Knitted Platinum Alloy Gauzes

CATALYST DEVELOPMENT AND INDUSTRIAL APPLICATION

By B. T. Horner
Johnson Matthey, Materials Technology Division, Royston

The introduction of knitted catalyst gauzes into the nitric acid industry has had a major impact on both that industry and on the catalyst production procedures employed by Johnson Matthey. It is now two years since this technological advance was first reported and, because of this time interval, a summary of previous work is included here to serve as a background to this significant technical progress and the commercial acceptance that has taken place over the past few years.

The production of nitric acid is achieved by passing an ammonia-air gas mixture over a catalyst and absorbing the resultant gas in water. Most industrial plants use a platinum group metal catalyst, generally either rhodium-platinum or rhodium-palladium-platinum, to promote this reaction. The process is carried out at temperatures in the range of 800 to 940°C and at pressures of between 1 and 14 atmospheres. In order to realise optimum performance the catalyst is usually in the form of gauze, woven from wire. This structure was developed in 1909 (1), and until very recently little change in design had taken place.

Platinum behaves well as a catalyst, and early catalyst development involved the use of pure platinum (2) a relatively weak material. Among the first alloys considered for ammonia oxidation was platinum-iridium (2) and platinum containing 10 to 20 per cent palladium. Economic appraisal of these catalysts showed that none of these alloys was suitable for use in nitric acid plants, but platinum-rhodium alloys containing 5 to 10 per cent rhodium were subsequently found to have the best combination of properties in terms of ammonia conversion efficiency and economic performance; the rhodium increasing the relatively low tensile strength of pure platinum. That was 60 years ago.

Now platinum-rhodium alloys are at the heart of the nitric acid production process and as such have been the subject of much discussion. The sharp increase in the price of rhodium during the period 1989–1991, see Figure 1, led many nitric acid producers to consider reducing the rhodium content of their catalysts. The use of 10 per cent rhodium-platinum woven 1024 mesh gauze was well established (3), however, and alloys with lower rhodium content had reduced strength and a potential for increased metal loss.

The introduction of knitted catalyst gauzes had a major impact on catalyst producers and users. The production of knitted gauze and its performance, compared with that of traditional woven gauze, is discussed here.

Rotary Knitting Machine Development

After successful commercial trials of knitting gauzes, a full-scale production system was developed (3).

The circular knitting frame on the first production machine was 76.2 cm in diameter, with

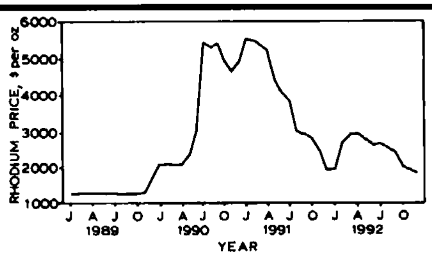

Fig. 1 The sharp increase in rhodium prices during 1989–1991 led producers to assess the rhodium content of the rhodium-platinum alloy catalyst gauzes

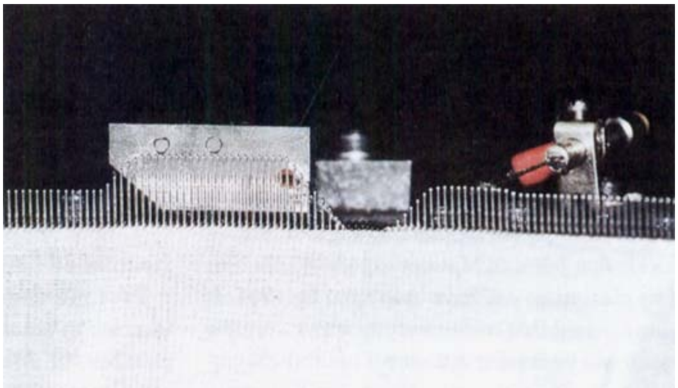

Fig. 2 One of the four knitting heads on the first production machine for knitted gauze showing the disposition of the needles as the platinum alloy wire and polyester carrier are co-knitted

approximately 1990 needles around the circumference, see Figure 2, the size being determined by the need to reduce wastage and minimise seam fabrication. Having already determined the optimum density of the cloth on the earlier development machine, the needle spacing and stitch length were maintained to achieve continuity.

