Platinum Recovery by Palladium Alloy Catchment Gauzes in Nitric Acid Plants

THE MECHANISM OF PLATINUM RECOVERY

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Since the introduction of palladium-gold catchment gauzes for the recovery of the platinum lost from the catalyst gauzes used in the manufacture of nitric acid, the mechanism by which these high palladium content alloys catch and recover the platinum has been of interest to both researchers and manufacturers, alike. Using analyses of the surface chemical species which form on palladium, both in flowing oxygen and during the ammonia oxidation reaction, this paper describes how the surface of the palladium, at temperatures above 800°C, is a multilayer structure with the bright palladium metal surface being covered by a thin layer of palladium metal vapour and then by a layer of palladium oxide vapour. The mechanism of the platinum recovery is related to the surface state of the palladium, and the high recovery rate by the palladium alloy catchment gauze is attributed to this unique multilayer structure and to the ability of palladium to reduce platinum oxide. Damage to either the surface multilayer structure or the oxidation characteristics of palladium decreases the platinum recovery rate. Thus, catchment gauzes made from palladium alloys containing high concentrations of base metal solutes, such as nickel, cannot be expected to have such a high platinum recovery rate.

The platinum-rhodium or platinum-rhodium-palladium catalyst gauzes used in the production of nitric acid lose weight due to the formation of volatile platinum oxide (PtO_2). Previously, the lost platinum was recovered by such methods as entrapment by a glass wool filter or a marble bed, as well as Raschig rings. In the 1960s, a new platinum recovery technique using palladium-gold catchment gauzes was introduced into ammonia oxidation apparatus (1). Since then, palladium-gold catchment gauzes have become widely used in nitric acid production plants (2, 3).

More recently, metals from Groups VIII and IB have been suggested as substitutes for the gold (4). This has led to the development of high content palladium alloys containing copper, nickel, etc., and their use in catchment gauzes (5, 6). It has been confirmed that catchment gauzes made of high content palladium alloy have a large platinum recovery rate during nitric acid production; this has caused interest in their recovery mechanism.

We suggest that the recovery mechanism is related to the surface states of the palladium or the high palladium content alloys at the operating temperatures. Therefore, the surface chemical species of palladium in a flowing oxygen atmosphere and of palladium in palladium-5 per cent nickel alloy catchment gauzes used in ammonia oxidation apparatus have been studied, and the mechanism by which they recover platinum is discussed here.

Surface Chemical Species of Palladium

Changes in the relative weight and heat absorption-heat release curves of palladium metal in oxygen flowing at a rate of 50 to 60 ml/minute have been determined by analysis of thermal

gravimetry and differential scanning calorime-
try, see Figure 1. In the temperature range from
0 to 348°C, it can be seen that the palladium
lost weight. This was the result of the volatili-
sation of any volatile material it contained and
was an endothermal process which continued
until the temperature reached 260°C, after which
exothermal palladium oxidation occurred.
However, the small weight gain which took place
on palladium oxidation was not sufficient to
compensate for the weight loss caused by the
volatilisation, until the temperature reached
348°C.

In prior literature, 348°C is thought to be the
temperature at which palladium oxide starts
to form. In fact, palladium oxidation begins at
260°C, and a gain in weight first becomes
detectable at 348°C. Weight gain occurs over
the temperature range 348 to 750°C with
increasing thickness of the palladium oxide film;
this was identified as PdO by X-ray diffraction
analysis (7). However, the curve of the weight
gain was clearly hysteretic, corresponding to the
curve of the heat changes.

In the region corresponding to 720 to 790°C
on the heat change curve, and to 750 to 800°C
on the weight change curve, the strong endother-
mal reaction and the notable weight loss should
be attributed to the decomposition of the oxi-
dised palladium, which proceeds as the
following reversible reaction (8):

$$PdO = Pd + 1/2O_2$$

Above 820°C, the exothermal palladium oxi-
dation reaction resulted in a relative gain in
weight by the sample. However, above 877°C
the palladium oxide and palladium metal evap-
orated. The decomposition pressure of PdO was
101.325 kPa (8) and the vapour pressure of pal-
ladium metal rapidly increased, due to the quite
low sublimation enthalpy (340 kJ/mol (9)) of
palladium; this resulted in a weight loss in the
system. Hence, the oxidation of palladium and
the evaporation of palladium and its oxide
showed that gain and loss of weight exist simul-
taneously, and result finally in complete loss
of weight at high temperatures.

