Platinum Loss from Alloy Catalyst Gauzes in Nitric Acid Plants

THE IMPORTANT ROLE OF THE PALLADIUM COMPONENT IN METAL CAPTURE DURING AMMONIA OXIDATION

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The loss of platinum from the catalyst gauzes used for the oxidation of ammonia in the manufacture of nitric acid has been studied for many years by catalyst producers and by users. In this paper, platinum losses from binary platinum-rhodium and ternary platinum-palladium-rhodium alloys, as well as from catalyst gauzes made of these materials, have been studied under laboratory and industrial conditions in atmospheric and medium pressure units, which are commonly found in P. R. China, and the rates of platinum loss and weight losses have been established. Adding a palladium component to the platinum-rhodium alloys or increasing the palladium content in platinum-palladium-rhodium alloys is clearly shown to decrease the rate of weight loss and the amount of platinum lost. This is attributed to the passive action of the palladium which accumulates on the surface and enriches the surface layer of the alloys, affecting both the platinum oxidation and platinum oxide reduction.

During the manufacture of nitric acid by the oxidation of ammonia, platinum-rhodium and platinum-palladium-rhodium alloy gauzes are used as catalysts. Traditionally the process is carried out in the temperature range 750 to 950°C and pressures of 1 to 10 atmospheres, and under such conditions the volatile oxides of platinum, palladium and rhodium, PtO_2, PdO and RhO_2, respectively, are formed on the catalyst surfaces (1–8). The volatilisation and mechanical attrition can cause the catalyst alloys to lose weight. As the catalyst gauzes contain less palladium and rhodium than platinum, the formation rates and amounts of the volatile oxides, PdO and RhO_2, formed are smaller. The weight lost from the catalyst gauzes is thus mainly due to platinum loss. In fact, apart from ammonia consumption, the major factor affecting the cost of nitric acid production is the loss of platinum.

The platinum lost from catalyst gauzes during nitric acid production depends on the properties of the catalyst alloys, the operating conditions (temperature and pressure) and the technical control. However, it is also dependent on the structure of the catalyst: whether the gauze has been knitted or woven.

Some twenty-five years ago it was established that the rate of platinum loss from platinum-10 per cent rhodium binary alloy gauzes varied from 0.05 gram ton^{-1} of nitric acid produced in plants operated at atmospheric pressure to 0.45 gram ton^{-1} of nitric acid produced in some high pressure plants (9). However, there is a shortage of data on the influence of the alloying components on platinum loss and on the comparative behaviours of platinum-rhodium and platinum-palladium-rhodium catalyst gauzes.

We have now completed a comparative study of platinum losses from platinum-rhodium and platinum-palladium-rhodium alloys and gauzes in industrial and laboratory conditions and results are presented here. While gauzes with

high palladium content have been shown to increase the production of nitrous oxide, our investigations were undertaken to discover the effects of the palladium component in the alloy on the platinum loss.

Experimental Procedure

Weight changes and platinum losses from the binary and ternary alloy gauzes commonly used in P. R. China for nitric acid production were selected for study; see Table I for the compositions of the alloys and the gauzes made from them. The weight changes of the alloys were determined by differential thermal analysis-thermal gravimetry (DTA-TG) in a pure oxygen atmosphere with a flow rate of 50 to 60 ml min^{-1}.

Heating at 80 K min^{-1} was used first to raise the temperature from ambient temperature to 900°C, then isothermal heating was applied to maintain the temperature for measured lengths of time. The sensitivity of the thermal gravimetric analysis was 1 mg and experimental details have been reported previously (10). Tests were also performed at three industrial nitric acid plants: "TY", "LY" and "KY", see Table I, where platinum losses from the woven catalyst gauzes were determined at atmospheric and medium pressures.

