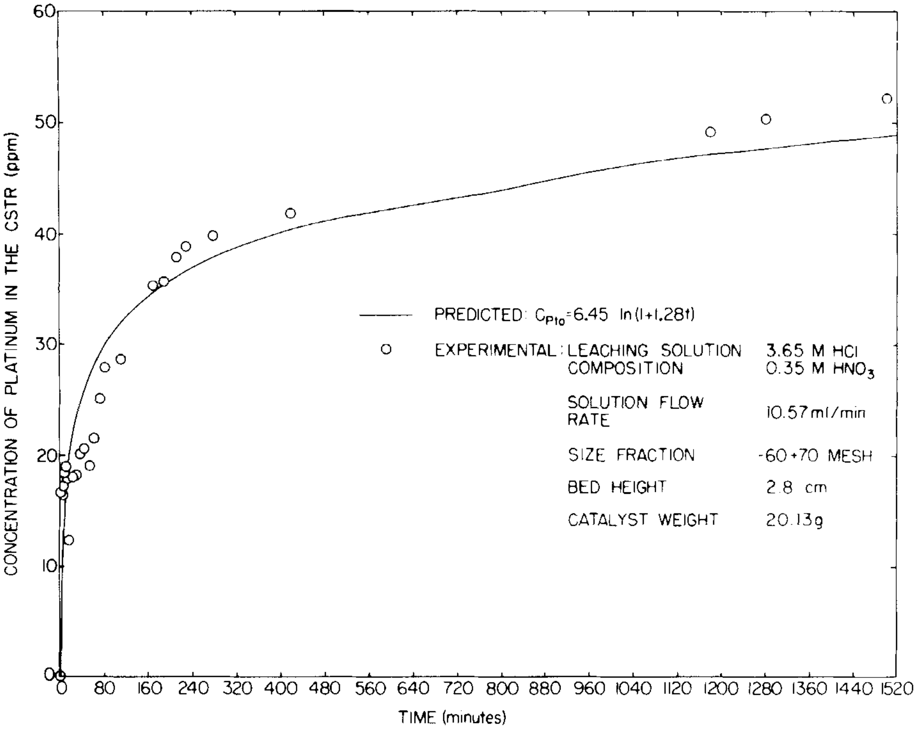


Figure 3. Concentration of palladium in the CSTR versus time for run 3.

$$r_{Aj} = (Av_0/W)[(V_j/v_0)[B/(1 + B'z)] + \ln[(1 + B'z)/(1 + B'(z-1)]] \qquad z > 1 \qquad (17)$$

In Eq. (16), V varies with z in an arbitrary way, causing r_A to be determined in a point-wise fashion at each time that a sample was removed. Thus, for an accumulation of 610.0 ml, $V_j = 610.0 - 5(j-1)$ for j = 1, ... n. Also, allowance is made for $V_0 = V_1 = 610.0$ ml, where V_0 is volume of accumulation at t = 0, such that $r_{Ao} = 610.0$

AB/W. In the region of $0 \leq z \leq 1$, the leaching solution has yet to complete the recycle loop, whereas in the region of $z > 1$, the closed loop system is fully employed.

The curve fitting program for $C_{Ao} = A \ln(1 + Bt)$ determined the values for A and B for each run, and the results are tabulated in Table 2. The reliability of these rate expressions depends on how well the empirical curve fits the C_{Ao} and time data.

The plots representing Eq. (17) for both platinum and palladium are given in Figure 4 and 5 respectively. The initial rate of reaction was 250.4 g/min-g_{cat} for platinum and 222.6 g/min-g_{cat} for palladium. In both cases, the rate value decayed rapidly. The rate became very low and nearly constant for platinum at times of about 110 minutes or more. For palladium the rate became very low and nearly constant at times of about 50 minutes or more.

Extent of Reaction

The extent of reaction, e_A, is defined by:

$$e_A = \frac{W_A^s}{W_A^o} \tag{18}$$

where W_A^s is the total mass of platinum or palladium dissolved from the catalyst, and W_A^o is the mass of platinum or palladium on a given weighed amount of unleached catalyst. Since each 5 ml sample removes platinum or palladium from the system, determination of weight would be based on the concentrations of all the removed samples. The number of samples removed from the CSTR can be represented by n and the concentration of the j^{th} sample ($j = 1,\ldots,n$) removed from the CSTR can be represented as C_{Aoj}. After completion of a run the remaining solution in the system has a volume of (900-5n) ml. On the assumption that the concentration of the nth sample represents the concentration of all the solution remaining in the closed loop system, the following equation is derived:

$$W_A^s = 5 \sum_{j=1}^{n-1} C_{Aoj} + [900-5(n-1)]C_{Aon} \tag{19}$$

A weighed amount of unleached catalyst was analyzed following the procedure of Potter (32) to determine the amount of platinum and palladium initially present in the catalyst. If C_A^{cat} represents the ppm of platinum or palladium on the unleached catalyst, the expression for W_A^o becomes:

