

# Redistribution of Platinum Metals within an Ammonia Oxidation Plant

## CATALYST AND CATCHMENT SYSTEMS INVESTIGATED

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*The powder recovered from the catalyst and catchment systems in a high pressure ammonia oxidation plant has been studied by a variety of analytical means. From this investigation it can be concluded that the powder results from the in-depth degradation of the platinum-rhodium catalyst gauzes and the palladium-copper catchment gauzes, together with impurities arising from the reactor constructional materials. The results indicate two different transport mechanisms, and the study may assist in the development of more stable platinum-based catalysts and catchment packages for nitric acid plants.*

The heart of medium and high pressure ammonia oxidation plants is a chemical reactor containing a platinum-based catalyst pack and an associated catchment system, which allows the ammonia oxidation reaction to take place efficiently. This reaction is considered to be a three-stage process involving the burning of ammonia gas with air over platinum-rhodium alloy gauzes to form nitric oxide, followed by the oxidation and then the absorption of this gas in water to form nitric acid. Although the oxidation of ammonia with air is complex, the overall process can be summarised as follows:



This reaction, which gives good yields at temperatures between 820 and 950°C, has been found to be sensitive to a number of variables including temperature, pressure, the presence of impurities and the rate of gas flow within the reactor, as well as on the nature and the position of the catalyst.

Under the severe operating conditions imposed by the high pressure ammonia oxidation pro-

cess, namely 920°C and 9 kg/cm<sup>2</sup>, the catalyst gauzes experience progressive deterioration, as shown by the restructured surface of the catalyst wires (1, 2, 3), the loss of catalytic activity (4-7) and the loss of catalytic materials, mainly platinum (8, 9, 10). An important part of the platinum removed from the platinum-rhodium alloy wires can be recovered at the outlet of the reactor by means of palladium gauzes. This palladium is usually alloyed with other metals, such as copper and nickel, to provide improved mechanical strength (11, 12, 13). This catchment process, which is based on the great ability of palladium to alloy with platinum, is not 100 per cent effective and a fraction of the platinum, and practically all of the rhodium lost by the catalyst wires, evades the catchment package and is then deposited in other parts of the plant, especially in the glass-wool filter placed at the outlet end of the reactor. In the same way as platinum and rhodium, palladium may experience similar losses, however to date no studies concerning the

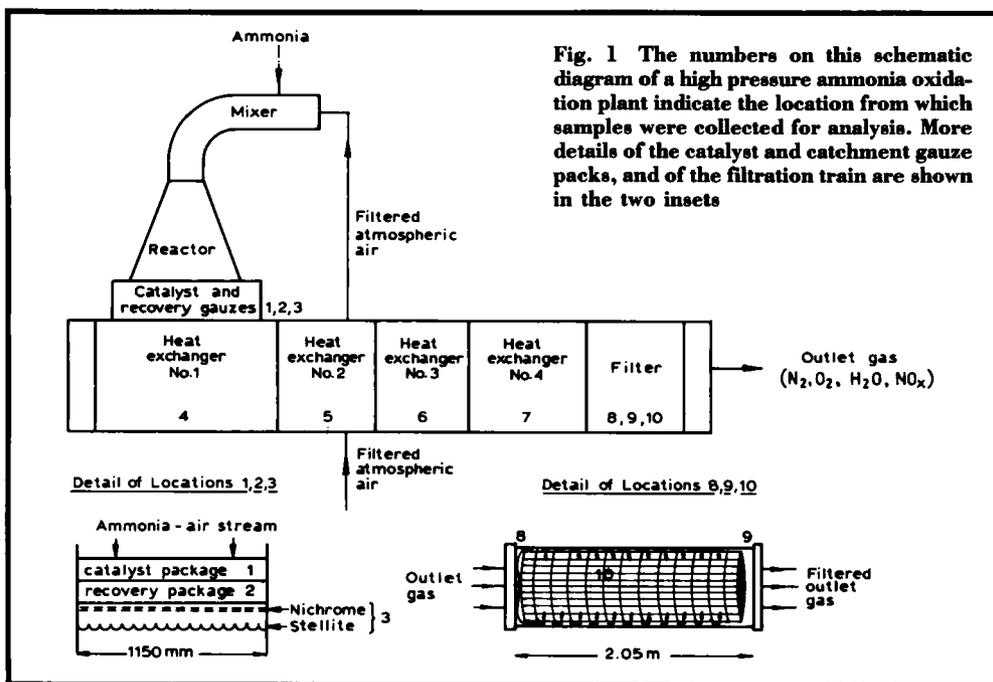


Fig. 1 The numbers on this schematic diagram of a high pressure ammonia oxidation plant indicate the location from which samples were collected for analysis. More details of the catalyst and catchment gauze packs, and of the filtration train are shown in the two insets

relocation of palladium to other parts of the plant are known.