Although a single feed system could probably cope with the anticipated demand, it was decided that a 4-feed system would give greater flexibility. Indeed, all Johnson Matthey machines are capable of accepting 8 feeds although a requirement for such production rates is unlikely.

The cloth is produced by co-knitting the platinum group metal wire with a multi-strand polyester yarn carrier which almost completely covers the wire and provides support during the knitting process (4), see Figure 3. The fabric is knitted in the form of a tube then split to give a cloth 2.4 metres wide which is cut to size. The polyester carrier is next removed and the catalyst is flamed with hydrogen to activate the surface. The carrier is not removed until this late stage of the process in order to give protection during storage; last minute cleaning also minimises the potential for contamination by dust. Any contaminants that are present during flaming could diffuse into the surface of the catalyst and subsequently cause problems during use.

During the carrier removal process no residues are left behind, but its composition is such that even if the gauze was installed without its removal the catalyst would still function efficiently.

Scale-up of the development process highlighted the problem of supplying the correct volume of material, at identical rates, to each of the four knitting heads, in order to obtain a cloth of uniform tension and with homogeneous density, see Figure 4. The introduction of computer control completely solved this problem. The reliability and efficiency of this knitting machine (which no longer resembles the original textile machine), together with the interest shown by customers has encouraged Johnson Matthey to

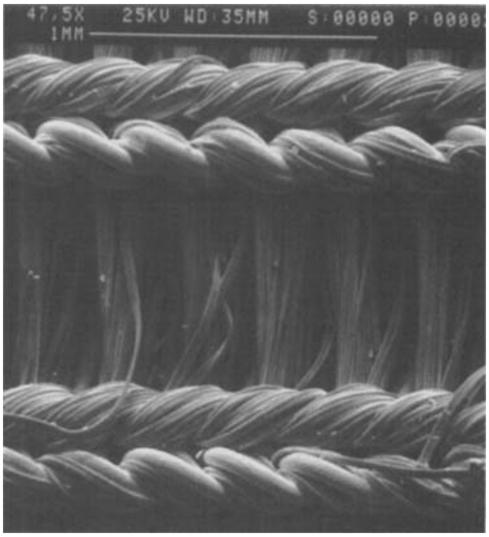

Fig. 3 The carrier is a multi-stranded polyester fibre which almost completely covers the platinum alloy wire during the knitting operation. The carrier is removed after the gauze is cut to size and before the catalyst is activated for use

purchase more machines for the production of knitted catalyst gauzes, as well as the catchment gauzes used in nitric acid production and in other similar chemical processes.

Industrial Application

Demand for knitted gauzes from the nitric acid industry has grown rapidly and is expanding so quickly that Johnson Matthey expects 80 per cent of its customers will have converted by 1994. It is anticipated that most catalysts which are now woven will be knitted in future. Other major catalyst manufacturers are already producing or planning to produce knitted catalysts either by rotary or flat bed knitting.

In a previous article the following list of potential benefits accruing from the use of knitted gauzes was given (2):

- Increased conversion efficiency
- Reduced rhodium oxide formation
- Stronger material
- Greater surface area for catalysis
- Fabric flexibility providing greater resistance to damage by thermal shock
- Choice of alloy
- Lower stock levels resulting from quicker response times

Since then two other major benefits have been observed, namely:

- Lower metal losses
- Extended campaign lengths.

These benefits will now be considered in greater detail to show why the adoption of knitted gauzes has been so rapid.

There are two main types of nitric acid production plants: a single pressure process performed at either medium pressure (4 to 6 atmospheres) or at high pressure (7 to 14 atmospheres); and a dual pressure process where ammonia oxidation is carried out at medium pressure, and absorption is completed at high pressure. The overall reactions are:

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

$$2NO + O_2 = 2NO_2 \quad \text{ammonia oxidation}$$

$$3NO_2 + H_2O = 2HNO_3 + NO \quad \text{absorption}$$

The ammonia oxidation stage uses a catalyst pack containing up to 36 platinum group alloy gauzes designed to optimise the efficiency of the reaction.

The whole process is fast, but a contact time of 10^{-4} seconds is needed between gas and catalyst to maintain process efficiency. The catalysts have typical service lives of 50 to 300 days, depending mainly upon the pressure of the system.

