

# Platinum Recovery in Ammonia Oxidation Plants

## A NEW PROCESS USING GOLD-PALLADIUM CATCHMENT GAUZES

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*This article describes a novel process for the recovery of platinum lost in ammonia oxidation plants for the manufacture of nitric acid. The process, based on the finding that the platinum lost is in vapour form, is particularly suitable for medium and high pressure plants in which the present methods of recovery are relatively inefficient.*

The first manufacture of nitric acid by the oxidation of ammonia, using platinum as a catalyst, was carried out in 1908 using Wilhelm Ostwald's process. From this small beginning a vitally important branch of the chemical industry has developed and with it the enormous artificial fertiliser and explosives industries.

For the ammonia oxidation reaction, the catalyst now takes the form of pads of gauzes, up to 4 m diameter, located horizontally in the ammonia burner. The ammonia oxidation reaction is highly exothermic and, once the gas stream has ignited and thermal equilibrium has been reached, the gauzes maintain themselves at their operating temperatures in the range 750 to 950°C.

The rhodium-platinum gauze wires roughen rapidly in service and there is considerable grain growth. In turn, rhodium and platinum are lost into the gas stream. In atmospheric plants this loss may range from 0.15 to 0.35 g/ton N and in plants operating between 3 and 9 atmospheres from 0.5 to 1.8 g/ton N. These losses have led to the use over many years of processes that recover part of the metal otherwise lost, such as glass-wool or other filters and Raschig rings. These techniques are, however, applied more generally to pressure plants and are limited in effectiveness.

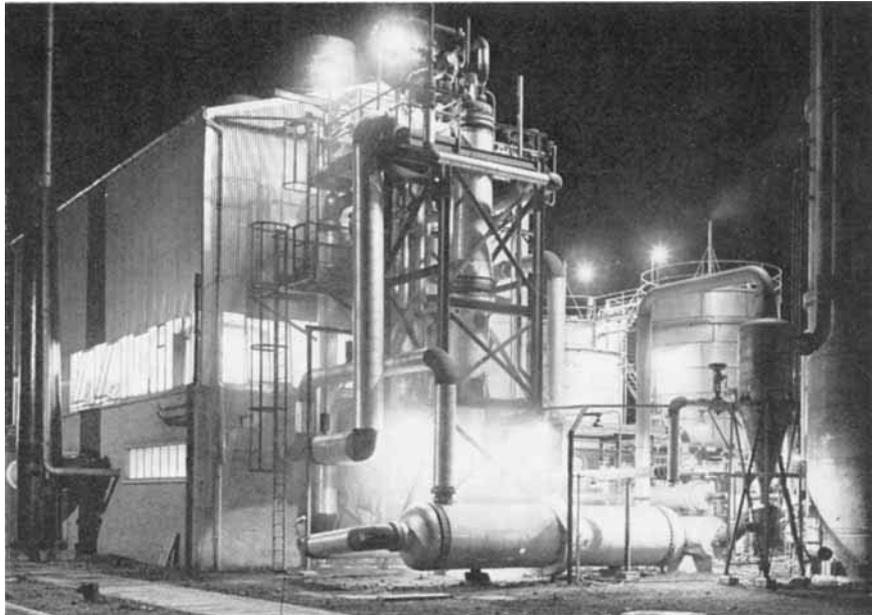
Research carried out by Degussa in

collaboration with several nitric acid producers and a plant construction company has now led to the development of a practical recovery process, suitable for medium and high pressure plants. A fuller account of the theory upon which this process is based, and of the experimental work leading to its successful development, has been given elsewhere by the present writer (1).

### Theory of Platinum Loss from Gauzes

The author does not agree with existing explanations of these phenomena, particularly with that of Figurowskii (2) who concluded that *particles* detached themselves mechanically from the gauze. Instead he suggests that the loss can be explained by the intermediate formation of a volatile platinum oxide.