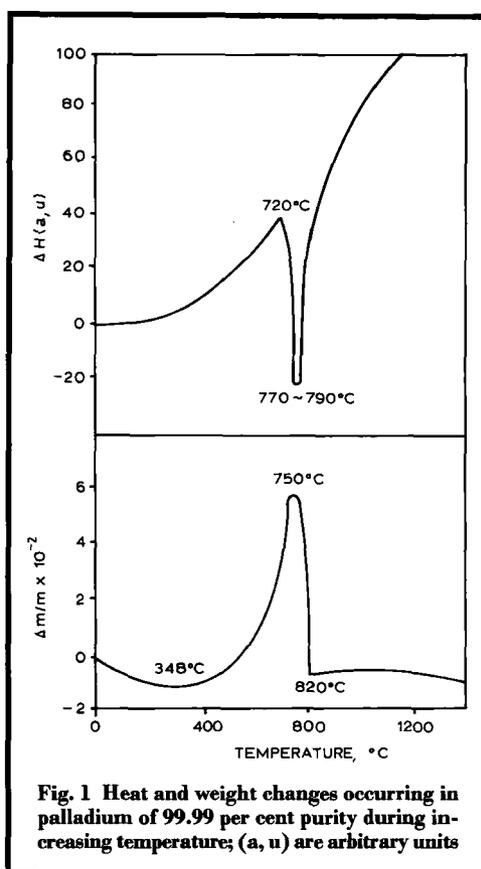In brief, palladium gains weight because it is

Fig. 1 **Heat and weight changes occurring in
palladium of 99.99 per cent purity during in-
creasing temperature; (a, u) are arbitrary units**

oxidised at temperatures below 750°C, and loses
weight because its oxide decomposes at
temperatures above 750°C.

X-ray photoelectron spectroscopic (XPS)
analysis has been used to determine the surface
chemical species of two kinds of palladium sam-
ples. Sample [1] was heated at 850°C for 2 hours
in air and then quenched in ice water. Sample
[2] was also heated for 2 hours at 850°C but
was cooled slowly in the furnace. In the XPS
analysis, the magnesium K_α ray (h_ν = 1253.6
eV) and the carbon 1s line at 284.8 eV were used
as the excitation source and as the charge ref-
erence, respectively, to determine the binding
energies accurately. The XPS for Pd 3d
and O 1s are shown in Figure 2, and the cor-
responding values of the binding energy are listed
in Table I. It is clear that the surface of Sample
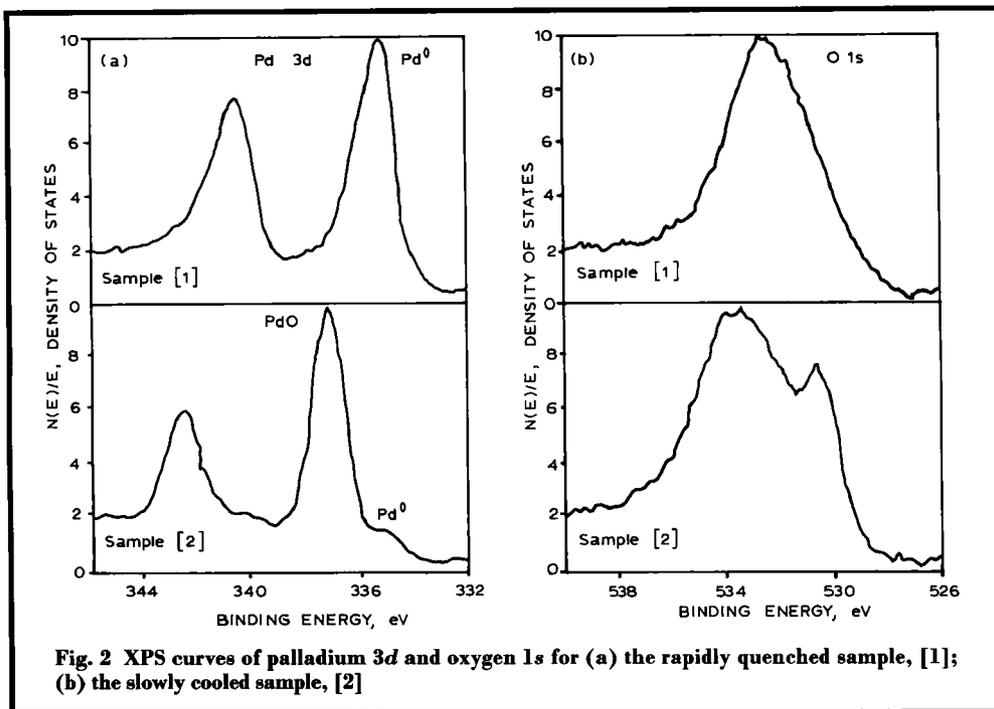[1] consists of palladium metal (Pd⁰) simply