Table 2. Empirical constants from C_{Ao} versus time plots using the expression: $C_{Ao} = A \ln(1+Bt)$

Run no.	Metal	A	B
1	Pt	3.633	7.648
	Pd	2.587	0.465
2	Pt	5.609	0.924
	Pd	2.919	0.275
3	Pt	6.451	1.281
	Pd	2.919	2.517
4	Pt	6.629	9.823
	Pd	2.135	7.881
5	Pt	10.269	2.444
	Pd	3.007	2.943
6	Pt	12.905	0.927
	Pd	3.352	3.770
7	Pt	11.225	1.376
	Pd	2.907	5.353

$$W_A^o = WC_A^{cat} \qquad (20)$$

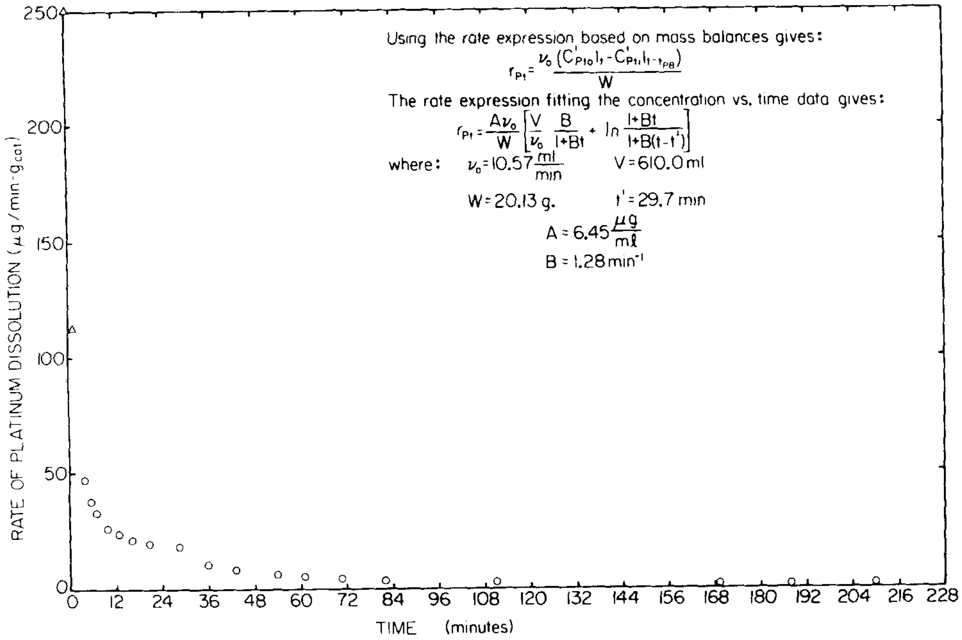
Upon substitution of Eq. (19) and Eq. (20) into Eq. (18), the following expression results:

$$e_A = \frac{5 \sum_{j=1}^{n-1} C_{Aoj} + [900-5(n-1)]C_{Aon}}{W\, C_A^{cat}} \qquad (21)$$

The extent of reaction for the different runs is given in Table 1. The other parameters which were varied include leaching solution composition, size fraction, and bed height/catalyst weight. The system's flow rate was not changed due to the risk of flooding the packed bed reactor.

Effect of Leaching Solution Composition

The data on the effect of leaching solution composition are given in Table 1. One group of experiments were carried out with 3.65 M HCl and 0.35 M HNO_3 and the rest of the experiments were car-



Using the rate expression based on mass balances gives:

$$r_{Pt} = \frac{\nu_0 \left(C'_{Pt0}|_t - C'_{Pt1}|_{t-t_{PB}}\right)}{W}$$

The rate expression fitting the concentration vs. time data gives:

$$r_{Pt} = \frac{A\nu_0}{W}\left[\frac{V}{\nu_0}\,\frac{B}{1+Bt} + \ln\frac{1+Bt}{1+B(t-t')}\right]$$

where: $\nu_0 = 10.57\,\frac{ml}{min}$ $V = 610.0$ ml

$W = 20.13$ g. $t' = 29.7$ min

$A = 6.45\,\frac{\mu g}{m\ell}$

$B = 1.28\ min^{-1}$

Figure 4. Rate of platinum dissolution versus time based on the empirical concentration relationship for run 3.

ried out with 3.0 M HCl and 1.0 M HNO_3. In both solutions, the H^+ concentration was 4.0 M in order to keep the leaching reactions under the same conditions.

