Platinum Recovery in Ammonia Oxidation Plants

EXPERIENCE OF THE GOLD-PALLADIUM CATCHMENT GAUZE SYSTEM

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Since the initial development of the gold-palladium catchment gauze system for platinum recovery in 1968 considerable practical experience has been obtained. The optimism expressed at that time proved to have been well founded, recovery figures in excess of 60 per cent of the gross platinum losses having been regularly obtained. Some initial problems with the mechanics of installation have now been overcome and this article describes the practical aspects of the recovery system and its effect on the economics of the ammonia oxidation process.

The manufacture of nitric acid by the oxidation of ammonia over a platinum or platinum alloy catalyst, as first carried out by Ostwald in 1908, is today one of the major cornerstones of the economy of the developed world. The enormous quantities of nitric acid that are produced annually – around 3,000,000 tons per year in the United Kingdom alone – are almost all consumed by the production of artificial fertilisers, explosives and man-made fibres, and the worldwide demand is increasing in parallel with the demand from underdeveloped countries.

The process of ammonia oxidation has been fully described in this journal and elsewhere (1-5) but in principle it consists of passing a mixture of air and anhydrous ammonia over a platinum or platinum alloy catalyst in the form of a number of gauzes maintained by the exothermic reaction at a temperature of between 750 and 950°C to produce nitric oxide and water vapour.

\[4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}\]

This is a simplified equation for the reaction since there is considerable debate over its exact form. The nitric oxide is further oxidised by excess air and is then absorbed by water to produce nitric acid. Plants may be operated at pressures ranging from one to ten atmospheres, depending on the design.

During the course of the ammonia oxidation reaction platinum and rhodium are lost from the catalyst in the form of volatile oxide vapours. These vapours are carried downstream and eventually decompose in cooler parts of the plant so that both platinum and rhodium are deposited as fine particles. Some of these particles may remain within the plant – commonly on the tubes of the steam superheater immediately below the gauze (these tubes usually collect sufficient platinum to warrant refining when they are removed for renewal) – or be lost with the tail gas, or deposited as a sludge within the nitric acid storage tanks. However, the amount of platinum recovered from superheater tubes and acid storage tanks represents a small percentage of the total losses and, particularly in the case of heat exchangers, the time interval between recovery opportunities is considerable.

The amount of platinum and rhodium lost varies from plant to plant but is generally less in plants operating at atmospheric pressure than in those operating at high
Fig. 1 Newly installed gauzes at the ammonia oxidation plant of Thames Nitrogen at Rainham. The six catalyst gauzes have been rolled back to show the position of the catchment gauze pack beneath them. By making its diameter about 50 mm less than that of the burner throat the pack is able to expand without restriction until at operating temperature the diameters are equal. This arrangement has proved very satisfactory.

pressures (6 to 10 atm). Typical platinum loss figures are 0.05 to 0.11 g/ton HNO₃ produced for plants operating at atmospheric pressure and 0.20 to 0.45 g/ton HNO₃ produced for high pressure plants.

Figure 2 shows the recorded platinum loss...
rates from a number of different plants located in various parts of the world. The higher band generally represents the losses from older plants, particularly in the case of the figures for 7 to 10 atm.

The intrinsic cost of these quantities of platinum represents a very small part of the cost of a ton of nitric acid. However, in terms of the total tonnage produced per year the cost is considerable. If an average loss figure of approximately 0.16 g/ton HNO₃ produced is taken for all the plants at present operating in the U.K. then the gross losses to the industry are about 480 kg per year. The price per kilogram of platinum provides a considerable incentive to recover these losses.

Various platinum recovery systems for ammonia oxidation plants have been available for many years, such as glass wool filters, Raschig rings and marble chips, which are placed below the catalyst. All of these systems recover platinum with varying degrees of success but they have significant operational disadvantages. The glass wool filtration system, being placed some way downstream from the catalyst, traps platinum as discrete metallic particles together with any other solid particles present in the gas stream. The pressure drop across the filter increases and eventually plant operation can be affected to the point of overriding any economies of platinum recovery. Glass wool filtration systems have occasionally been known to recover up to 50 per cent of the gross platinum losses but, because of particles other than platinum being present, an unacceptable pressure drop is often experienced before completion of the acid production campaign. The problem of rapid pressure drop can sometimes be overcome by using a coarser filter but this in turn leads to reduced platinum recovery efficiency. A general recovery efficiency of 10 to 20 per cent is representative of filtration systems. The use of glass wool filters in plants operating at atmospheric pressure is not common because of the extreme sensitivity of these plants to pressure drop.