Direct volatilisation can be discounted: even at 1570°C the vapour pressure of platinum is only  $6.76 \times 10^{-9}$  Torr corresponding with a loss on heating in vacuum of 10 g/cm<sup>2</sup>h. However, heating *in air* causes significant weight losses, even at temperatures under 1000°C, while in oxygen the losses are much higher. These phenomena are shown graphically in Figs. 1 & 2. However, in ammonia oxidation the loss of platinum is considerably higher than could be deduced from these data. The author's theory is that the volatile PtO<sub>2</sub> is formed during the reaction

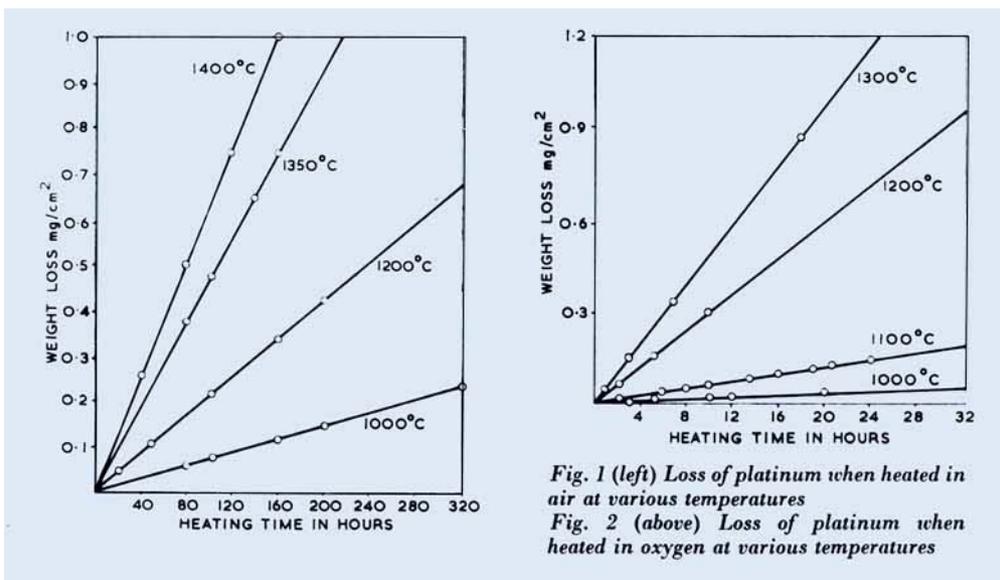


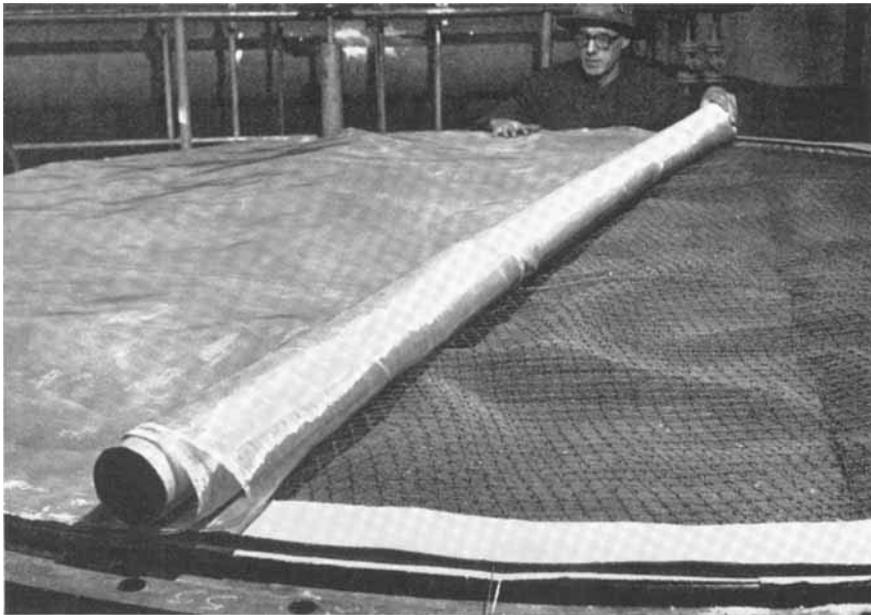
*The production of nitric acid by the oxidation of ammonia on rhodium-platinum gauzes constitutes one of the world's major chemical industries and well over twenty million tons of acid are made annually in plants such as this. Loss of platinum from these gauzes contributes significantly to the operating costs, and the development of a process for the recovery of a major proportion of the lost platinum is therefore of considerable potential value to the industry*

and that this accounts for the weight loss from the gauzes.