Considering only the experiments with a bed height of 2.8 cm, the extent of reaction for palladium for the 3.65 M HCl/0.35 M HNO_3 leaching solution was higher than for the other three. The presence of a higher concentration of Cl^- in the solution surrounding the catalyst surface resulted in a higher extent of reaction. This observation makes sense since, in an equilibrium dissolution reaction where one of the reactants is Cl^-, the shift in equilibrium would favor the products. In other words, more metal would go into solution.

For platinum, the extent of reaction was in the 90 percent range for the 3.0 M HCl/1.0 M HNO_3 leaching solution runs. Elucidation of the true mechanism using these oxidants could better explain the observed data.

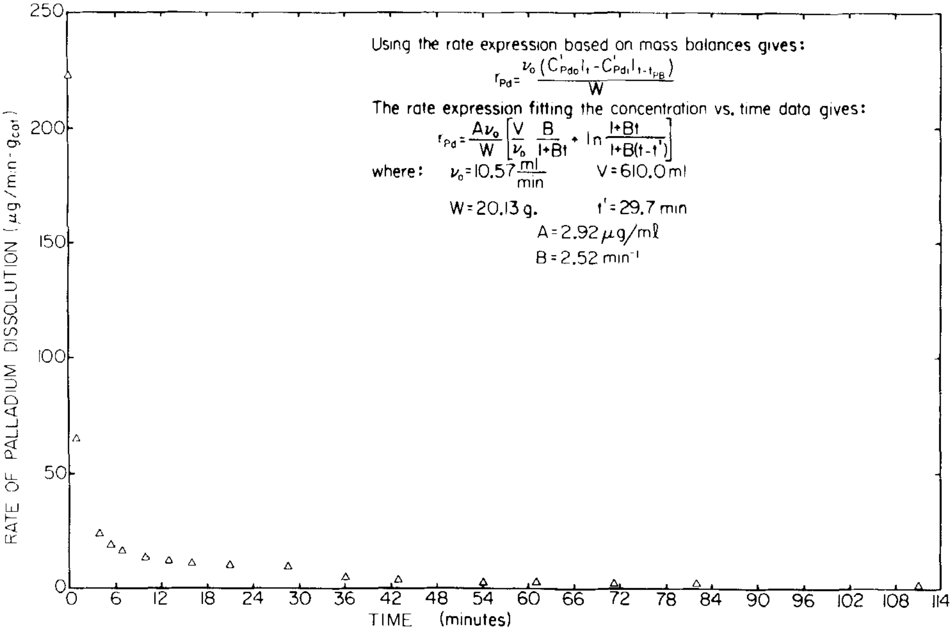


Figure 5. Rate of palladium dissolution versus time based on the empirical concentration relationship for run 3.

Effect of Size Fraction

The data on the effect of size fraction on the extent of reaction are given in Table 1. Consider the experiments performed at a constant bed height of 2.8 cm and a leaching solution composition of 3.0 M HCl and 1.0 M HNO_3. There appears to be no true correlation between size fraction and extent of reaction for palladium. The other experiment at a bed height of 2.8 cm, a leaching solution composition of 3.65 M HCl and 0.35 M HNO_3 and a size fraction of -60+70 mesh gave a higher extent of reaction for palladium than the smaller size fractions. The results from the last three runs in Table 1 indicate that the increase in the extent of reaction of the first run for palladium is due to the higher chloride ion concentration and not due to the size fraction.

For platinum the last three runs in Table 1 show that the extent of reaction stays relatively constant with decreasing particle size.

The extent of reaction for platinum using -60+70 mesh is much lower than the others listed in Table 1. This difference is due to the changes in the leaching solution compositions.

Effect of Bed Height and/or Catalyst Weight

The data illustrating the extent of reaction dependency on the bed height and/or catalyst weight are given in Table 1. The data were collected without setting the initial leaching solution concentration or the size fraction to any specified value. In other words, the leaching solution concentration and size fraction were considered to have negligible effect on the extent of reaction when compared to the effect of bed height and/or catalyst weight.