The oxygen feed gas is not completely used up by the ammonia oxidation reaction, consequently platinum, rhodium and palladium are all susceptible to oxidation (14, 15); and  $\text{PtO}_2$ ,  $\text{Rh}_2\text{O}_3$  and  $\text{PdO}$  are stable oxides of these elements. Accordingly, it is generally believed that major material losses occur in the form of these oxides although, presumably, different mechanisms may be involved. Without doubt a most important difference is the fact that under the operating conditions the oxides  $\text{PtO}_2$  and  $\text{PdO}$  are volatile, while  $\text{Rh}_2\text{O}_3$  is not (15). Therefore platinum can leave the reactor as  $\text{PtO}_2$  vapour; part of which is trapped in the palladium catchment system, while the remainder will probably condense in the colder sections of the plant. Similarly, palladium will leave the catchment gauzes as  $\text{PdO}$  and will follow the same route as  $\text{PtO}_2$ . However rhodium, in the form of small  $\text{Rh}_2\text{O}_3$  particles, will be carried from the reactor in the gas stream and will then be mechanically deposited in different parts of the plant, determined by

the particle size and by the rate of gas flow.

Recent work relating to the same high pressure ammonia oxidation plant has shown that the types of oxide mentioned above are present on the platinum-rhodium catalyst wires (17, 18), and on the palladium-based catchment gauzes (18). Nevertheless, the evolution and distribution of these oxides and impurities throughout the different components of the plant have not yet been studied and, hence, is the aim of this paper.

### Plant and Procedure

The samples for analysis were taken from selected areas in an industrial high pressure ammonia oxidation plant, a schematic diagram of which is shown as Figure 1. The reactor is fed with a preheated 8.5 to 9.5 per cent (v/v) ammonia:air mixture, at a pressure of 8 to 9  $\text{kg/cm}^2$ . Once the reaction starts it is self-sustaining at a temperature close to  $920^\circ\text{C}$ . Ammonia oxidation occurs on a catalyst pack made up of thirty circular platinum-rhodium gauzes, of 1150 mm diameter and 1024 apertures per  $\text{cm}^2$ . A second pack consisting of seven

Table I Ambient Conditions in Different Locations of the Plant		
Location	Pressure, kg/cm <sup>2</sup>	Temperature, °C
1,2,3	9.00	920
4	7.40	650
5	7.35	600
6	7.20	550
7	7.20	450
8,9,10	—	225

palladium-copper catchment gauzes is installed at the reactor outlet for the partial recovery of the platinum metals lost from the reactor. Within the catchment pack, adjacent palladium-copper gauzes are separated by stainless steel Megapyr (5Al-20Cr) gauzes, which provide the necessary mechanical strength. Additional Nichrome (80 Ni-20Cr) and Stellite (45Co-32Cr-17W-1Fe-1Si, and <2.7C) gauzes installed at the bottom of the catchment pack improve the overall mechanical strength. The effluent gases from the reactor, mainly nitrogen dioxide, oxygen, water vapour and nitrogen, are further cooled in four heat exchangers before being passed through a glass wool filter.

In Figure 1 the numbers refer to plant locations from which samples were taken for

analysis. The local temperature and pressure at each of these locations are summarised in Table I. The samples were withdrawn from the reactor after a four months' campaign, because it was known that both platinum-rhodium catalyst gauzes and palladium-copper catchment gauzes deteriorate badly after longer times. Samples for analysis were selected with the utmost care — only powder weakly bonded to the substrate qualified for the study.

The equipment and the conditions used for the scanning electron microscopy (SEM) morphological studies, energy dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS) have recently been given elsewhere (18).