Ceramic Raschig rings placed beneath the catalyst do not have a particularly high recovery efficiency. Very few Raschig ring beds recover sufficient platinum to warrant recovery, especially as the cost of extraction and refining is relatively higher than for other systems.

Marble chips 3 to 5 mm diameter placed immediately below the catalyst bed (the O.S.W. process) (6) can give high recovery figures. As the reaction temperature rises above 600°C they decompose to calcium oxide, which absorbs the volatilised platinum. However, below 600°C calcium oxide reacts with any water vapour present to form calcium hydroxide, a situation that will occur during plant shutdown. On subsequent reheating this reaction is reversed and the chips form a fine powder. The pressure drop through the powder is considerably greater than through the chips. Thus there is a pressure build-up in high pressure plants that could prove explosive. Hence the use of this process is precluded in high pressure plants where shutdowns are relatively frequent. The cost of extracting and refining the platinum recovered by this method is also relatively high.

The limitations of these recovery systems led to the development of the gold-palladium alloy catchment gauze recovery process by Degussa. Detailed accounts of the development of this system have been given in this journal and elsewhere (7, 8) but a brief account of the principal elements of the system will be given.

As previously stated, the loss of platinum and, to an extent, rhodium from catalyst gauze surface occurs primarily by the volatilisation of the oxide PtO₂ (8, 9). If this vapour is brought into contact with a suitable metallic surface maintained at an elevated temperature the vapour will decompose at the surface and platinum will diffuse into the bulk of the material. The material chosen for the “getter” must not form surface oxide films at the temperature of operation and must readily dissolve platinum. The choice of
materials was therefore either gold, palladium or platinum itself.

Trials were carried out using gold, palladium and various alloys of the two, woven into the form of gauze. The gauzes were placed immediately below the catalyst, being separated from each other and from the rhodium-platinum catalyst gauzes by a coarse austenitic stainless steel mesh. Pure palladium was found to give the highest platinum recovery efficiency but was mechanically unsatisfactory. Eventually an alloy of 20 per cent gold-palladium was chosen as having the best combination of strength and recovery efficiency.

Gauzes woven from 20 per cent gold-palladium, separated by stainless steel mesh, were tried under varying plant conditions. It was found that the platinum recovery efficiency of a single gold-palladium gauze depended upon the gauze loading, as shown in Fig. 3. The efficiency of each individual gauze in the pack was found to be the same in terms of presented platinum, i.e. if the first gauze of a pack collected 20 per cent of the gross platinum losses then the second gauze collected 20 per cent of the remaining platinum which was presented to it or 16 per cent of the gross platinum losses. Hence, for a recovery system using more than one gauze the total percentage recovery of the gross platinum losses is expressed by:

\[ S = \left[ 1 - \left(1 - \frac{a}{100}\right)^n \right] \times 100, \]

where \( S \) is the total recovery of the gross losses by all the gauzes, \( a \) is the percentage recovery of the gross losses by the first gauze and \( n \) is the number of gauzes used in the pack.

The rate of platinum recovery was found to be constant up to a certain point, which may be termed the saturation point. For practical reasons the saturation point is taken as the point where the recovery constant \( K_r \) in the following expression is 80 per cent.

\[ K_r = \left( \frac{\text{weight of platinum recovered}}{\text{weight of catchment gauzes when new}} \right) \times 100. \]

It was also found that a certain percentage of the palladium was lost, to the extent of roughly 33 per cent by weight of the platinum recovered.