Increased Conversion Efficiency

Pilot plant trials indicated that a 4 per cent increase in ammonia conversion efficiency was possible (3). Most industrial nitric acid plants claim conversion efficiencies of 96 to 99 per cent, but if these figures are accurate then a 4 per cent increase in efficiency is clearly impossible. It is, however, important to appreciate that pilot plant trials only indicate potential.

The majority of nitric acid plants measure the conversion efficiency of the overall system, not of the burner. Following the installation of knitted gauze catalyst packs, detailed production information has not been made available but, without exception, all the plants have reported no drop in conversion efficiency, and some have recorded reduced ammonia usage, which indicates an improvement in efficiency. Indeed, an increase in conversion efficiency must occur because less rhodium oxide and lower impurity levels have been recorded.

Reduced Rhodium Oxide Formation

Rhodium enrichment of a catalyst gauze occurs as a consequence of the loss of platinum from the catalyst surface. Platinum oxidises and volatilises at high temperatures in oxidising atmospheres; rhodium also oxidises, but does not volatilise as readily. When a 10 per cent rhodium-platinum alloy is in use, platinum is lost at a rate approximately 19 times faster than rhodium, so resulting in a natural enrichment of rhodium. However, if the actual catalyst is PtO_2 and not platinum, then the need for replenishment and oxidation of the platinum is important.

When the initial composition of the gauze is 10 per cent rhodium-platinum, the final analysis of the bulk material can be 13 per cent rhodium-87 per cent platinum. An important factor in the catalytic process is the amount of RhO_2

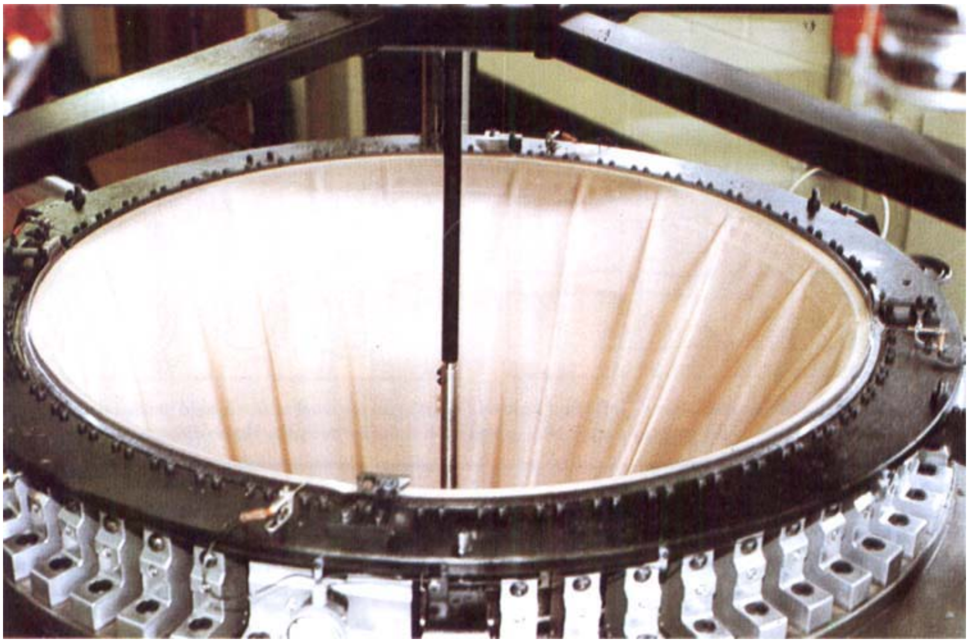

Fig. 4 The four knitting heads are supplied with fibres at a computer-controlled constant rate to produce a knitted tubular gauze, of uniform tension and homogeneous density. The first production knitting machine was 76.2 cm in diameter and had approximately 1990 needles around the circumference

present at the catalyst surface. Although rhodium enrichment is regarded as a natural phenomenon other factors also can influence its formation. For instance, if the platinum-rhodium gauzes are operated at low temperatures (< 800°C) then a decline in catalyst activity can occur. The formation temperature of RhO_2 is 600°C and it dissociates over the temperature range 1050 to 1150°C. Poisoning causes a loss in activity which slows the kinetic processes relative to the rate of gas diffusion transfer; thus the gauze contaminated by poison, usually the lead gauze, only allows limited diffusion. Visual evidence that this is happening is the appearance of a dull patch on an otherwise bright gauze. This low operating temperature and the subsequent increase in the oxygen partial pressure stabilises the rhodium oxide, which then rapidly accumulates at the surface. Efforts to reduce the RhO_2 by raising the temperature of the gauze have only a limited success since, as stated above, the temperatures required to achieve this dissociation are high.