A scheme of the atmospheric pressure unit at the "TY" nitric acid plant is shown in Figure 1. Each of the two burners contains three gauzes, TG$_1$, TG$_2$ and TG$_3$. The gauzes in burner I
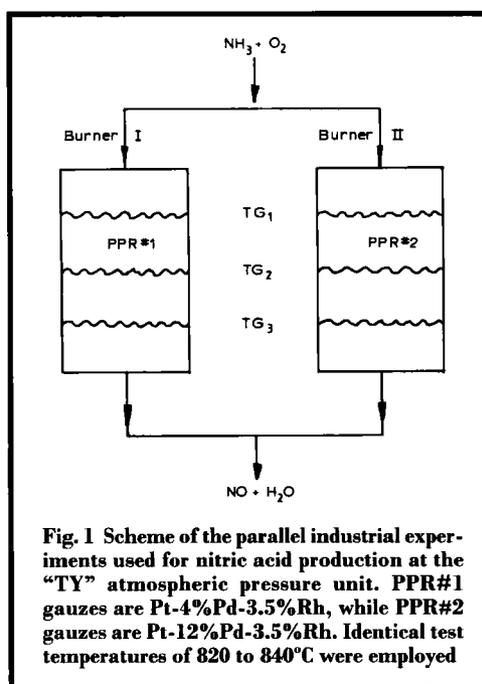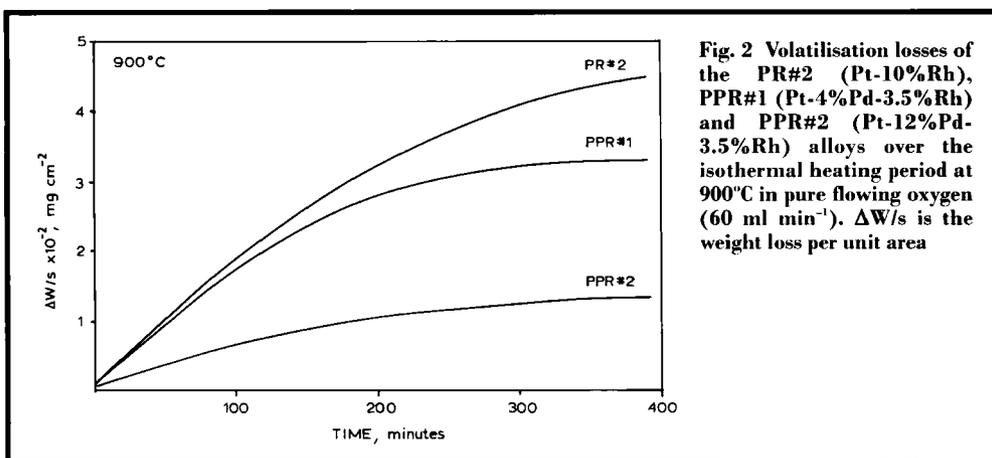

Fig. 1 Scheme of the parallel industrial experiments used for nitric acid production at the "TY" atmospheric pressure unit. PPR#1 gauzes are Pt-4%Pd-3.5%Rh, while PPR#2 gauzes are Pt-12%Pd-3.5%Rh. Identical test temperatures of 820 to 840°C were employed

are made of PPR#1 alloy and the gauzes of burner II are PPR#2 alloy. The gauzes, of diameter 2875 mm and 1024 mesh cm^{-2}, respectively, were woven from wire of diameter 0.09 mm at Kunming Institute of Precious Metals (KIPM). Gauzes PPR#1 and PPR#2 in burners I and II, respectively, were tested simultaneously under identical conditions of: pressure 0.098 MPa, temperature 820 to 840°C, ammonia concentration in the ammonia-air mixture 10.5 to 11.5 per cent and the burning intensity of ammonia is 600 to 800 kg m^{-2}. The gauzes were removed from the burners after a fixed time, cleaned in an aqueous solution of hydrochloric acid and then weighed.