It was, therefore, on the assumption that platinum is principally carried into the gas stream as *vapour*, and not as discrete particles,

that work on new recovery techniques was initiated. The basic principle was to "getter" the platinum atoms at the high temperatures in the burner, immediately below the catalyst gauzes.





*A rhodium-platinum catalyst gauze being installed in an ammonia oxidation plant. Normally a number of gauzes is used in the form of a pad*

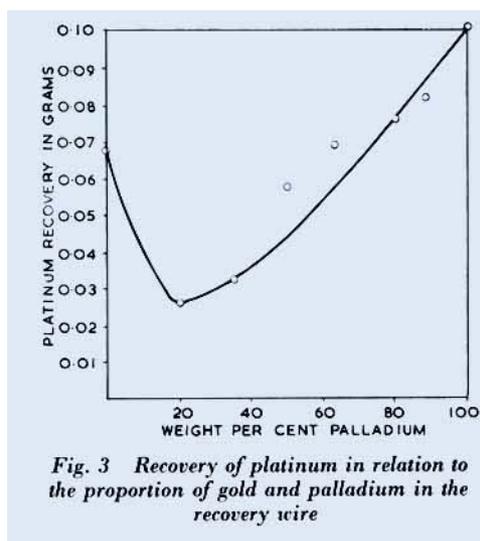
To translate this principle into practice, it was necessary first to choose metals that did not form oxides at temperatures of about 950°C and which would not react with the gases in the stream (NO, O<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>). Moreover, the gauze form seemed ideal, so that ductility of the metal chosen was essential. On these considerations the choice lay finally between gold, palladium and platinum.

In fact platinum was rejected primarily on the grounds of price, so that the choice appeared to lie between gold and palladium. For the trials described below fine gold and fine palladium, together with a series of binary alloys of these two metals, were evaluated as wire 0.125 mm diameter, placed through a coarse mesh gauze of an austenitic stainless steel. This gauze was installed immediately below the rhodium-platinum gauzes in a 7 atmosphere plant and was, in turn, supported by a second similar, stainless steel gauze. Its location ensured an operating temperature of 940°C.

The purpose of these trials was to determine whether the wires could collect platinum and to establish whether or not they would

survive. A similar assembly was also tested in a cooler zone of the burner at 800°C.

The results were significant: at 800°C the wires appeared unaffected and had collected little platinum. At 940°C they had the furred appearance associated with used catalyst gauzes but they had collected worth-while amounts of platinum, as shown in Fig. 3.



*Fig. 3 Recovery of platinum in relation to the proportion of gold and palladium in the recovery wire*

It will be seen that pure palladium is the most effective, but this could not be used as the palladium wire was mechanically damaged. The 20 per cent gold-palladium alloy wire seemed to provide the best compromise between optimum recovery and mechanical properties, and subsequently this alloy formed the basis of all tests. Other alloying constituents were also tried, but while they improved mechanical properties they were less effective in terms of recovery.

### Confirmation of the Theory

In the author's opinion the presence of platinum vapour was confirmed by the fact that the platinum had collected uniformly on the wires, not solely on the face opposite the gas stream. Microsection showed apparent pitting, with crystal formation on the surface identified as solid solutions from the diffusion between the gauze alloy and the "captured" platinum at prolonged high temperature. It was, however, impossible to identify phases.

Two explanations are offered for the poorer results at 800°C: the "getter" effect is reduced with decreasing temperature and, in the cooler zone, less platinum is present in the vapour phase.

At 940°C the platinum recovery was partly offset by losses of catchment material. The gold loss was minimal but the palladium losses were more significant. The author cannot precisely explain the phenomenon, particularly the relationship between palladium lost and platinum recovered. The vapour pressure of palladium in vacuum, even at 1200°C, is so low that it cannot provide the explanation. In practice the 20 per cent gold-palladium gauze loses roughly one-third of a gramme of palladium for every gramme of platinum recovered. (If account is taken of the relative intrinsic values and densities, this appears less significant.)