The structures of woven and knitted catalyst are shown in Figure 5. The more open knitted structure achieves the same weight as the closer woven structure, due to its bulky three-dimensional nature. This open structure also offers less resistance to gas flow, which enables the reaction to take place further into the gauze and ensures a more even temperature profile across the catalyst.

This improved distribution of the catalytic activity reduces the metal loss per gauze, with a subsequent drop in the formation rate of rhodium oxide. The results given in Table I indicate significant reductions in RhO_2 formation over the entire range of plant pressures, when using knitted gauzes. This is particularly significant since the major cause of campaign cessation in Example 3 (a high pressure plant) was the high levels of RhO_2 formation.

Another major factor contributing to the formation of rhodium oxide is the presence of contaminants, the most common of which is iron. High surface levels of iron reduce catalytic activity, promote the breakdown of nitric oxide and increase the surface concentrations of RhO_2. It

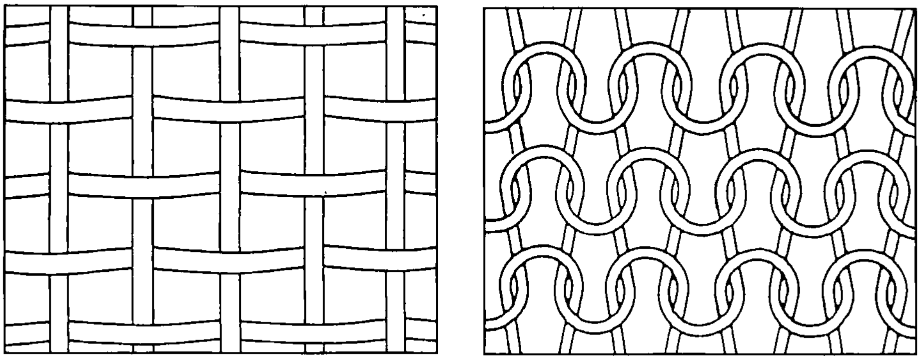

Fig. 5 Typical structures of woven (left) and knitted (right) gauzes used in nitric acid production. The more open structure of the knitted material is compensated for by its bulky three-dimensional nature

is generally believed that the campaign life may be extended by increasing the number of gauzes in a pack, so that contamination of the leading gauzes results in the transfer of the reaction zone to a greater depth, without causing any loss of efficiency. This does not happen, however, since the ammonia is less selectively oxidised to nitric oxide; instead more is oxidised to nitrogen as the level of contamination increases.

The levels of iron impurity on the gauzes are listed in Table I. The improved gas flow through the knitted gauzes results in less solid particles being trapped and hence less RhO_2 is formed due to iron contamination. Example 1 shows that there has been no drop in iron impurity levels (0.56 per cent during a woven campaign and 0.54 per cent during a knitted campaign) but the significant factor is the greatly reduced amount of impurity present on the surface of the knitted catalysts. This phenomenon is seen in all campaigns using knitted gauzes.

Stronger Material

When woven catalyst gauzes are removed from an oxidation rig they are often in a fragile state, once the clamping supports and weights are removed. This does not occur with knitted gauzes, indeed many plant managers have commented on the catalyst integrity at the end of a campaign.

The strength of the catalyst is important, not only for high pressure plants but also for medium and low pressure ones. Catalysts are designed to be supported horizontally, but in high pressure units the support basket often deforms to such an extent that the edge of the burner wall cuts into the catalyst, sometimes causing it to tear. This also happens in low and medium pressure units which usually employ rashing ring support. During operation the rings may migrate to the centre, causing the catalyst to "dome". This leaves the catalyst unsupported around its edge, which tends to result in tearing.