Experiments at medium pressure were performed at the "LY" nitric acid plant in a unit imported into China. In this unit seven PPR#2 alloy gauzes, 2540 mm in diameter and 1024 mesh cm^{-2}, woven from 0.07 mm diameter wire at KIPM, were installed and operated for 115 days at a pressure of 0.5 MPa, temperature 860 to 870°C and ammonia concentration of 10.5 per cent. After use they were removed, cleaned and then weighed. Binary alloys: platinum-5 per

Table I Catalyst Gauze and Nitric Acid Plants		
Alloy used for gauze		Gauze name
Pt-5%Rh		PR#1
Pt-10%Rh		PR#2
Pt-4%Pd-3.5%Rh		PPR#1
Pt-12%Pd-3.5%Rh		PPR#2
Nitric acid plant	Pressure	Gauzes tested
"TY"	Atmospheric	PRR#1, PRR#2
"LY"	Medium	PR#1, PR#2, PPR#2
"KY"	Atmospheric	PPR#1

Fig. 2 Volatilisation losses of the PR#2 (Pt-10%Rh), PPR#1 (Pt-4%Pd-3.5%Rh) and PPR#2 (Pt-12%Pd-3.5%Rh) alloys over the isothermal heating period at 900°C in pure flowing oxygen (60 ml min⁻¹). ΔW/s is the weight loss per unit area

cent rhodium (PR#1) and platinum-10 per cent rhodium (PR#2) were also used in the unit, as originally designed.

Volatilisation Losses in Flowing Oxygen

Volatilisation losses for PR#2, PPR#1 and PPR#2 alloys during isothermal heating at 900°C in pure flowing oxygen are shown in Figure 2.

The weight loss per unit area is highest for PR#2 and lowest for PPR#2. After five hours, the weight loss per unit area for PPR#2 is about one third of that for PPR#1 and about one quarter of that for PR#2 alloy.

The dependence of the weight loss per unit area (ΔW/s) on the heating time (t) shown in Figure 2 can be expresses as:

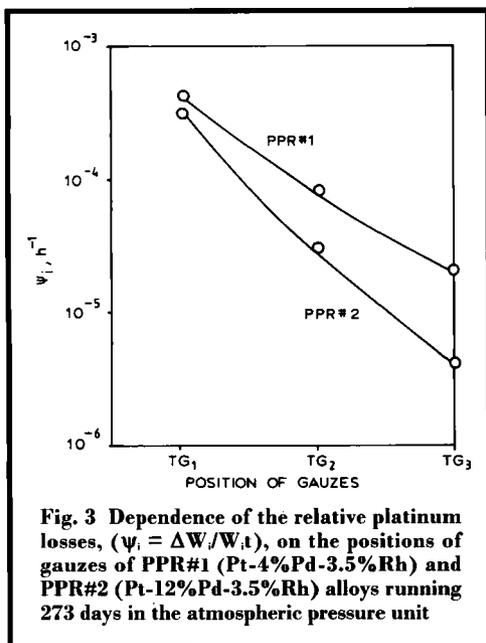$$\Delta W/s = K_1 t^{2^{-1}} \qquad (i)$$

where K_1 is the weight-loss rate constant. The values of K_1 for the three alloys are shown in Table II. The volatilisation losses for these three alloys, heated isothermally at 900°C in flowing oxygen, clearly follow the same pattern, and only the weight-loss rate constants are different. The same pattern is attributable to the weight-loss mechanism controlled mainly by PtO_2 volatilisation. The difference in the weight-loss rate constants is due to the effects of the rhodium and palladium components in the alloys on the formation rate of PtO_2. Values of the formation rates of PtO_2 (r_{PtO_2}) and the weight-loss rate constants (K_1) are listed in Table II. The r_{PtO_2} values were determined by Rubel and colleagues on gauze samples of size 5×55 mm^2 held at a temperature of 890°C for 70 hours under oxygen at 0.094 MPa pressure (6, 7). Although the K_1 values, determined in the present work, are larger than the r_{PtO_2} values (due to different alloy

Table II

The PtO₂ Formation Rate (r_{PtO_2}) and Weight-Loss Rate Constant (K_1) for Oxidation and Volatilisation Measurements of Alloys in Oxygen