Fig. 2 XPS curves of palladium 3d and oxygen 1s for (a) the rapidly quenched sample, [1]; (b) the slowly cooled sample, [2]

as metal, with the binding energy of Pd $3d_{5/2}$ = 335.2 eV, accompanied by absorbed oxygen; no palladium oxide was observed. Thus, Sample [1] retains its bright metal surface.

However, the surface of Sample [2] is covered by palladium oxide with binding energy of Pd $3d_{5/2}$ = 337.1 eV; this was identified as PdO, as mentioned above, and only a minute quantity of palladium metal (Pd^0) was found on the surface.

The experimental results shown in Figures 1

and 2 clearly indicate that the oxidation of palladium at temperatures above 800°C should produce a multilayer surface structure: with the bright palladium metal surface being covered (directly) by a thin layer of palladium metal vapour that is itself covered by a layer of palladium oxide (PdO) vapour, which is in contact with air or oxygen. This conclusion agrees fully with the view of Chaston (12).

Precisely because of this the palladium will retain a bright metal surface when it is either

Table I

Surface States and Binding Energies for Rapidly Cooled Palladium [1] and Slowly Cooled Palladium [2], from 850°C, eV

Sample	Pd $3d_{3/2}$		Pd $3d_{5/2}$		O $1s$	
	Pd^0	PdO	Pd^0	PdO	Bonded state	Absorbed state
Sample [1]	340.3	–	335.2	–	–	532.2
Sample [2]	–	342.3	335.1 (weak)	337.1	530.3	533.6
Refs. (10, 11)	340	–	335.1–335.4	336.3–336.9	529.3 (PdO)	–

held at, or quenched from, temperatures above 800°C, but will retain a tarnished surface covered by a palladium oxide film when it is either held at, or quenched from, temperatures below 800°C.

Palladium Chemical Species in Palladium-Nickel Catchment Gauzes

XPS was used to determine the chemical species of palladium that are present in the palladium-5 per cent nickel catchment gauzes used in ammonia oxidation apparatus operating at a pressure of 4 atmospheres and a temperature of 850°C. The gauzes, used for 5 and 8 months, were named (G-5) and (G-8), respectively. In the downstream direction, the surfaces of two sheets of gauzes were marked [a], [b], [c] and [d] from the front surface of the top gauze to the back surface of the bottom gauze. Details of the ammonia oxidation and the palladium-5 per cent nickel gauzes have been described here before (12). The XPS curves of palladium $3d$ are shown in Figure 3. The distinct shoulder peaks can be observed on the XPS trace of all the gauze surfaces, except for (G-5)[a] and (G-5)[d]. Binding energy values for palladium $3d_{5/2}$ and $3d_{3/2}$ are listed in Table II. The binding energies for palladium $3d_{5/2}$, in the range 335.15 to 335.29 eV, are in agreement with binding energy values of Pd^0, although bind-
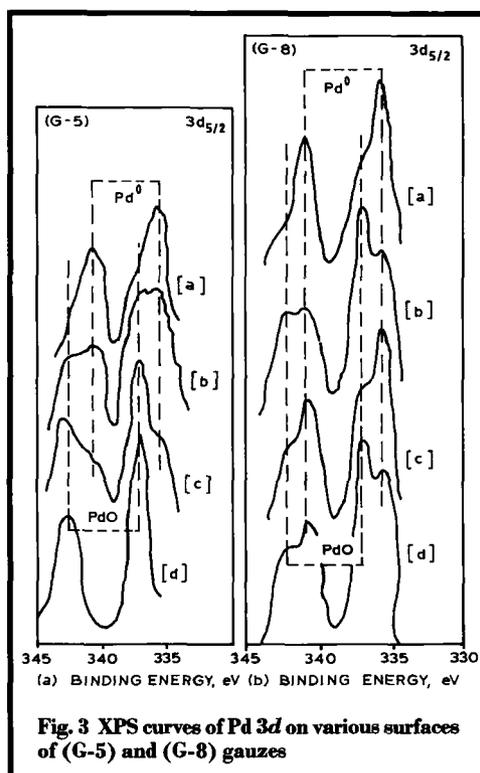