Pilot plant trials established that the ammonia to nitric oxide conversion efficiency was unaffected and that by keeping the value of \( K_r \) to 80 per cent the pressure drop was not significant. From these results it was clear that an extremely efficient system of platinum recovery was now available.
Production Installations

Following the development of the catchment gauze recovery system by Degussa, Johnson Matthey & Co Limited were appointed sole licence agents for the process in the United Kingdom. In the period since 1968 Johnson Matthey has gained great experience in the installation and operation of these catchment gauzes, following detailed discussions with nitric acid producers in Great Britain and elsewhere.

Having proved the system viable on an experimental basis, the next step was to introduce the recovery system to producers of nitric acid and to obtain confirmation of the experimental results. The initial trials were for convenience carried out on plants with fairly small diameter ammonia burners. The plants chosen were fairly old high-pressure designs producing about 50 tons of nitric acid per day. Platinum loss rates were in the order of 0.45 g/ton HNO₃ produced and the length of the acid-making campaign was typically two to three weeks. Owing to the high gauze loading of these plants, the individual gauze recovery potential was low, in the order of 12 per cent of the presented platinum, meaning that six gold-palladium gauzes would give about 50 per cent recovery, a convenient target. A trial pack was made up of six gold-palladium gauzes of 200 mesh/cm², 0.18 mm wire diameter, separated by seven austenitic stainless steel (25 per cent Cr-20 per cent Ni-Fe) gauzes of 49 mesh/cm², 0.4 mm wire diameter. Results were extremely promising, 55 per cent recovery being attained with no detectable change in operating efficiencies.

During the first trial the gold-palladium and stainless steel gauzes had all been of the same diameter as the overall diameter of rhodium-platinum catalyst gauzes, the whole catalyst/catchment pack being held by the normal clamping mechanism (Fig. 4). A further trial was carried out with gold-palladium gauzes having a diameter the same as the contact diameter of the rhodium-platinum gauzes, these being carefully aligned in the burner throat between the layers of stainless steel gauzes (Fig. 5). This, it was hoped, would make the maximum use of the gold-palladium gauzes without affecting their recovery efficiency. The results of this trial showed that this system recovered as much platinum as during the first trial while reducing the intrinsic cost of the catchment gauzes.

Another benefit noticed in both trials was that the uniform support given by the catchment gauze pack left the catalyst gauzes in much better condition than usual at the end of a campaign, while there was also some evidence that gas mixing was improved.

Having proved the system on a small commercial plant a further trial was carried out on a medium pressure plant having a
contact diameter of 2.1 metres and an acid-making campaign of four months’ duration. The catchment gauze pack for this plant consisted of two gold-palladium gauzes interleaved between three stainless steel gauzes. Calculations showed that the catchment gauzes, because of the lower platinum losses of the plant, would not become saturated in one campaign but could, in fact, be left in for two campaigns, i.e. a total of eight months’ running time. The recovery of the gross platinum losses was calculated as being 60 per cent. At the end of the first campaign the stainless steel gauzes showed signs of quite marked oxidation but were considered to be suitable for a further four months’ running. At the end of the second campaign the pack was removed for refining, the stainless steel by this time having become quite brittle. On refining the gauzes a weight of platinum equivalent to 63 per cent of the gross catalyst losses was recovered along with rhodium equivalent to 5 per cent of the gross losses. Palladium losses from the catchment gauzes were found to be equivalent to 35 per cent of the weight of platinum recovered.

From the recovery aspect the trial had been a complete success with no detectable deleterious effects upon the operation of the plant. However, the embrittlement of the stainless steel gauzes presented a potentially difficult problem because the gold-palladium gauzes become fragile quite quickly and rely upon the support of the stainless steel gauzes to prevent tearing. A stainless steel of improved oxidation resistance was needed. This trial also showed that, because the individual gauze recovery efficiencies were high (in the order of 40 per cent), the top gold-palladium gauze was nearing saturation long before the gauze below it, this having recovered \( \frac{100 - 40}{100} \times 40 \) per cent of the gross losses (24 per cent). As the saturation weight of the gold-palladium gauze is related to the weight of platinum recovered by it, a lighter weave could thus be used for the second gauze. A second type of standard weave was produced with 1024 mesh/cm² from 0.09 mm wire having a weight of 0.546 kg/m² compared with 0.960 kg/m² for the original “heavier” gauzes. Thus by using heavy gauzes for the top of a pack and light gauzes towards the bottom of the pack the gold-palladium would be used to its maximum capacity, thereby keeping manufacturing, refining and intrinsic costs to a minimum. Subsequent trials elsewhere confirmed the advantage of using gauzes of two different weaves in many medium pressure plants, there being no detectable difference in the recovery efficiency between the weaves.