Parameter	Experimental conditions	Alloy gauze		
		PR#2	PPR#1	PPR#2
K_1, μg cm^{-2} h^{-1} (present work)	900°C, 60 ml min⁻¹ pure flowing oxygen	13.2	11.6	4.6
r_{PtO_2}, μg cm^{-2} h^{-1} (Refs. 6, 7)	890°C, 0.094 MPa oxygen pressure	0.78	0.70	PPRR* 0.67

* PPRR is Pt-15%Pd-3.5%Rh-0.5%Ru alloy

Fig. 3 Dependence of the relative platinum losses, ($\psi_i = \Delta W_i/W_i t$), on the positions of gauzes of PPR#1 (Pt-4%Pd-3.5%Rh) and PPR#2 (Pt-12%Pd-3.5%Rh) alloys running 273 days in the atmospheric pressure unit

components, sample states and experimental conditions) – they tend to change in the same way. The results indicated that adding palladium to platinum-rhodium binary alloys or increasing the palladium concentration in platinum-palladium-rhodium ternary alloys resulted in a decrease in the formation rate for PtO_2 and thus the weight-loss rate constants are reduced for these alloys in the oxidation and volatilisation processes.

Platinum Loss
Ternary Alloy Catalyst Gauzes Operated at Atmospheric Pressure

During the industrial trials of PPR#1 and PPR#2 alloy gauzes in the atmospheric pressure units of the "TY" nitric acid plant, the catalyst gauzes were removed from the units on days 200, 273, 384 and 585, then cleansed in a dilute hydrochloric acid solution. Each gauze sheet was weighed and the weight loss found.

Taking the average value of the relative platinum loss each day, $\psi = \Delta W/Wt$, (where ΔW is the weight loss, W is the starting weight and t is time) as a parameter, the extent and pattern of the platinum lost from the PPR#1 and PPR#2

gauzes in the pack could be then compared.

In Figure 3 is shown the dependence of the parameter ψ_i ($i = 1, 2, 3$) for gauzes TG_1, TG_2 and TG_3 run for 273 days, on their positions in the pack. The ψ_i values of the first gauzes (TG_1) for both PPR#1 and PPR#2 alloys are the largest and are of the order of 10^{-4}. For PPR#1 gauze, from TG_1 to TG_3, the ψ_i values drops to 10^{-5}, while for PPR#2 gauze the ψ_i value drops to 10^{-6}. The ψ_i value of each gauze in the PPR#2 package is less than that of corresponding gauze in the PPR#1 package. PPR#2 alloy catalyst gauzes clearly lose much less platinum. The relationship of ψ_i values determined at other running times for the other packages of PPR#1 and PPR#2 gauzes in these positions are similar to the plots in Figure 3.

The dependence of Ψ_Σ, which is the total relative platinum loss per day for the three PPR#1 and three PPR#2 gauzes, on the running times is shown in Figure 4. This can be written as:

$$\Psi_\Sigma = K_2 t^{2/3} \qquad \text{(ii)}$$

where K_2, the platinum-loss rate constant, is 3.95×10^{-2} per day for PPR#1 alloy gauze and 2.95×10^{-2} per day for PPR#2 alloy gauze. $\Delta W/s$ and Ψ_Σ in Equations (i) and (ii), respectively, represent the weight loss and platinum loss in
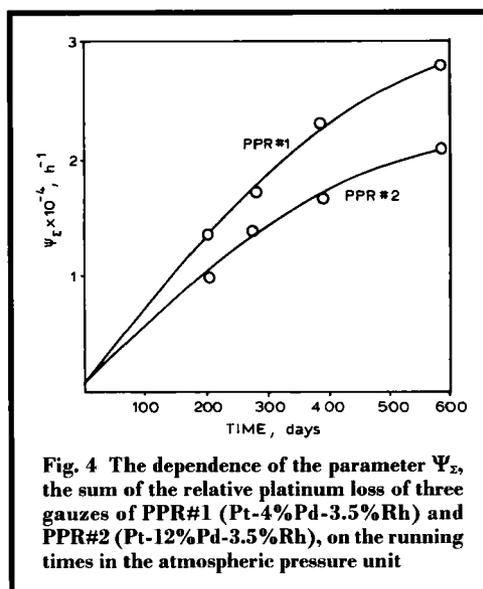