Fig. 3 XPS curves of Pd $3d$ on various surfaces of (G-5) and (G-8) gauzes

ing energies for PdO in the range 336.94 to 337.10 eV, listed in Table II, are higher than those reported in References 10 and 11 in Table I. The diffraction peaks of PdO were found in

Table II

Binding Energies of Palladium $3d_{5/2}$ and Concentration Distributions of Pd^0 and PdO on the Surfaces of (G-5) and (G-8) Gauzes

Surface of gauze	Pd^0		PdO	
	$3d_{5/2}$, eV	at.% Pd	$3d_{5/2}$, eV	at.% Pd*
(G-5)[a]	335.15	50	—	0
(G-5)[b]	335.29	45	337.0	23
(G-5)[c]	335.24	48	337.05	28
(G-5)[d]	—	0	337.10	88
(G-8)[a]	335.27	40.36	337.08	7.70
(G-8)[b]	335.28	35.88	337.05	34.3
(G-8)[c]	335.27	48.63	336.94	20.71
(G-8)[d]	335.22	42.40	337.05	37.19

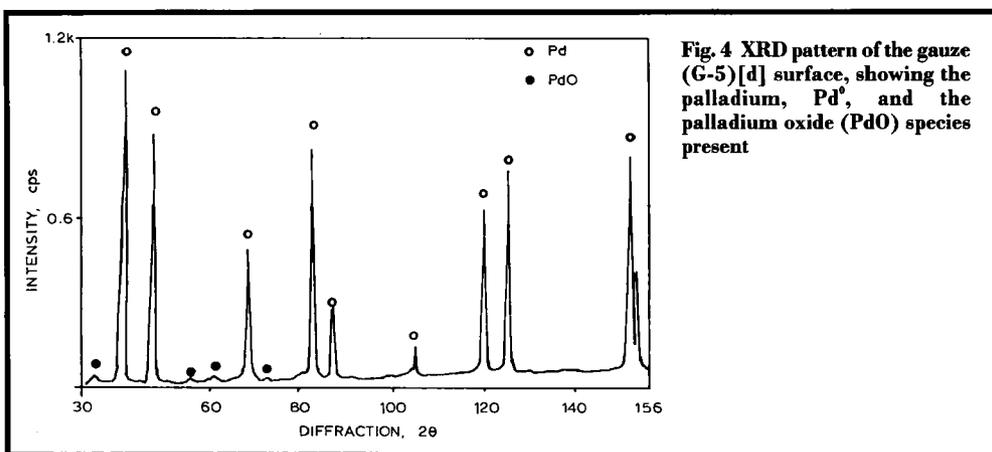*The values in this column are the palladium concentrations in palladium oxide (PdO)

the X-ray diffraction pattern of the (G-5)[d] gauze, see Figure 4. These results show that there are clearly two palladium chemical species, Pd° and PdO, present on the various surfaces of palladium-5 per cent nickel gauzes.