## Results and Discussion

The concentration of the platinum metals was determined by EDX analysis of the powder collected from different parts of the plant. As shown in Figure 2, the concentration depends largely on the location from which the sample was collected. However, rhodium seems to behave differently to platinum and palladium. In fact, the rhodium concentration is very high in the catalyst gauzes but decreases greatly away from the reactor, except in the terminal filter (positions 8, 9 and 10) where it increases again. Whereas, the platinum concentration is high in the powder recovered from the catalyst gauzes, but becomes almost undetectable at

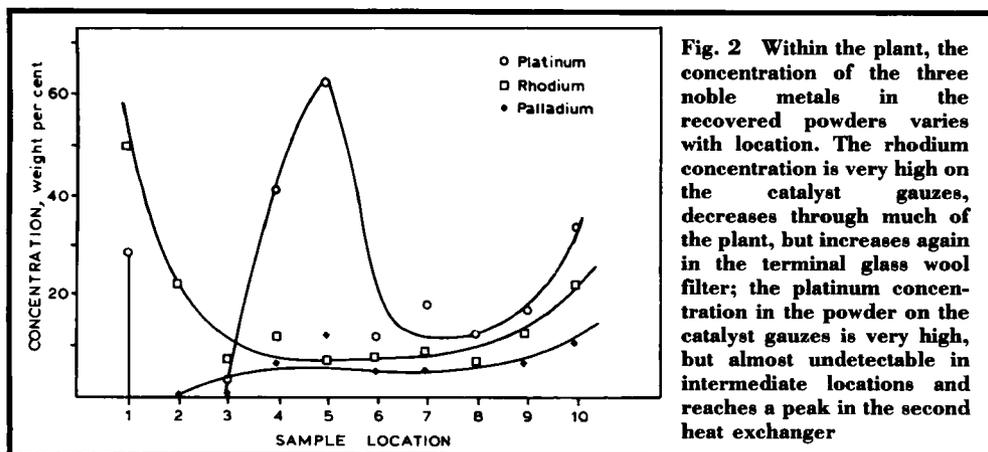
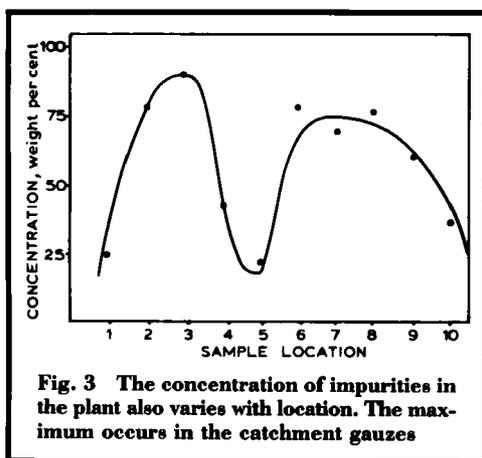


Fig. 2 Within the plant, the concentration of the three noble metals in the recovered powders varies with location. The rhodium concentration is very high on the catalyst gauzes, decreases through much of the plant, but increases again in the terminal glass wool filter; the platinum concentration in the powder on the catalyst gauzes is very high, but almost undetectable in intermediate locations and reaches a peak in the second heat exchanger



intermediate locations and reaches the highest level in the second heat exchanger. The palladium concentration follows the same trend as that of platinum, with an enrichment in the second heat exchanger, although this concentration increase is much smoother. It is noteworthy that the overall platinum and palladium concentrations in this second heat exchanger (position 5) represent approximate 70 per cent of the sample composition. Other elements including magnesium, aluminium, silicon, sulphur, potassium, calcium, chromium, iron, cobalt, nickel and copper have been detected by EDX, associated with impurities. From the nature of the more abundant