Fig. 4 The dependence of the parameter Ψ_Σ, the sum of the relative platinum loss of three gauzes of PPR#1 (Pt-4%Pd-3.5%Rh) and PPR#2 (Pt-12%Pd-3.5%Rh), on the running times in the atmospheric pressure unit

Table III

**Concentration Changes and Platinum-Loss Rate for PPR#1 and PPR#2 Gauzes
Used for 384 Days at Atmospheric Pressure**

Catalyst gauzes	Concentrations				Platinum-loss rate,
	[Pd], wt.%	[Rh], wt.%	[Pt], wt.%	[Pt]:[Pt]$_o$, wt.%	gram ton^{-1} nitric acid
PPR#1 alloy					
New gauze	4.02	3.40	92.58	–	–
TG$_1$*	4.33	3.78	91.89	0.9925	
TG$_2$	4.42	3.65	91.93	0.9929	0.061
TG$_3$	4.18	3.62	92.20	0.9959	
KG$_1$**	5.89	3.72	90.39	0.9763	
PPR#2 alloy					
New gauze	12.05	3.58	84.37	–	–
TG$_1$*	12.10	3.40	84.50	1.0015	
TG$_2$	12.00	3.48	84.52	1.0018	0.044
TG$_3$	10.86	3.51	85.63	1.0149	

* TG$_1$, TG$_2$ and TG$_3$ are three sheets of gauzes in the down stream direction, taken from "TY" plant, see Figure 1.
**KG$_1$ is the first sheet of PPR#1 gauze used for 2 years in "KY" plant

PPR#1 and PPR#2 alloys and their catalyst gauzes; their values are controlled by the mechanisms of PtO$_2$ formation and volatilisation.

The volatilisation loss, Equation (i), and the platinum loss, Equation (ii), follow the same pattern. In Equation (ii), the K$_2$ value for PPR#2 alloy gauzes is 25 per cent smaller than for PPR#1 alloy gauzes, showing that the relative platinum loss for PPR#2 gauzes during industrial operation is smaller than for PPR#1 gauzes. This can be seen in Figure 4, where the $\Delta\Psi_\Sigma$ value, obtained by subtracting Ψ_Σ for PPR#2 gauzes from Ψ_Σ for PPR#1 gauzes, becomes increasingly larger with prolonged running time, and reaches an average increase of 40 per cent on day 585.
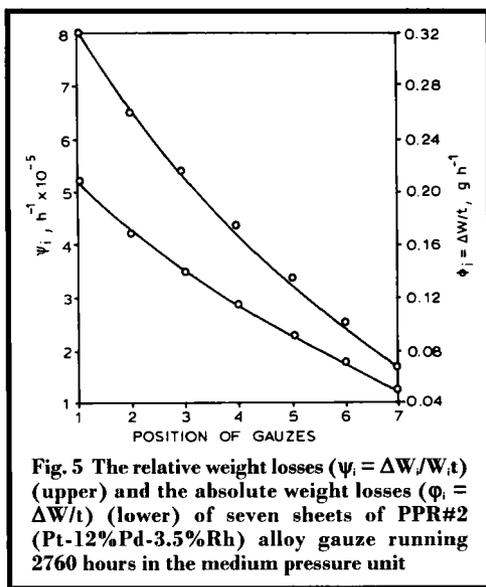
In Table III are listed the changes in composition of platinum, palladium and rhodium in PPR#1 and PPR#2 gauzes after 384 days in the "TY" plant. To show the effect of operating time on the composition, the components of a KG$_1$ gauze made of PPR#1 alloy, which had been used for two years in the "KY" nitric acid plant, are also listed. Compared with their initial concentrations in new gauze, the palladium and rhodium concentrations in the three sheets of PPR#1 gauzes have increased, while the platinum concentration has decreased. For KG$_1$

gauze, the palladium concentration increased from 4.02 per cent to 5.89 per cent, while the platinum content decreased from 92.58 per cent to 90.39 per cent. The platinum loss in the gauzes increases with operating time, thus increasing the palladium and rhodium concentrations.