### Production Trials

As already mentioned, the 20 per cent gold-palladium alloy appeared to be the best proposition, and for production trials wire of this alloy 0.09 mm diameter was woven into 1024

mesh/cm<sup>2</sup> gauzes. These gauzes were tested in a 7 atmosphere plant comprising two ammonia burners connected in parallel, each with a throughput of 23 ton of nitrogen per day. The loss of platinum from the catalyst gauzes was approximately 1 g/ton N. The 20 per cent gold-palladium "catchment" gauzes were mounted in the burners below the catalyst gauzes, and coarse mesh gauzes of stainless steel were used to separate the recovery gauzes from each other and from the pad of rhodium-platinum gauzes.

The following conclusions were drawn from these trials:

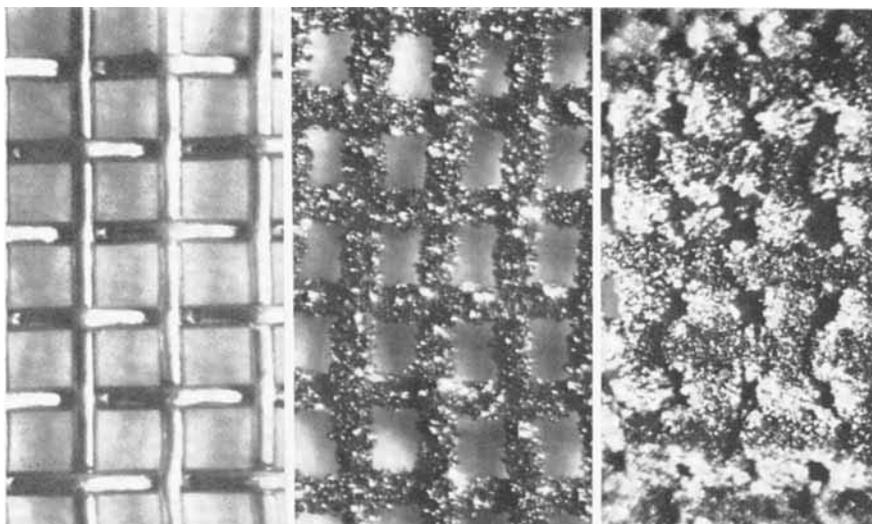
- (1) Under these operating conditions the first recovery gauze collected about 23 per cent of the platinum otherwise lost.
- (2) The next gauze, lying under the first, collected 17.5 per cent, i.e. 23 per cent of the 77 per cent remaining from the first gauze. In fact, each gauze collected 23 per cent of the platinum presented to it. The following equation expresses total recovery percentage:

$$S = \left[ 1 - \left( 1 - \frac{a}{100} \right)^n \right] \times 100 \quad (\text{Equation I})$$

Where S is the total recovery percentage of all gauzes  
 a is the percentage recovery of the first gauze  
 n is the total number of recovery gauzes used.

Although *a* varies according to plant conditions, this exponential equation applies broadly to *all* plants.

- (3) As a result of examination after 35 and 68 days, it was established that the *rate* of recovery after 68 days was almost the same as after 35 days, thus the limit of recovery was not reached within that trial period.
- (4) The 68-day period was the better economic proposition. Nearly twice as much platinum was recovered, but many of the fixed costs (e.g. catchment gauze manufacturing and refining) were spread over nearly twice as much recovered platinum.



The gold-palladium catchment gauze is fitted in the converter immediately behind the rhodium-platinum gauzes in order to recover the rhodium and platinum carried away in the gas stream. Left, a gold-palladium gauze as installed. Centre, the same gauze after 90 days in operation, and, right, after 190 days, showing the effect of the collected platinum

Tests were subsequently conducted on other plants with operating conditions ranging from 9 atmospheres to atmospheric. These tests revealed unexpected variations from plant to plant in the percentage of platinum recovered. In high pressure plants with a specific load of nearly 30 ton N/m<sup>2</sup>/day each single catchment gauze recovered about 22 per cent of the platinum presented to it: in medium pressure plants (3 atmosphere) this figure rose to about 45 per cent and in atmospheric plants to about 60 per cent. It was, therefore, apparent that more gauzes would be necessary in high pressure plants than would be required in low pressure and atmospheric plants.