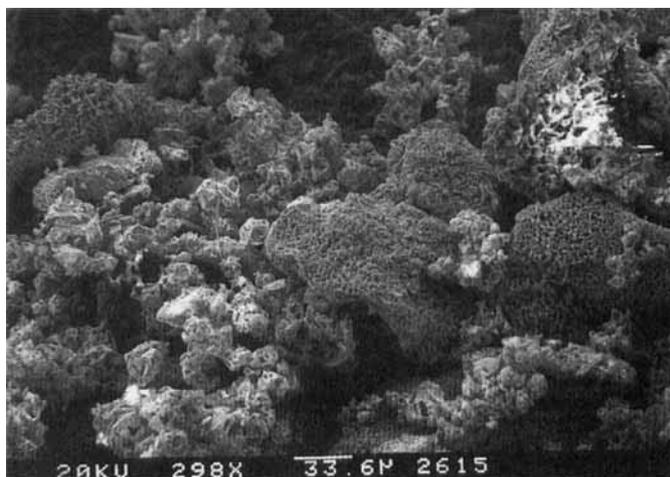
of these elements, it may be inferred that a considerable part of these impurities have a common origin—resulting from the thermal degradation and corrosion by nitric oxide of the materials from which the reactor is built. The presence of other foreign elements suggests that some impurities are probably carried into the reactor by the air stream, but have then not been trapped by the sophisticated inlet filter systems. As can be seen in Figure 3, a large percentage of these impurities accumulate in the catchment gauzes, where the temperature is high, and which may act as a filter especially when the surfaces have been severely roughened during use. The further accumulation of such impurities in the cooler parts of the plant may be due to the absence of any significant amounts of noble metals and/or preferential settling, as determined by particle size.

For a better understanding of the processes involved throughout the plant, a detailed analysis of the morphological and chemical aspects of the powder collected from various parts of the system is required.

### Powder in the Catalyst Gauzes

The morphological aspect of the powder weakly held on the platinum-rhodium alloys (positions 1 and 2) is depicted in Figure 4. Two types of particles are clearly distinguishable: polyhedral shaped particles with extended

**Fig. 4 Examination by scanning electron microscopy shows that the powder on the platinum-rhodium gauzes consists of two forms: polyhedral shaped particles with extended crystal faceting and highly porous particles**





**Fig. 5** This large irregularly shaped particle with a highly altered surface, recovered from the catalyst gauzes, consists essentially of iron. All the features suggest that it originated from part of the reactor wall, and had been degraded by the arduous operating conditions

crystal faceting, and highly porous particles. Both of these are similar to particles already described (17, 18, 19). The SEM-EDX analysis of these two particle types indicates that the platinum:rhodium atomic ratio is remarkably smaller than that of fresh platinum-rhodium gauze, especially in the porous particles where platinum is almost undetected. The impurities found in this location are composed, essentially, of iron. The shape and morphology of such an impurity is illustrated in Figure 5, which shows a large iron particle of irregular shape and with a highly altered surface. All these features appear to demonstrate that the particles have originated from the reactor walls, which become damaged due to the severe operating conditions, including very high temperatures and corrosive atmospheres.

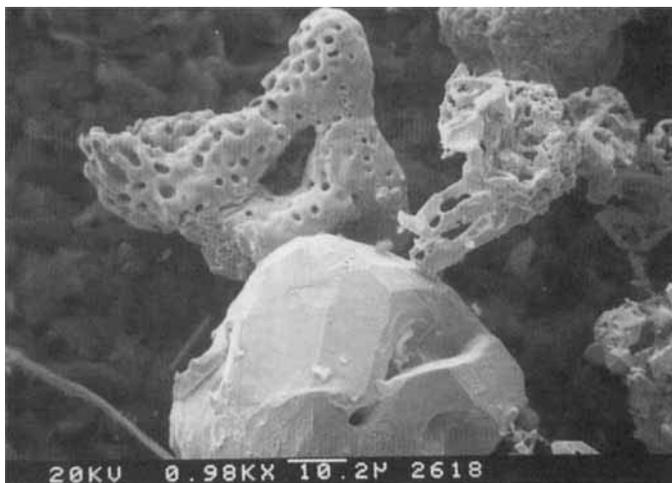
X-ray diffraction was found to be a useful technique for revealing the crystalline phases

present in the powder. As summarised in Table II, Pt<sup>0</sup>, Rh<sup>0</sup>, Rh<sub>2</sub>O<sub>3</sub> and α-Fe<sub>2</sub>O<sub>3</sub> are the main crystalline phases occurring in this location of the plant. In the light of these results it is reasonable to ascribe the rhodium-rich polyhedral particles mentioned above to fragments of platinum-rhodium catalyst wires separated from the gauzes during long periods on-stream. Similarly the porous particles containing nearly 100 per cent rhodium are assigned to Rh<sub>2</sub>O<sub>3</sub>, and the iron impurities to α-Fe<sub>2</sub>O<sub>3</sub>.