However, for the three sheets of PPR#2 alloy gauze the platinum concentration did not decrease. Further, comparing the concentration ratio [Pt]:[Pt]$_o$, where [Pt] is the concentration of platinum in each used gauze and [Pt]$_o$ is the original platinum concentration in a new gauze, it has been found that:

[a] [Pt]:[Pt]$_o$ values for PPR#1 gauzes decreased with prolonged running time. For example, [Pt]:[Pt]$_o$ decreased from 0.9925 (TG$_1$ gauze in "TY" plant) after 384 days to 0.9763 (KG$_1$ gauze in "KY" plant) after 2 years.

[b] For two groups of gauzes of PPR#1 and PPR#2 alloys, the [Pt]:[Pt]$_o$ values increased from TG$_1$ gauze to TG$_3$ gauze. In other words, the platinum losses decreased gradually from the top gauze through the second gauze to the bottom gauze in the down-stream direction, which agrees with the change in ψ_i. This is probably related to both the more intense catalytic reaction and higher operating temperature on

Fig. 5 The relative weight losses ($\psi_i = \Delta W_i/W_i t$) (upper) and the absolute weight losses ($\varphi_i = \Delta W/t$) (lower) of seven sheets of PPR#2 (Pt-12%Pd-3.5%Rh) alloy gauze running 2760 hours in the medium pressure unit

the upper gauze and to the catchment and the recovery of platinum on the lower gauze.

[c] For three sheets of PPR#1 the values $[Pt]:[Pt]_o < 1$, but for three PPR#2 gauzes $[Pt]:[Pt]_o > 1$. This shows that platinum loss in PPR#2 gauzes is less than in PPR#1 gauzes. In fact, for three PPR#1 gauzes the platinum-loss rate is 0.061 gram platinum per ton of nitric acid produced, and for PPR#2 alloy the platinum-loss rate is 0.044 gram platinum per ton nitric acid, after 384 days at atmospheric pressure. The latter is 28 per cent lower than the former.

The weight loss of the gauzes includes the losses of platinum, palladium and rhodium. However, as the palladium and rhodium contents of the gauzes are much smaller than the

platinum contents, the weight loss is mainly due to platinum. In general, for woven gauzes, most of the reactions take place in the top half of the gauze pack.

Ternary Alloy Catalyst Gauzes Operated at Medium Pressure

Seven sheets of PPR#2 alloy gauzes each weighing in the range 2675 to 2685 grams were operated for 2760 hours in the medium pressure apparatus of the "LY" nitric acid plant. The nitrogen loading on the burner at medium pressure was 30 to 32 tons m^{-2} per day. Using the same method as applied to the atmospheric pressure plant, the relative weight losses per hour ($\psi_i = \Delta W_i/W_i t$) and the absolute weight losses ($\varphi_i = \Delta W_i/t$) were obtained for each gauze, see Figure 5. It can be seen that the ψ_i and φ_i values of the gauzes decrease smoothly from Gauze 1 to Gauze 7, showing the same pattern as the ψ_i values obtained at atmospheric pressure in Figure 3. Platinum losses decrease gradually from the upper to the lower gauze.

The rates of platinum loss and ammonia consumption for PPR#2, PR#1 and PR#2 alloy catalyst gauzes in the medium pressure apparatus are listed in Table IV. The platinum-loss rate for PPR#2 alloy is about 20 per cent less than for PR#1 and PR#2 alloys, and the rate of the ammonia consumption for PPR#2 is 3 to 7 per cent smaller.