These trials showed that whereas, given enough gauzes, 99 per cent recovery of gross...
platinum losses was possible theoretically, in general the economic recovery was about 55 to 70 per cent, depending on the type of plant. Above this range the cost of manufacturing and refining the additional gauzes needed outweighed the value of the platinum that could be recovered.

Following the success of the initial trials installations were arranged on plants of various types and diameters and it became clear that the choice of stainless steel for the separating gauzes had been an unfortunate one. While the low oxidation resistance of 25 per cent Cr-20 per cent Ni-Fe could be accepted in many plants, the high expansion coefficient presented mechanical problems in those of large diameter. Also the type of catalyst pre-ignition heating system needed consideration and, if necessary, slight modification before installing a catchment gauze pack.

Simultaneous trials at two large-diameter plants showed that the expansion of the stainless steel gauze was relieved by wrinkling. During any shutdown the gauze cooled rapidly and contracted, causing tension on the clamping mechanism. This tension was relieved more easily by gauze movement in the clamping flange than by straightening the wrinkles. Gauze expansion could exceed 50 mm on 3 metres diameter, i.e., gauze movement in the clamp grips could reach 25 mm, and if the clamping ledge shown in Fig. 5 was less than 25 mm the gauzes were likely to pull out completely. Even if the ledge was wide enough to accept this movement the first time, the problem was likely to occur during a subsequent shutdown owing to a “ratchet” effect.

While awaiting an acceptable stainless steel a catchment gauze pack was tested that was not gripped in the clamping flanges. Pack diameter was 40 to 50 mm less than burner throat diameter, as shown in Figs. 1 and 6. This pack could move without restriction during expansion, its diameter increasing until it equalled that of the burner throat at the operating temperature. The pack shrank somewhat during cycling but no operational problems occurred nor were recoveries affected, the area not covered by the pack being only a small fraction of the catalyst working area at the operating temperature. Figure 7 shows this pack after one catalyst campaign. Figure 8 shows the appearance of the gold-palladium after use.

Megapyr 2 (5 per cent Al-22 per cent Cr-Fe) stainless steel has now been adopted.

Fig. 6 The arrangement of an unclamped gold-palladium catchment gauze pack. The top stainless steel separating gauze has a larger diameter than the others. It is wrapped round the edge of the pack to present a smooth edge to the catalyst gauzes.
Fig. 7 An unclamped catchment gauze pack in a large medium-pressure ammonia burner. It has shrunk somewhat after one acid-making campaign but is still perfectly operational and platinum recovery will not be affected when the pack expands again on reheating.

Fig. 8 Close-up of the edge of the catchment gauze pack shown in Fig. 7. Apart from minor tears along the edge the gold-palladium gauze is in good condition. It is ready to undertake recovery of platinum during a second acid-making campaign. The operator is holding one of the stainless steel gauzes, which are in good order.
Fig. 9 Damage caused to a catchment gauze pack when the fixed air-hydrogen ring burner used to pre-heat the catalyst gauzes before ignition burned for too long thereby causing extreme localised overheating.

for the separating gauzes. It has a thermal expansion coefficient of \(14 \times 10^{-6}\) between 100 and 900°C, a maximum continuous operating temperature of 1300°C and outstanding oxidation resistance, since the aluminium forms an adherent surface oxide film which prevents further oxidation of the steel. Although its cost is about 50 per cent higher than the original stainless steel, it reduces operating costs because the separating gauzes can be used for a longer time. The adoption of Megapry 2, combined with clamping modifications, has fully overcome the problems of excessive expansion and embrittlement of the support gauzes.