From the above results it can be concluded that the fine powder weakly held on the platinum-rhodium catalyst arises from the chemical and morphological transformation of the wire induced by the high operational temperature (17), and from the accumulation of ferric oxide originating from the reactor walls. The presence of the iron oxide impurities on

<b>Table II</b>				
<b>Peak Intensity Ratio Measured on the X-ray Diffraction Patterns</b>				
<b>Location</b>	<b>α-Fe<sub>2</sub>O<sub>3</sub> d = 0.269 nm</b>	<b>Pt d = 0.226 nm</b>	<b>Rh d = 0.220 nm</b>	<b>Rh<sub>2</sub>O<sub>3</sub> d = 0.062 nm</b>
1	1.00	0.67	0.40	0.22
2	1.00	0.22	0.36	0.47
5	1.00	16.60	—	1.30

**Fig. 6** The morphology of typical particles in the powder recovered from catchment gauzes, and the presence of rhodium as the main element, indicates that this material originated from the platinum-rhodium catalyst gauze pack



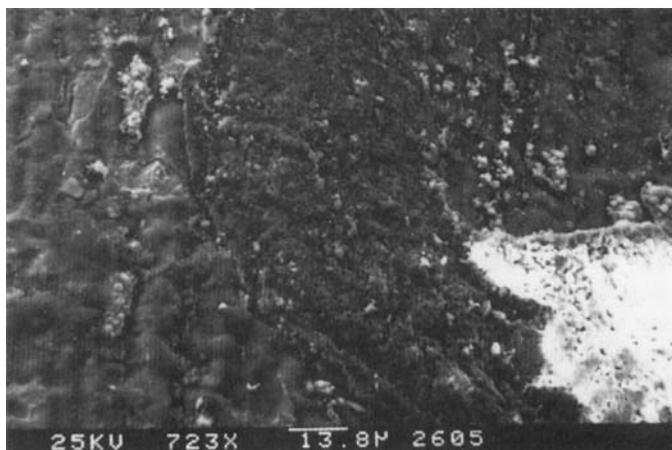
the surface of the catalyst wires is detrimental to catalyst activity because it blocks the active  $\text{Pt}^0$  sites at the surface of the wires. In practice periodic shutdowns are required to enable the iron oxide impurities to be removed from the platinum-rhodium catalyst gauzes, by a hydrochloric acid treatment (19).

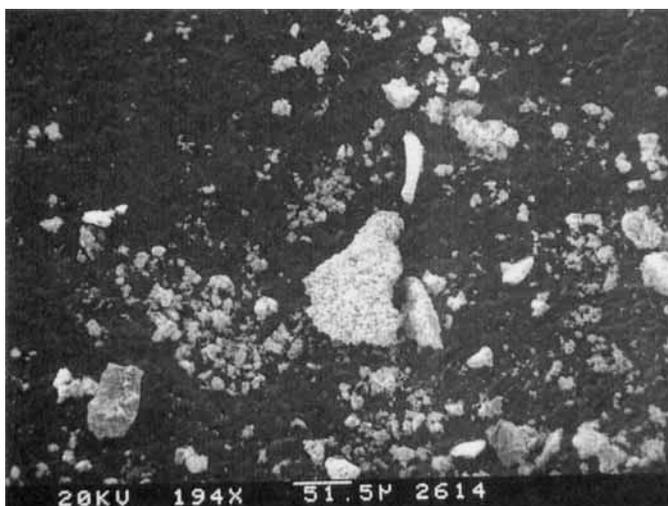
### **Powder in the Catchment Gauzes**

The powder particles weakly held on the surface of the palladium-based catchment gauzes, in area 2, have also been examined by SEM-EDX. The results show, surprisingly, that no significant amounts of either platinum or palladium are observed in the powder coating