The lower rates of platinum loss and ammonia consumption for PPR#2 alloy means that using gauzes made of PPR#2 can prolong service life, save platinum and reduce the production cost of nitric acid. Also, when used in a high pressure apparatus at 0.88 MPa pressure

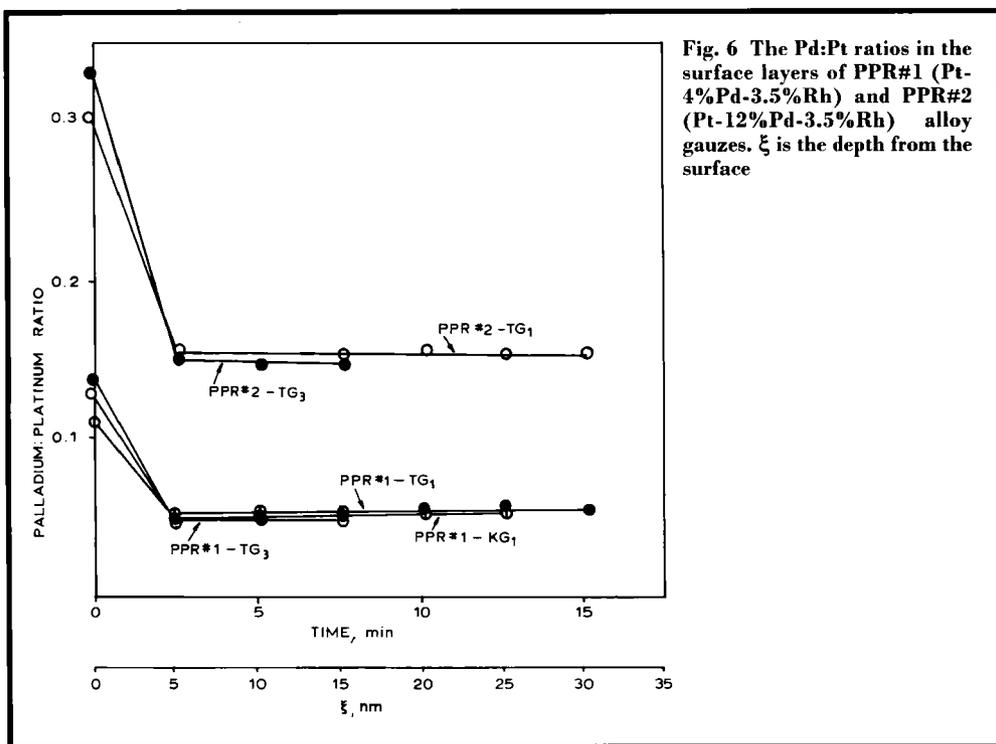| Table IV			
Platinum-Loss Rate and Ammonia Consumption for the Binary Alloys and PPR#2 Ternary Alloy at Medium Pressure			
Catalyst gauzes	Operation times, h	Platinum-loss rate, g ton^{-1} nitric acid	Ammonia consumption rate, kg ton^{-1} nitric acid
PR#1	2717	0.150	301
PR#2	1939	0.153	290
PPR#2	2760	0.121	281

Fig. 6 The Pd:Pt ratios in the surface layers of PPR#1 (Pt-4%Pd-3.5%Rh) and PPR#2 (Pt-12%Pd-3.5%Rh) alloy gauzes. ξ is the depth from the surface

and temperature of 920 to 940°C, the platinum losses from PPR#2 alloy gauzes are lower than from the platinum-rhodium binary alloys.

Discussion

These experimental industrial results have confirmed that adding palladium to platinum-rhodium binary alloys or increasing the palladium concentration in platinum-palladium-rhodium ternary alloys considerably reduces the weight loss and platinum loss in the catalyst gauzes. This may be an option for some nitric acid plants to adopt.