Tensile tests were carried out to determine the strength of knitted and woven catalyst gauzes, the results being given in Figure 6. Significantly more energy can be absorbed by the knitted structure than by woven gauze, as shown by the areas

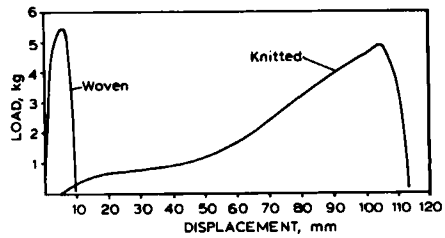

Fig. 6 Strips of knitted and woven gauze (25 mm × 180 mm) were subjected to tensile testing, with constant gauge length and cross-head speed. The knitted alloy was found to absorb more energy. Both gauzes are 10 per cent rhodium-platinum, 0.076 mm diameter wire; the gauze is 1024 mesh or equivalent

Table I

Example 1: Low Pressure Plant

Gauze type	Composition, per cent		Rhodium surface, per cent	Impurity on gauzes, per cent	Impurity in catchment, per cent	Total impurity per cent	Metal loss, grams/tonne of acid produced
	Platinum	Rhodium					
Knitted trial 1	89.31	10.64	8.9	0.05	-	0.05	0.116
Knitted trial 2	89.18	10.78	12.1	0.06	0.48	0.54	0.115
Typical woven gauze pack 3	88.31	11.33	18.7	0.36	0.2	0.56	0.112

Example 2: Medium Pressure Plant

Gauze number	Levels of rhodium and iron at the surface of the gauze					
	Type of gauze and composition					
	Woven 10% rhodium-platinum		Knitted 10% rhodium-platinum		Knitted 5% rhodium-platinum	
	Rhodium, per cent	Iron, per cent	Rhodium, per cent	Iron, per cent	Rhodium, per cent	Iron, per cent
1	56	0.2	28	0.1	10	trace
2	58	0.2	27	trace	7	0
3	61	0.1	25	0	8	0
4	62	0.1	30	0	8.5	0
5	68	0.1	32	0	8.7	0
6	76	trace	32	0	10.0	0
7	75	0.3	34	0	10.0	0
8	68	0.1	31	0	11.0	0

Example 3: High Pressure Plant

Gauze number	Surface levels of rhodium oxide			
	Type of gauze and position in pack			
	Woven 10% rhodium-platinum		Knitted 10% rhodium-platinum	
	Front	Back	Front	Back
1	29.7	38.2	20.1	14.6
2	36.3	59.9	19.1	13.8
3	37.2	61.9	21.2	14.3
4	43.2	66.0	15.5	11.1
5	46.9	63.8	14.8	12.6
6	51.5	63.6	15.2	15.5
7	55.0	62.5	19.9	17.5
8	58.8	63.8	21.7	19.2
9	60.5	61.3	14.6	13.1
10	61.4	65.9	12.4	12.9
11	60.5	64.9	12.8	11.4
12	63.6	61.3	13.3	11.7
13	63.1	65.1	13.6	12.1
14	62.1	64.3	11.7	12.2
15	63.6	64.5	12.9	11.7
16	59.2	60.0	12.8	13.1
17	56.4	54.3	14.2	14.2