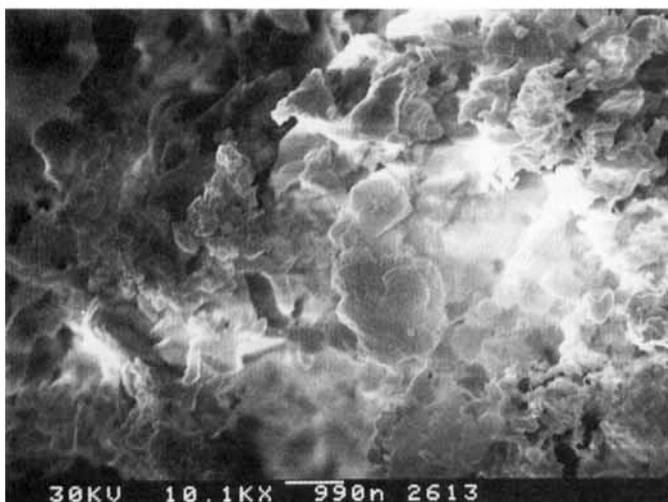
on the surface of these gauzes, see Figure 2. On the other hand, the presence of rhodium as the major element in the powder, as well as the characteristic particle morphology—which is illustrated in Figure 6—indicate that the powder deposited on the surface of palladium-based catchment gauzes arises from the platinum-palladium catalyst gauzes situated upstream. The concentration of impurities increases markedly due to the very high temperatures, as can be seen from the data in Figure 3. At very high temperatures the stainless steel Megapyr gauzes located between pairs of palladium-based catchment gauzes become severely damaged, see Figure 7, although nickel and

**Fig. 7** The stainless steel Megapyr gauzes, used to increase the strength of the catchment gauzes, are altered by the severe operating conditions





**Fig. 8 Powder recovered from the second heat exchanger includes large Megapyr particles, and other much smaller particles which may agglomerate on the stainless steel or remain highly dispersed**



**Fig. 9 Some of the smaller particles which occur in the powder from the second heat exchanger consist entirely of platinum and palladium**

chromium are only detected in other areas downstream.

### **Powder in the Heat Exchangers**

The analysis of powder recovered from areas 4 to 7 is crucial to an understanding of the mechanism by which noble metals are lost from both the platinum-rhodium catalyst and the palladium-based catchment packs, because here the temperature of the gases decreases markedly, and thus volatile oxides, namely PdO and PtO<sub>2</sub>, can condense. As shown in Figure 2, the powder in the heat exchangers is mainly composed of platinum and palladium.

This finding provides support to the mechanism proposed earlier to account for the rhodium enrichment at the surface of the platinum-rhodium catalyst wires (8, 10, 17, 18). In short, platinum is lost through evaporation of PtO<sub>2</sub>, which is carried away by the gas stream, at temperatures close to 900°C. It condenses, however, to a large extent in the first two heat exchangers, where the temperature decreases by more than 250°C.

As can be seen in Figure 8 this powder is composed of some large particles, inferred from the presence of both iron and chromium to be Megapyr alloy. In addition there are much

**Table III**  
**Binding Energies of Core Electrons in the Atoms of Samples Collected in Different Locations, eV**

Location	Rh 3d <sub>5/2</sub>	Pd 3d <sub>5/2</sub>	Pt 4f <sub>7/2</sub>	Ni 2f <sub>3/2</sub>	Si 2p	Fe 2p <sub>3/2</sub>	Cl 2p <sub>3/2</sub>	Na 1s	N 1s	S 2p
4	308.9	335.2	70.7 (73.7)	854.6	102.7	710.1	—	—	—	—
9	—	—	74.0	855.5	—	—	198.8	1072.7	407.9	168.9

Parenthesis refers to shoulder

smaller particles, shown in Figure 9, which consist exclusively of platinum and palladium, as major and minor components, respectively; and finally there are other particles ascribed to rhodium oxide. A careful examination of these platinum and palladium particles reveals that they may eventually cover the Megapyr substrate, as shown in the centre of Figure 8, or else remain highly dispersed. The complete absence of rhodium in these particles, their colloidal size and their random distribution over the Megapyr particles provide further evidence of the mechanism of deposition of both platinum and palladium from the gas phase. The X-ray diffraction patterns show that the powder at this location contains Pt<sup>0</sup> and Rh<sub>2</sub>O<sub>3</sub> phases. Palladium, however, was not detected, perhaps due to its much lower abundance. As X-ray diffraction is a bulk technique, no conclusion can be drawn about the chemical state of the atoms at the particle surface. This type of information has been obtained from X-ray photoelectron spectroscopy.