The surface chemical states of PPR#1 and PPR#2 ternary alloy gauzes operated for 1 year in the atmospheric pressure apparatus at "TY" plant were determined by the X-ray photoelectron spectroscopy (XPS). An Ar^+ spray was used to remove the surface to 2 nm depth (ξ) per minute. The platinum content on the gauze surfaces was found to be low, while the palladium content and thus the Pd:Pt ratio was found to be high. The larger the palladium content in the

alloy, the bigger is the Pd:Pt ratio, see Figure 6. The heat of sublimation of palladium (340 kJ mol^{-1}) is much lower than those of platinum and rhodium (about 565 kJ mol^{-1}) (11). In the ammonia oxidation reaction and the temperature range 800 to 950°C, palladium preferentially vaporises and is oxidised to palladium oxide (PdO). The surface of the catalyst thus becomes covered by a layer of palladium metal and also PdO vapour (12), the latter is almost passive toward oxygen and probably reduces the formation rate of volatile platinum and rhodium dioxide (6). The palladium metal vaporised directly and that released by the decomposition of PdO can reduce PtO_2 to platinum:

$$2Pd + 2PtO_2 \rightarrow 2PdO + Pt$$
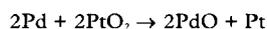
The reduced platinum can deposit on the surface of the catalyst gauzes, which gradually increases the size of parameter $[Pt]:[Pt]_o$ from the upper to the lower gauze, especially for alloys containing higher palladium content, and thus platinum loss is decreased. The mechanism of

reduction for palladium is similar to that for platinum recovered by palladium alloy catchment gauze (13).

Conclusions

In flowing oxygen atmospheres and in an ammonia oxidation environment used for nitric acid production at 800 to 950°C, the weight losses and the platinum losses from platinum-rhodium binary and platinum-palladium-rhodium ternary alloys and their catalyst gauzes obey Equations (i) and (ii):

$$\Delta W/s = K_1 t^{2/3} \text{ and } \Psi_z = K_2 t^{2/3}$$

and are controlled by the formation and volatilisation of PtO_2.

The different values for rate constants K_1 and K_2 are mainly due to the different effects of the palladium component on the formation rate of PtO_2. Adding palladium to platinum-rhodium alloys and increasing the palladium content in platinum-palladium-rhodium alloys clearly decrease platinum losses, and K_1 and K_2. This is due to palladium enrichment and the formation of palladium metal and a PdO vapour layer on and over the alloy surface, which is passive to platinum oxidation and can reduce PtO_2 to platinum, thus reducing the formation rate of PtO_2.

Results of industrial experiments for nitric acid production show that the rate of platinum loss from platinum-12 per cent palladium-3.5 per cent rhodium alloy gauzes is 0.044 gram platinum ton⁻¹ nitric acid at atmospheric pressure and 0.121 gram platinum ton⁻¹ nitric acid at medium pressure, the former being about 28 per cent lower (0.061 grams of platinum per ton of nitric acid) than for platinum-4 per cent palladium-3.5 per cent rhodium alloy gauzes, which in turn is about 21 per cent lower (0.15 to 0.153 grams of platinum per ton of nitric acid) than for platinum-5 per cent rhodium and platinum-10 per cent rhodium binary alloys.

The rate of ammonia consumption of platinum-12 per cent palladium-3.5 per cent rhodium alloy gauzes is about 3 to 7 per cent lower than for platinum-5 per cent rhodium and platinum-10 per cent rhodium binary alloys. The low rates of platinum loss and ammonia consumption of the platinum-12 per cent palladium-3.5 per cent rhodium ternary alloy mean that using the alloy can prolong the service life of the catalyst gauzes, save platinum metal and reduce the costs of nitric acid production.

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Ruthenium Photoactive Dendrimers

Dendrimers are highly defined macromolecules with large tree-like structures, which can be attached to simpler metal complexes, to make use of a physical property of the metal complex.

Scientists from universities in Italy and Germany have now synthesised photoactive dendrimers built around a luminescent $[Ru(bpy)_3]^{2+}$ core (bpy = 2,2′-bipyridine), with 12 and 24 luminescent naphthyl units in the periphery (M. Plevoets, F. Vögtle, L. De Cola and V. Balzani, *New J. Chem.*, 1999, **23**, (1), 63–69).

The larger dendrimer core fluoresces three times more than the basic ruthenium complex, showing that very efficient energy transfer is taking place from the naphthyl units to the metal core (antenna effect). This has various applications, such as antenna systems for harvesting energy in sunlight.