These figures relate to the percentage of platinum recovered from the gas stream (a in Equation I). However, in considering the overall economies of the use of catchment gauzes it is also necessary to relate the weight of metal recovered to the weight of the catchment gauzes when new. This can be treated as a percentage and known as  $K_r$  (recovery constant), where:

$$K_r = \frac{\text{Weight of Platinum Recovered}}{\text{Weight of Catchment Gauzes when New}} \times 100$$

To assess the viability of the process, account must also be taken of the *time* in which an acceptable amount of platinum is recovered. A value for  $K_r$  of 80 per cent

Platinum Offer and Operational Period (Wire 0.09 mm diameter)		
Operating pressure (atmospheres)	Pt offered per m <sup>2</sup> g/day	Average Period to attain $K_r=80$ with 0.09 mm diameter wire (1024 mesh/cm <sup>2</sup> )
9	162	19 days
7	23	75 days
3	4	9 months
0	0.5	4 years

provides a good basis for comparison but does not represent the limit of the process.

Whereas the atmospheric plants have the advantage of requiring fewer catchment gauzes than the high pressure plants because each gauze collects a higher percentage of the platinum presented, it must be remembered that the *rate* of presentation of platinum is very much lower. Consequently, with gauze woven from 0.09 mm diameter wire they may take an uneconomically long time (because of interest charges) to attain this notional 80 per cent recovery (see above). The table compares the *averaged* level of platinum offered per day in typical plants of different operating pressures and shows the time required to achieve this figure of 80 per cent.

In fact this table illustrates the fact that the time taken to attain the notional 80 per cent recovery figure with gauzes woven from wire 0.09 mm diameter is uneconomically long in the lower pressure plants. This is best overcome by using smaller diameter wire for the catchment gauzes. Subsequent tests showed that by using 0.06 mm diameter wire in gauzes of the same mesh (1024 mesh/cm<sup>2</sup>) the percentage of platinum recovered from the gas stream (a in Equation 1) was not greatly affected—despite the reduction in surface area—but the recovery times were reduced to about 43 per cent. These reduced recovery times make the process viable for the lower pressure plants.

### Limits of Recovery

Although it is established that 20 per cent gold-palladium gauzes woven from either 0.09 mm or 0.06 mm diameter wire can capture 80 per cent of their original weight of platinum (i.e.  $K_r = 80$ ), the *limit* of recovery has not yet been established. Nevertheless, the *rate* of recovery has remained more or less constant in all tests so far conducted.

An important factor in assessing this rate of recovery is the increase in surface area of the gauze as platinum atoms diffuse into the wire and so cause “roughening”—with consequent increase in surface area. The

importance of this “roughening” was confirmed in an experiment with a gauze manufactured from wire in which 10 per cent of platinum had already been alloyed. This captured far less platinum than a normal 20 per cent gold-palladium gauze which had in service already collected 10 per cent of platinum.

### Experience So Far

Degussa have gained experience with atmospheric and medium pressure plants that are representative in operating conditions of nearly all such current plants in use. With high pressure plants they have, as yet, no experience with daily loadings in excess of 30 tons of nitrogen per square metre of burner, nor with plants operating at pressures greater than 7.5 atmospheres—but preparations are in hand for these tests.

Certainly the installation of the catchment gauzes is simple in that they are easily mounted—together with their stainless steel support gauzes—in the same flange as the catalyst gauzes. Adequate mechanical support is essential throughout their operating life.

### Economics of the Process

At a time when interest rates and metal prices are subject to fluctuation, it is impossible to cite examples of the overall savings achieved by this process. Nevertheless, it is worth while to consider which factors contribute to overall viability.

Second only in cost to the ammonia used in the production of nitric acid is the cost of the metal lost from the catalyst gauzes. Discussion so far has concerned platinum losses but in practice rhodium is also lost. Some rhodium is recovered by this process: typically 1.5 to 3.5 per cent of rhodium (as a percentage of the platinum recovered) is recovered from gauzes containing 10 per cent of rhodium.