The installation of catchment gauzes in two particular plants produced unexpected problems. Melting of both the stainless steel and the gold-palladium gauzes occurred, caused by difficulties with the air-hydrogen burners used to pre-heat the catalyst gauzes before the introduction of ammonia. While these burners are designed to heat the gauzes to a temperature sufficient only for ignition under practical commercial plant conditions, i.e. in the order of 800 to 900°C, (although during research ignition has been achieved at less than 300°C), the ring burners in question produced locally extreme temperatures. In one case the temperature was sufficient on a number of occasions to melt even the 10 per cent rhodium-platinum catalyst gauzes (melting point 1850°C). As the melting point of both the gold-palladium and the stainless steel is in the order of 1500°C, melting readily occurred during the light-up sequence, the molten catchment gauze pack fusing to the bottom of the catalyst gauzes.

In one case the problem was overcome by fitting a lockable pressure-reducing valve on the hydrogen line and by ensuring that the gauzes are heated for no longer time than is necessary for ignition. Modifications are in hand on the second of these plants to raise the ring burner within the hood. This will increase the gap between the gauzes and the
burner, the two being at present in close proximity. Figure 9 shows the pattern of damage caused to the catchment gauze pack.

The two most suitable gauze pre-heating systems in this context have been electrical and rotating air-hydrogen burners. It is important with the latter to ensure that the burner is kept rotating at all times while lit to prevent the risk of local overheating.

In all but one instance such problems have now been overcome and it is expected that this plant will also be using catchment gauzes soon when the modifications to the gauze pre-heating system now in hand have been completed.

Examples of the catchment gauze packs now in use in various typical ammonia oxidation plants, together with the platinum recovery figures obtained, are shown in Table III.

Pressure Drop

While maintaining $K_r=80$, the pressure drops recorded across various types of catchment gauze packs during the final stages of installation have remained within acceptable limits. (See Table I). If the acid making campaign is likely to be extended significantly beyond its normal period the catchment pack may be designed with $K_r=70$ to give a margin of flexibility.

Table I
Pressure Drop across Catchment Gauze Packs

<table>
<thead>
<tr>
<th>Pad Configuration (Number of Gauzes)</th>
<th>Pressure Drop across Pad at Saturation $(K_r=80)$</th>
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<tbody>
<tr>
<td>1 Au-Pd+2 stainless steel</td>
<td>20 mm H$_2$O</td>
</tr>
<tr>
<td>4 Au-Pd+5 stainless steel</td>
<td>100 mm H$_2$O</td>
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Palladium Losses

During the initial trials it was found that about one gram of palladium was lost for every three grams of platinum recovered by the gauze. Subsequent experience has shown that palladium losses vary with the type of plant, as shown in Table II. Gold losses have been minimal, usually amounting to about 20 to 30 g in a large pack.

<table>
<thead>
<tr>
<th>Gauze Loading tons N/m$^3$.day</th>
<th>Pd Loss:Pt Gain</th>
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<tbody>
<tr>
<td>40-60</td>
<td>40-45</td>
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<tr>
<td>25-35</td>
<td>30-35</td>
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<tr>
<td>5-10</td>
<td>20-25</td>
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Design of the Catchment Gauze Pack

As shown in Fig. 3, the recovery efficiency of a single catchment gauze is dependent upon the gauze loading. Once the single gauze recovery efficiency is known the total recovery of a number of gauzes can be readily determined from the following formula:

$$R = 1 - (1-q)^n$$

(1)

where $R$=total recovery factor, $q$=single gauze recovery factor, and $n$=number of gauzes.

To determine the number of gauzes required to give a recovery of 60 per cent ($R=0.6$), this becomes:

$$n = \frac{\log (1-0.6)}{\log (1-q)}$$

(2)

For example, if the gauze loading of a plant is 40 tons of nitrogen per square metre per day, the single gauze efficiency will be 16 per cent (see Fig. 3), so $q=0.16$.

Substituting this in equation (2) gives:

$$n = \frac{\log (0.4)}{\log (0.84)} \approx 5$$

Thus five gauzes will be needed.

In a plant with contact area 2.22 m$^2$ producing 400 tons of acid per day with a loss of 0.24 g Pt/ton over a campaign length of 25 days, the gross platinum losses per campaign are $400 \times 0.24 \times 25 = 2400$ g. Re-
vertent to equation (1), the actual total recovery for five gauzes will be 58.17 per cent.