For palladium the extent of reaction remained about the same at 96 percent for bed heights between 1.6 cm and 1.7 cm and about 75 percent between 2.5 cm and 2.8 cm. However the extent of reaction decreased from around 96 to 75 percent when bed heights were changed from 1.7 cm to 2.5 cm.

The data in Table 1 also illustrate the results for platinum. With 3.76 M HCl/0.35 M HNO_3 leaching solution concentration, the extent of reaction for the bed heights of 1.6 cm and 1.7 cm increased from 73 to 80 percent. The extent of reaction dropped to 57 percent for a bed height of 2.8 cm. For the leaching solution concentration of 3.0 M HCl/1.0 M HNO_3, the extent of reaction also decreased from 98 to 93 percent with increase in bed height from 2.5 cm to 2.8 cm.

SUMMARY AND CONCLUSIONS

A kinetic expression was determined empirically for the experimental data. The equation which fit the concentration-time data was $C_{Ao} = A \ln(1 + Bt)$. The rates of reaction started at relatively high values and then dropped off very quickly with respect to time. Thus in order to get the maximum rate out of the process the reaction should be carried out with very short residence time.

From the results obtained it is apparent that as bed height and/or catalyst weight increases the extent of reaction decreases. This effect holds true for both platinum and palladium. This result stems from the recycling effect which decreases available chloride ion. This result also indicates that the use of smaller multiple packed bed reactors would be more efficient than using one large packed bed reactor. On a large scale, cost determinations and reaction characteriation would dictate the number and size of the reactors to be used for obtaining the highest extents of reaction in the least amount of time.

The extent of reaction of palladium increased, while that of platinum decreased when the chloride ion concentration was increased and the nitrate ion concentration was decreased. This observation would indicate a difference in the mechanisms surrounding the dissolution of palladium and platinum. The difference exists because platinum undergoes a redox reaction while in the ionic state while palladium only goes from the metal to the ion.

For constant bed height and constant leaching solution composition the extent of reaction for platinum and palladium does not change in any particular manner for decreasing particle sizes. There is no correlation between the extents of reaction and particle size for either platinum or palladium.

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NOMENCLATURE

A	empirical constant in the equation which fit the curve of C_{Ao} versus t, (ppm)
B	empirical constant in the equation which fits the curve of C_{Ao} versus t, (ppm)
B'	empirical constant in the equation which fits the curve of C_{Ao} versus t, (ppm)
C_A^{cat}	solid concentration of platinum or palladium on the unleached catalyst, (ppm)
C_{Ai}	platinum or palladium concentration in the inlet stream to the CSTR, (ppm)
C_{Aij}	platinum or palladium concentration in the inlet stream to the CSTR for the j^{th} reading, (ppm)
C_{Ao}	platinum or palladium concentration in the outlet stream from the CSTR (ppm)
C_{Aoj}	platinum or palladium concentration in the outlet stream from the CSTR for the j^{th} reading, (ppm)
C_{Aon}	platinum or palladium concentration in the outlet stream from the CSTR for the last reading of a run, (ppm)
C_A'	platinum or palladium concentration through the packed bed reactor, (ppm)

C'_{Ai}	platinum or palladium concentration at the entrance of the packed bed reactor, (ppm)
C'_{Ao}	platinum or palladium concentration at the exit of the packed bed reactor, (ppm)
e_A	extent of reaction for platinum or palladium
j	number corresponding to the individual samples of a run
n	total number of samples removed for a run
r_A	rate of dissolution of platinum or palladium based on weight of catalyst sample, $g/min\text{-}g_{cat}$
r_{Aj}	rate of dissolution of platinum or palladium based on weight of catalyst sample for the j^{th} reading, $g/min\text{-}g_{cat}$
t	time, (min)
t_a	average time required for an element of fluid to travel from the outlet of the packed bed reactor to the inlet of the CSTR, (min)
t_{PB}	average time required for an element of fluid to travel through the packed bed reactor, (min)
t'	average time required for an element of fluid to travel from the outlet of the CSTR back to the inlet of the CSTR, (min)
V_j	total volume of accumulation in the CSTR after the j^{th} sample is removed, (ml)
v_o	volumetric flow rate of the leaching solution through the system, (ml/min)
W	mass of the catalyst sample in the packed bed reactor prior to leaching, (g)
r_A	rate of reaction of platinum or palladium in packed bed reactor based on weight
W_A^o	mass of platinum or palladium on the catalyst sample prior to leaching, (g)
W_A^s	total mass of platinum or palladium dissolved from the catalyst sample, (g)
z	dimensionless time, t/t'

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