The concentrations of palladium (Pd°) and palladium oxide (PdO) calculated from individual peak areas are listed in Table II. Two single chemical species, Pd°, on the (G-5)[a] surface and PdO on the (G-5)[d] surface were observed. It is clear that the concentrations of Pd° on the [a] and [c] surfaces facing the gas stream are higher than those on the [b] and [d] surfaces, whereas the concentrations of palladium oxide (PdO) on the [a] and [c] surfaces are lower than those on the [b] and [d] surfaces for both (G-5) and (G-8) gauzes. On removing the (G-5)[d] surface layer by argon ion bombardment for 3 minutes, the PdO spectrum seen by XPS disappears. This indicated that the PdO species existed only in the surface to a depth of less than 6 nm. Clearly, the surface state of palladium in palladium-5 per cent nickel alloy

catchment gauzes during the ammonia oxidation reaction is the same as that of palladium in a flowing oxygen atmosphere, as mentioned above. Hence, the surface states of high palladium content alloys, which are operated at the temperatures of the ammonia oxidation reaction, consist of a similar multilayer structure: bright palladium metal surface is covered by palladium metal vapour and palladium oxide (PdO) vapour.

## Mechanism of Platinum Recovery by High Palladium Content Alloys

The platinum:palladium ratios on various surfaces of the (G-8) gauzes were determined by electron probe microarea analysis (EPMA) and are listed in Table III. The platinum:palladium ratios of the [a] and [c] surfaces are higher than those of the [b] and [d] surfaces; in other words, the front surfaces facing the gas stream recover more platinum than the back surfaces.

This is due to the platinum, which is lost from the catalyst gauzes, being deposited by gas

Table III				
Platinum:Palladium Ratios on Various Surfaces of (G-8) Gauze				
Positions	[a]	[b]	[c]	[d]
Platinum:palladium ratios*	1.5	1.0	1.3	0.6

*The ratio values were calculated using weight percentages

Fig. 5 The surface multilayer structure of palladium and the reduction of platinum oxide (PtO₂) to platinum on the surface is shown. Platinum then alloys with palladium
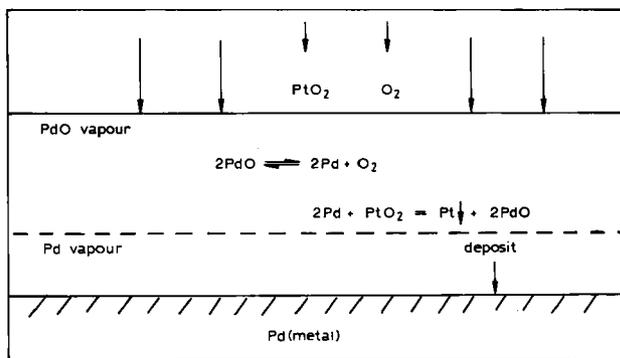
transportation preferentially on the front surfaces.

The recovery of platinum by palladium alloy catchment gauzes is a process in which the volatile platinum oxide, PtO_2, that forms in the catalytic gauzes, is transported by the gas stream to the catchment gauzes where it is reduced to platinum metal. The platinum is deposited on the surfaces of the catchment gauzes and then alloys with palladium to form new palladium(platinum) solid solutions (13, 14).

When the platinum oxide (PtO_2) vapour is transported to the catchment gauze surfaces, it first comes into contact with palladium oxide (PdO) vapour in the multilayer structure on the surfaces of the high palladium content alloys. Since the affinity of palladium to oxygen is stronger than that of platinum, the palladium released by the decomposition of palladium oxide (PdO) could remove the oxygen from the platinum oxide and reduce it to platinum:

$$2PdO = 2Pd + O_2\uparrow \qquad (i)$$
$$2Pd + PtO_2 = Pt\downarrow + 2PdO \qquad (ii)$$

Palladium metal vapour is also likely to participate directly in the reaction.