The catchment process described in this article has, in fact, shown itself to be viable in several plants operating in various parts of the world, in that it recovers so much more platinum from the gas stream than the

methods hitherto employed that its cost is well justified. Obviously account must be taken of the manufacturing costs of the catchment gauzes, the interest that must be paid on their intrinsic values and the costs of their subsequent refining, but overall experience so far points to the promise of universal adoption of the process in nitric acid plants in the years to come.

The benefits of the process are simply assessed. A catchment gauze pack can be installed in a burner and after a short period of service removed for analysis and refining.

The analysis provides an immediate indication of the recovery rate and this can be related to the additional costs involved.

The process described above is internationally patented. (British Patent No. 1082105 applies in the U.K.) Johnson Matthey & Company Limited and their overseas subsidiaries are appointed licence agents for the process in the United Kingdom and all other countries in the world except those of North America, the European Common Market and Spain.

### References

- 1 H. Holzmann, *Chem.-Ing.-Tech.*, 1968, **40**, 1229
- 2 N. A. Figurovskii, *Zh. prikladnoi Khim.*, 1936 **9**, 37; 1938, **11**, 1440

## Economics of Platinum Catalysts in Fuel Cells

The advantages of employing platinum metal electrocatalysts in fuel cells continue to be debated, but a paper by K. R. Williams, of "Shell" Research, presented at the Sixth International Power Source Symposium at Brighton, gives a useful guide to the economics of their use in certain types of systems.

Starting from the basis of using methanol or hydrocarbons in a low temperature system in the range 1 to 5 kW, the author compared the costs and performance of cells fuelled by pure hydrogen, impure hydrogen and methanol. Pure hydrogen may be obtained by steam-reforming methanol in a fluidised bed reactor and extracting the hydrogen by means of a silver-palladium diffusion cell. This system produces a very pure hydrogen fuel. Methanol can also be reformed to yield impure hydrogen; the cost of a diffusion cell and associated equipment would be saved, but the system weight would scarcely be reduced since more reforming catalyst is required to achieve an adequately low carbon monoxide concentration. Obtaining hydrogen by hydrocarbon reforming necessitates the use of a two-stage system - a reforming stage in the temperature range 500 to 700°C, followed by a shift reaction at lower temperatures to increase the hydrogen content of the gas.

Ruthenium-platinum electrocatalysts applied to electrodes comprising microporous plastics coated with a conductive metallic layer have been demonstrated to show a number of advantages in this type of system. In 6N KOH systems at platinum loadings of 1 mg/cm<sup>2</sup> power outputs of 100 mW/cm<sup>2</sup> can be achieved with hydrogen fuel, compared

with only 40 mW/cm<sup>2</sup> with less expensive nickel catalysts. The ruthenium-platinum catalysts, moreover, can deal effectively with impure hydrogen, as well as with methanol directly, at a small cost of slightly increased electrode polarisation. When total system costs are compared for fuel cells operating with ruthenium-platinum and nickel catalysts, a 1 kW battery would cost around £60 in the former case (with two-thirds of this sum being attributed to the platinum) and about £50 in the latter instance. There is thus only a slight saving when non-platinum catalysts are used, due to the increased construction costs that almost completely offset the savings in electrocatalyst. The weight of such a system, moreover, is increased significantly.

In acid electrolytes the catalyst loading has a very marked effect on cell performance. Ruthenium-platinum electrocatalysts operate best around 70°C when impure hydrogen is used as fuel, but—in general—construction costs are much higher when acid electrolytes are employed due to corrosion problems.

From an analysis of costs and performances of the systems reviewed, the author concludes that although the least expensive system at the 5 kW level is that using a methanol reforming system giving pure hydrogen and non-platinum catalysts in an alkaline electrolyte, the additional cost of using platinum catalysts is minimal and bestows significant advantages in increased performance/weight parameters. The system using impure hydrogen is about 2½ times as expensive; most expensive is that using methanol directly in an acid medium.

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