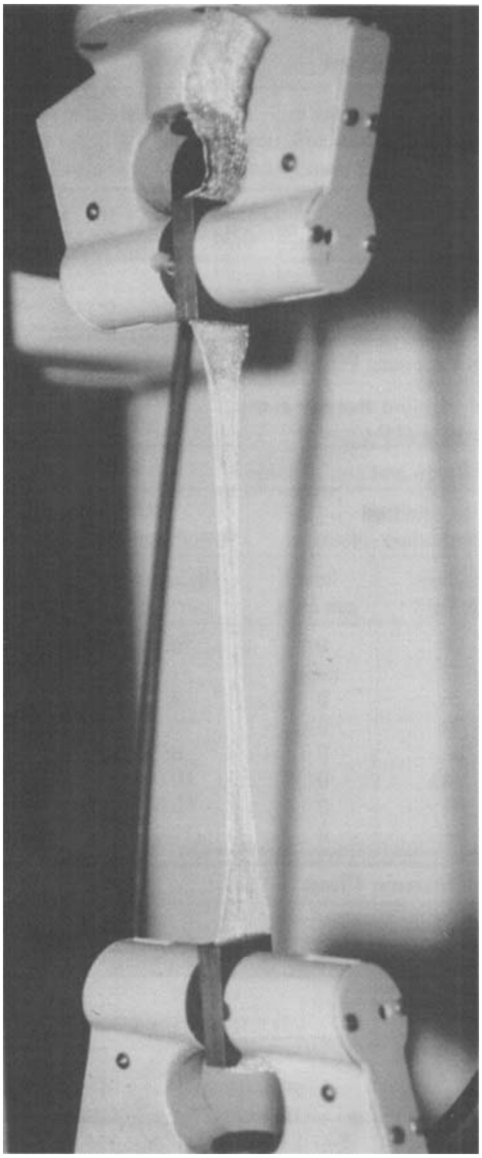

Fig. 7 A tensile test sample of knitted gauze stretched significantly before fracture, which usually occurred at the clamping jaws

under the two curves. This is further illustrated in Figure 7; Figure 8 shows almost instant tearing of the herringbone – the strongest of all the conventional weaves – which results in rapid failure. A knitted sample stretches considerably before fracture, which usually occurs at the clamp interface and not within the gauze length. Flaws of different types, such as holes and cuts, were deliberately introduced into the knitted gauze with the aim of making the fracture occur within the gauze length, but without success. A simple analogy is to try tearing a knitted jumper compared to tearing a woven shirt.

Greater Surface Area for Catalysis

The knitted gauzes have more surface area available for catalysis because of their bulky three-dimensional structure. In woven gauzes the potential area for catalysis is masked, when compared to the knitted structure. Mathematical modelling was used to estimate the surface area available for catalysis for both types of gauze, and values of 83 per cent (17 per cent masked) for woven and 93 per cent (7 per cent masked) for knitted gauzes were obtained. In knitted gauzes the gas circulates around the wire, which provides more active sites for catalysis. This increases the potential for oxidation and reduces localised metal loss (wire thinning), so the wire retains its strength, which results in a longer life.

Fabric Flexibility

The flexibility of the knitted structure allows the catalyst to remain essentially fluid when subjected to start-up and shut-down procedures.

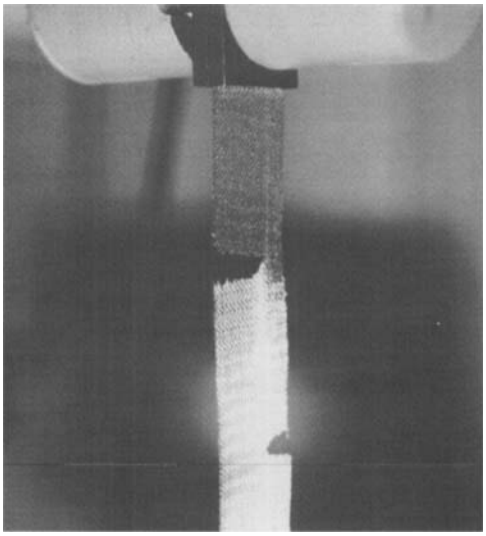

Fig. 8 Although the herringbone structure is considered to be one of the strongest conventional weaves, a tensile test sample tore almost instantly when under load

When in use the catalyst gauze is held rigidly in a burner, but some distortion occurs with temperature change. The catalyst will contract or expand, which may cause deformation and/or tearing at the edges; if this does not happen the gauzes may slip from under the clamp allowing ammonia to by-pass the gauze. The flexible nature of the knitted gauze enables the metal to expand and contract readily without affecting its physical and catalytic properties.

Choice of Alloy

Historically the conventional alloy for ammonia oxidation has been 10 per cent rhodium-platinum woven gauze. Before weaving can commence on a loom between 50 and 100 kg of wire must be available, whereas a knitting machine only needs 5 kg of wire. This permits a more flexible approach to alloy composition and also allows a faster response to market changes. There are now four standard alloys in production: 5 per cent rhodium-platinum, 8 per cent rhodium-platinum, 10 per cent rhodium-platinum and 5 per cent rhodium-5 per cent palladium-platinum.

Lower Stock Levels

Due to the different alloys which can be accommodated and the reduced amount of wire required for start-up, the production of large quantities of "stock" catalysts has not been required, despite the increase in the number of alloys being supplied. It also follows that a quicker response to a request for any knitted alloy is possible. Knitting can commence as soon as wire is produced. Certain non-standard alloys have been and can be produced to suit particular customer requirements.