The reduced platinum immediately deposits on the bright surface of the palladium metal and alloys with the palladium, forming a solid solution. The process is shown schematically in Figure 5. It can be seen, on comparing the data in Tables II and III, that the platinum:palladium ratios are inversely proportional to the concentrations of palladium oxide on the various surfaces of (G-8) gauzes, see Figure 6. The same

tendency to inverse proportion is also found on (G-5) gauzes. This indicates that the palladium oxide participates in the platinum recovery reaction, which leads to the decrease in the palladium oxide concentrations, especially on the front [a] and [c] surfaces of both catchment gauzes. On the other hand, the porous structure in the palladium alloy gauzes that formed during the operating period was caused mainly by oxygen released from the decomposition of PdO; this was used for the reduction of PtO_2.

The platinum recovery mechanism is related to the surface state of the palladium in the catchment gauzes. As a result of the reduction effect of palladium towards platinum oxide (PtO_2) and because palladium retains its bright metal surface at high temperatures, catchment gauzes
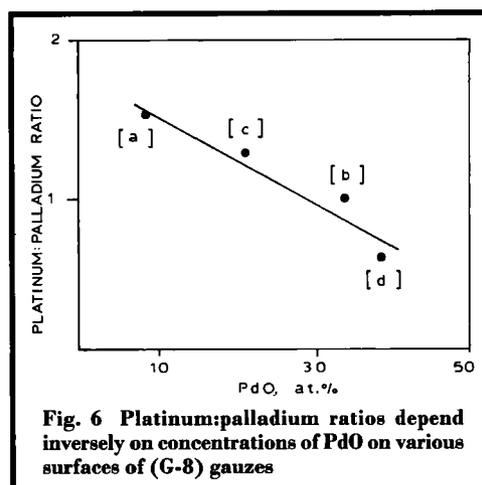

Fig. 6 Platinum:palladium ratios depend inversely on concentrations of PdO on various surfaces of (G-8) gauzes

made of palladium or high palladium content alloys can recover large amounts of platinum. Platinum and gold also retain bright metal surfaces at high temperature, but the surface state of gold does not have the ability to reduce platinum oxide. Platinum, however, is still oxidised to PtO_2 at the operating temperatures of the catchment gauzes, so the platinum recovery rate for palladium-gold gauzes is lower than that of palladium gauzes (2). Other metals, such as nickel, copper and iron, are not suitable for use as catchment gauze because they are quickly oxidised and are eventually lost under the conditions of ammonia oxidation (14).

A high content of base metal solutes is not suitable in the palladium alloys used for catchment gauzes. This is because the oxide film of the base metal solutes covers the surface of the palladium or palladium alloy, damages the characteristic multilayer structure of the palladium and decreases the platinum recovery. For example, the platinum recovery rate of catchment gauzes made of palladium-40 per cent nickel alloy used in the present experiment was only 32 per cent, whereas the platinum recovery rate of the (G-8) gauzes is 73 per cent, for the same length of time and under the same experimental conditions.

It is worth pointing out that the mechanism of recovery does not ignore any partial reduction of PtO_2 by remnant ammonia (6).

Conclusions

When palladium is heated at the rate of 5 K/min in an oxygen atmosphere, an exothermal oxidation reaction occurs at 260°C and palladium oxide is formed, resulting in a detectable weight gain at 348°C. The palladium oxide film becomes thicker with increasing temperature. The palladium oxide decomposes at 750°C, giving palladium and oxygen, which results in a loss of weight due to the release of oxygen. This is a reversible reaction and palladium can be continuously oxidised. Above 877°C, palladium metal and its oxide evaporate and the decomposition pressure of the palladium oxide and the vapour pressure of the palladium metal increase rapidly. Therefore, at temperatures above 800°C, a multilayer structure forms on the surface of the palladium and the bright palladium metal surface becomes covered immediately by a thin layer of palladium metal vapour and then by palladium oxide vapour.

Two kinds of chemical species of palladium: palladium metal (Pd^0) and palladium oxide (PdO) exist on the surfaces of the palladium-5 per cent nickel catchment gauzes used in medium pressure ammonia oxidation apparatus. The thickness of the oxide film is less than 6 nm. The platinum:palladium ratios on various surfaces of the catchment gauzes are inversely proportional to the concentrations of palladium oxide on these surfaces. Clearly, palladium oxide participates in the platinum recovery process.