Binding energies of core electrons in the powder samples collected from the first heat exchanger are summarised in Table III. The binding energy of the Rh 3d<sub>5/2</sub> peak at 308.9 eV is typical of Rh<sup>3+</sup> ions, which is in agreement with the above XRD and SEM-EDX results. In the case of palladium and platinum the situation is somewhat more complex. The Pd 3d<sub>5/2</sub> peak at 335.2 eV showed a small shoulder in the high binding energy side at about 1.0 eV, which indicates the presence of palladium as a major species and of a very small fraction of Pd<sup>2+</sup> ions. In a similar manner, the Pt 4f<sub>7/2</sub> peak at 70.7 eV showed another small peak placed at

3.0 eV higher binding energy than the most intense peak, which means that Pt<sup>0</sup>, as a major species, and Pt<sup>4+</sup>, as a less abundant species, appear simultaneously. The existence of both Pd<sup>0</sup> and PdO, and Pt<sup>0</sup> and PtO<sub>2</sub> species can be explained assuming that the volatile oxides condense at the temperature of the heat exchanger, about 600°C, and then undergo some further reduction by the unconverted ammonia in the gas stream (17, 18). In addition, the impurities contain all the elements from the reactor materials, especially iron, nickel and silicon, but not chromium and cobalt which were not detected by XPS. An indication of the reducing environment in the region of the first heat exchanger is provided by the observation of Fe<sup>2+</sup> ions in the XPS spectra of Fe 2p core levels of the samples, instead of Fe<sub>2</sub>O<sub>3</sub>, see Table III.

### Powder in the Glass Wool Filter

The data presented in Table I shows that the temperature of gases in the glass wool filter (areas 8, 9 and 10) is relatively low and, therefore, other compounds which have travelled through the reactor in the gas phase, either as feed air contaminants or as reaction products, can condense in this location.

The SEM-EDX analysis clearly demonstrates that an important accumulation of sulphur occurs in the filter. It is very likely that the origin of this sulphur is atmospheric sulphur dioxide, present as a contaminant in the environment of the industrial area where the high pressure ammonia oxidation plant is located. However, the low atomic number elements carbon, oxygen and nitrogen have not been detected by this method of analysis, possibly due to adsorption

by the beryllium window; neither have other elements with characteristic peaks in strongly overlapping spectral regions, such as chlorine. The X-ray photoelectron spectra were conclusive on this point.

As data which are summarised in Table III show, a substantial proportion of sodium, chlorine, nitrogen and sulphur, and lesser amounts of nickel and platinum were detected. Judging from the binding energy values, the chemical states of these elements seem to be  $\text{Na}^+$  and  $\text{PtO}_2$ . In order to understand which salts are dominant an estimation of the atomic ratios of these elements has been calculated. The Na:Cl and Ni:(N + S) ratios, determined from the intensity ratios and published atomic sensitivity factors (20) for these levels, were 1.07 and 0.87, respectively. These results suggest that the most plausible  $\text{Ni}^{2+}$  salts are nitrates and sulphates, while sodium chloride seems to be the most abundant sodium salt. The origin of sodium chloride in the filter is difficult to explain in the light of the above results alone, and further research is needed to understand the route by which this salt is incorporated into the outlet stream.

## Conclusions

The data presented here legitimise the statement that the powder weakly held on the catalyst gauzes is composed of rhodium-enriched oxidised particles and impurities, mainly  $\alpha\text{-Fe}_2\text{O}_3$ , arising from reactor materials. The powder on the catchment gauzes comes mainly from the catalyst gauzes, carried by the gas stream. The additional deterioration of Megapyr, Nichrome and Stellite contributes to the increase in the impurities which accumulate downstream. Because the temperature in the first heat exchangers is sufficiently low the volatile oxides  $\text{PtO}_2$  and  $\text{PdO}$  condense, thus giving support to the mechanisms currently proposed to account for the platinum and palladium losses. In the final filter impurities accumulate, some of which result from the polluted air, others from the reactor materials and yet others resulting from interaction with the reaction products.

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## Electroless Osmium Deposition

The unique properties of osmium including hardness, high reflectivity, extremely high melting point, and good chemical resistance make it a suitable material for use in non-oxidising atmospheres. None the less it does not find wide industrial application. A recent communication from the National Tsing-Hua University, Taiwan, however, reports the successful deposition of an amorphous osmium thin film on to single crystal silicon by electroless deposition from a hypophosphite-based bath (Y.-S. Chang and M.-L. Chou, *Mater. Chem. Phys.*, 1989, **24**, (1-2), 131).

The process ensures the cleanliness of the interface between the osmium and the silicon. The interface is abrupt, flat and without porosity, and annealing techniques may facilitate the growth of epitaxial silicide/silicon Schottky diodes. Tentative mechanisms for the growth of the film are proposed and discussed.