Lower Metal Losses

The actual nature of the metal lost from catalysts has been the subject of speculation for a number of years. There appear to be two main types of metal loss: platinum volatilisation and mechanical removal. The platinum which is lost as PtO_2 can be collected by installing palladium-based catchment systems, which can recover up to 95 per cent of the total platinum losses. Platinum is also lost by mechanical removal caused by vibration during plant operation, and this can be further compounded on start-ups and shut-downs. There may also be temperature differences in a catalyst bed which can result in increased losses.

The general conclusion from many studies is that volatilisation is the main contributor to platinum loss (3, 5–7). In order for platinum to be volatilised it must come into contact with oxygen molecules; therefore volatilisation is dependent upon the conversion of ammonia and hence on the production of acid. Assuming constant conversion efficiencies, the metal loss should be fixed and therefore the only possible reason for reduced metal loss must be smaller losses due to mechanical removal.

Table II

Typical Production Data

Gauze No. 2 knitted	Removal date Acid production Metal loss Metal loss/tonne of acid produced Surface rhodium	31.12.90 11345, tonnes 20.07, per cent 0.032, grams 14.2, per cent
Gauze No. 3 woven standard	Removal date Acid production Metal loss Metal loss/tonne of acid produced Surface rhodium	31.12.90 11345, tonnes 21, per cent 0.042, grams 34, per cent

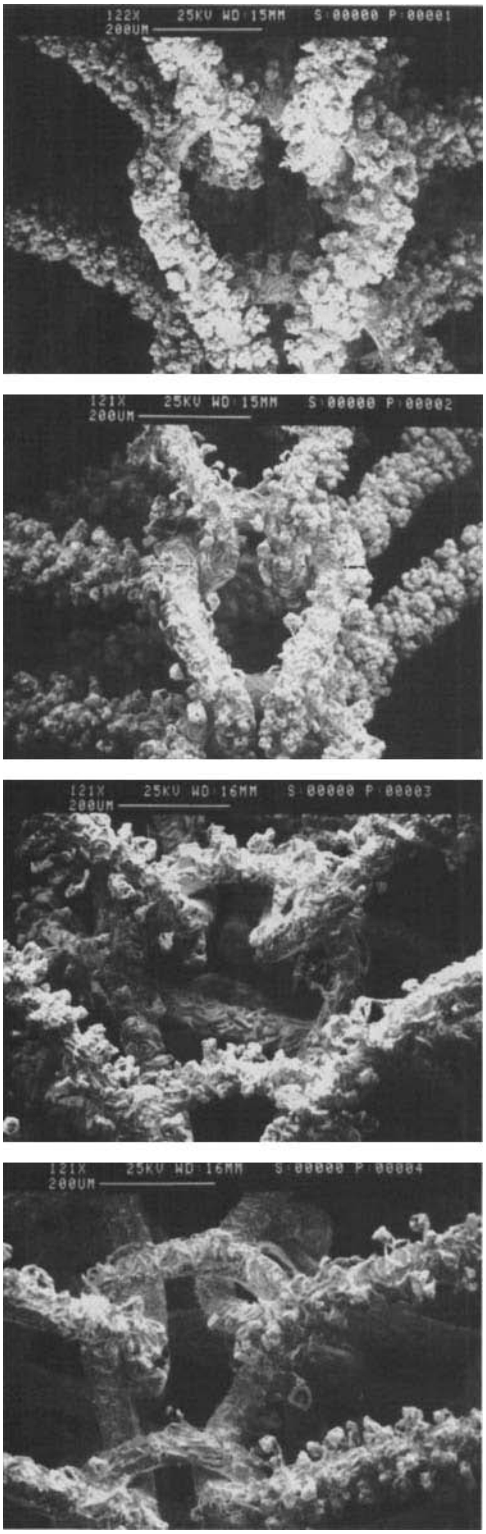

Fig. 9 After use for ammonia oxidation both woven and knitted gauzes show restructuring of the surface. Fragile "cauliflower" like formations grow on both types of catalyst but on knitted gauzes the structural rearrangement is widely dispersed throughout the catalyst pack leading to a more even temperature distribution, less mechanical damage and reduced metal loss, compared to the woven gauze