The individual gross recoveries of each gauze are as follows:

- gauze 1: 16 per cent, 384 g
- gauze 2: 13.44 per cent, 322.5 g
- gauze 3: 11.29 per cent, 270 g
- gauze 4: 9.48 per cent, 228 g
- gauze 5: 7.97 per cent, 191 g

Thus the first gauze recovers twice as much platinum as the fifth gauze. The saturation level $K_r$ of each type of gauze is a function of the gauze weight. In this case the weight of a 200 mesh/cm² 0.18 mm wire gauze will be $2.22 \times 960 \text{ g} = 2130 \text{ g}$ and $K_r = 1700 \text{ g}$.

Therefore the number of catalyst campaign periods for which the top gauze could be installed is $\frac{1700}{384} = 4.4$. Hence the gauzes will be installed for four acid campaigns or 100 days running time. The platinum recovered by each gauze during these four campaigns is:

- gauze 1: 1536 g
- gauze 2: 1290 g
- gauze 3: 1080 g
- gauze 4: 912 g
- gauze 5: 764 g

To make full use of the gold-palladium the bottom two gauzes of the pack could be of the lighter weave 1024 mesh/cm² 0.09 mm wire weighing 546 g/cm², $K_r$ in this case being $0.8 \times 546 \times 2.22 = 960 \text{ g}$. The addition of a sixth gauze, which would have a recovery of 6.69 per cent of the gross losses over the installation time, would recover an additional 642 g, bringing the total recovery to 64.86 per cent of the gross losses.

If for some reason the installation of a pack of catchment gauzes for this length of time is inconvenient, a pack of differing configuration might be used. Should it be more convenient to change the pack every two acid-making campaigns, the pack would then best be made up entirely from lighter weave gauzes. If a catchment campaign equivalent to three acid-making campaigns is envisaged then the top two gauzes would be of the heavier weave and the bottom of the lighter weave. Thus catchment gauze packs can be easily tailored to give optimum efficiency taking account of differing plant requirements, as shown in Table III.

Now that the minor installation problems experienced during the early trials have been overcome the gold-palladium catchment gauze recovery process is widely accepted in Western Europe and the U.S.A., giving reliable and trouble-free service. For optimum results each installation must be considered separately and a pack must be tailored to suit the plant. Regular use of catchment gauzes presents no administrative or operating problems. It produces considerable savings in the catalyst costs of ammonia oxidation plants without any add-
verse effect on plant performance; indeed, there is some evidence to show that by improving gas mixing and by providing uniform support for the catalyst gauzes the overall plant efficiency is increased.

References
6 Nitrogen, 1970, (66), 41
7 H. Holzmann, Chem.-Ing.-Tech., 1968, 40, (24), 1229

Strain Measurement at High Temperatures

Safe and successful operation of pressure vessels and boilers working at high temperatures, for example in the electricity supply industry, requires a knowledge of the strains to which they are subject under such conditions. Conventional strain gauges have used a resistive sensing method but this has not been ideal at high temperatures in adverse environments.

G. V. Planer Ltd of Sunbury-on-Thames have now developed with the Central Electricity Research Laboratories a gauge which operates instead by sensing changes in capacitance. The CERL-Planer gauge is attached to the test surface by micro spot-welding at two points only. Strains cause changes in gauge length and these are mechanically amplified, thus varying the separation of the electrodes of an air capacitor. Capacity changes measured on a capacitance bridge record the degree of strain present. Platinum electrodes were chosen for the air capacitor because platinum is well able to withstand the operating temperatures of up to and above 650°C without being affected by corrosive atmospheres. The capacitor is mounted inside a body made of alloys stable both mechanically and thermally. Cables and other accessories are available for use with the gauges.

The illustration shows a pair of the new gauges with connections to specially terminated mineral insulated cables. They are installed on a high pressure steam turbine housing. Gauges have a strain range of 10,000 microstrain. Typically the drift of gauge type CI at 600°C is less than 70 microstrain per week, although drifts of less than 20 microstrain per week have been recorded for this gauge.