A mechanism by which platinum is recovered by high palladium content alloy catchment gauzes is thus proposed and shown schematically in Figure 5. The high platinum recovery rate of the palladium or high palladium content alloy catchment gauzes is attributed to the unique multilayer surface structure and the reduction ability of palladium towards platinum oxide (PtO_2). Any factor damaging the oxidation characteristic and surface structure of palladium will decrease the amount of platinum recovered by the catchment gauzes. Thus, catchment gauzes made of palladium alloys with large concentrations of base metal solutes should not be expected to have high rates of platinum recovery.

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Iridium Apparatus for XRF Fusions

The properties required of containment materials used for X-ray fluorescence analysis (XRF) applications include good chemical resistance to the borate fluxes commonly used in the preparation of samples, sufficient hot strength to give an acceptable service life, and good wetting resistance. It must also be possible to work the material into the required form. Therefore, platinum, gold-platinum and gold-rhodium-platinum were widely used for this purpose, and the good surface finish on sample beads produced in ZGS 5 per cent gold-platinum casting moulds resulted in improved analytical accuracy (*Platinum Metals Rev.*, 1982, **26**, (3), 98).

Even these materials can be damaged, however, by the fusion of certain matrices, including some sulphides and unoxidised base metals. Now a paper from the Geoservices Centre of the Ministry of Northern Development and Mines, Canada, describes preliminary tests made to find if iridium could be used for the fusion of specific samples for XRF analysis (A. Martin, in "Summary of Field Work and Other Activities", 1995, Ontario Geological Survey, Miscellaneous Paper, 164, pp. 233–236).

The samples tested contained unoxidised base metals, sulphides, carbides and arsenides. Although the iridium crucibles contained manufacturing flaws, they did survive the fusion processes. Experiments were also performed to determine if iridium suffered from the "memory effect", where elements present in one melt would enter into the containment material and be released into subsequent samples. While iridium possesses wetting properties, it showed little or no loss of surface integrity during these metal permeability tests.

Thus, analytical sample beads have been produced in iridium crucibles from materials that would have significantly damaged and contaminated platinum apparatus. Further tests are to be carried out on new flaw-free iridium crucibles and the results are awaited with interest.

Ruthenium/Platinum in Water Electrooxidation

The oxidation of water is a basic reaction in photosynthesis, and for artificial photosynthesis any improvements to water oxidation systems must be welcome. Various systems can produce oxygen from water using metal oxides, RuO_2, IrO_2, PtO_2, and heterogeneous and homogeneous systems with metal complexes acting as the molecule-based catalyst. The trinuclear ruthenium complex, $[(NH_3)_5Ru-O-Ru(NH_3)_4-O-Ru(NH_3)_5]^{6+}$ (Ru-red) is one of the most active molecule-based catalysts. However, such catalysts have inefficient charge transfer between the electrode and the metal complex.

Researchers from Ibaraki University, Mito and the Institute of Physical and Chemical Research, Wako, Japan, have now designed a very active catalyst system for electrochemical water oxidation (M. Yagi, I. Ogino, A. Miura, Y. Kurimura and M. Kaneko, *Chem. Lett. Jpn.*, 1995, (10), 863–864). Ru-red was adsorbed onto platinum black (Pt-black) electrodeposited onto the surface of a basal-plane pyrolytic graphite (BPG) electrode, and electrochemical water oxidation tests were performed. The BPG/Pt-black [Ru-red] displayed an exceptionally steep rise in anodic current for oxygen evolution above 1.2 V. The current size after one hour at 1.3 V was 7.4 mA/cm^2, almost 10 times that for a BPG/Pt-black electrode. Additionally, oxygen began to evolve at 150 mV lower than for BPG/Pt-black, and the maximum oxygen evolution occurred when the ratio of Pt-black:Ru-red was $6.0 \times 10^{-6}:9.3 \times 10^{-3}$.

The high activity of the system is ascribed to each Ru-red molecule oxidising water in a 4-electron oxidation, as long as the trinuclear structure of the ruthenium red complex is maintained. The electrode matrix also strongly affects the activity of the Ru-red. When adsorbed on the Pt-black surface, charge is directly and efficiently injected from the Pt-black to the Ru-red complex; accounting for the high catalytic activity.