Metal losses from woven and knitted catalyst gauzes per tonne of acid produced are shown in Table II. The differences in metal loss can be partly explained by the restructuring that takes place on all gauzes, see Figure 9. The cauliflower-like formations that grow on the catalyst are very fragile, and become more so with increasing size; clearly, the more fragile the structure the greater its susceptibility to mechanical damage. With knitted gauzes there is widespread structural rearrangement throughout the catalyst pack and therefore less susceptibility to mechanical damage. This widely distributed restructuring also leads to a more even temperature distribution, and the increased structural flexibility enables it to withstand thermal shock more readily, which accounts for the reduced metal losses.

In some industrial plants, however, little or no reduction in metal loss has been seen, and therefore it can be concluded that these plants do not experience any significant loss of metal by mechanical removal.

Extended Campaign Length

One of the main requirements in ammonia oxidation plants is long catalyst life which permits extended campaign lengths. There are three factors affecting the catalyst life: material strength, rhodium oxide formation and contamination. Improvements in all these area have been observed as a result of using knitted gauzes. Various types of plant are now running extended campaigns. Typical examples are:

Low Pressure	from 180 to 240 days
Medium Pressure	from 120 to 200 days
High Pressure	from 50 to 80 days

When ammonia oxidation plants are running they are reasonably cost effective and reliable, but shut-downs to change the catalyst are costly in terms of both money and manpower, and invariably cause other problems of a mechanical nature. For a medium pressure plant, it is estimated that having one less change in the yearly schedule can result in a saving of £60,000 on the metal costs alone.

Summary

Knitting is rapidly gaining acceptance as a gauze manufacturing technique, and material fabricated in this way is also being applied to areas other than nitric acid production. Samples of knitted platinum group metals have been supplied for various specialist applications and to industries that deal predominantly in base metals.

Many of the early claims made for knitted catalysts have now been substantiated and, indeed, many other beneficial and unexpected results have been achieved. Further developments in the knitted structure and in the alloys involved are continuing, and the future for knitted gauzes looks assured.

References

1 K. Kaiser, *German Patent* 271, 517; 1909

2 S. L. Handforth and J. N. Tilley, *Ind. Eng. Ind.*, 1934 **26**, (12), 1287

3 B. T. Horner, *Platinum Metals Rev.*, 1991, **35**, (2), 58

4 Johnson Matthey PLC, *European Patent* 364, 153B

5 H. Connor, *Platinum Metals Rev.*, 1967, **11**, (2), 60

6 H. Holzmann, *Chem.-Ing.-Tech.*, 1967, **39**, (2), 89

7 H. Holzmann, *Platinum Metals Rev.*, 1969, **13**, (1), 2

Some Diverse Aspects of the Platinum Metals

Noble Metals and Biological Systems: their Role in Medicine, Mineral Exploration, and the Environment

EDITED BY R. R. BROOKS, CRC Press, Boca Raton, 1992, 392 pages, ISBN 0-8493-6164-8, U.S. $156, £94.50

The rise in interest in environmental issues over recent years has resulted in a significant increase in the number of papers related to the investigation of the distribution of materials in the environment, and particularly in biological systems. The above named book offers an extensive review of this literature in relation to gold, silver and the platinum group metals, with particular emphasis on exploration and medicinal use.

Because the noble metals occur at low concentrations in the earth's crust, trace analytical techniques are required for much of this work, and therefore the book begins with a chapter on the analysis of noble metals. This review is necessarily brief but highlights the improvements that have been made in recent years through the introduction of neutron activation analysis and inductively coupled plasma techniques, with emission or mass spectroscopy detection.

Much of the information gathered for this book deals only with silver and gold, due to their generally higher concentrations in the environment and their longer history of interest from exploration studies. Details and particularly interpretation of data on the platinum group metals is thus limited.

Two chapters discuss the determination of noble metal concentrations in biological material as an aid to mineral prospecting. Plants and microorganisms concentrate the noble metals from the soil, allowing evidence of underlying mineralisation to be obtained. Biological mobilisation of noble metals by microorganisms is reviewed as is the relationship of animals and noble metals. This section is then summarised by a general discussion of noble metals in the environment.

The final part of the book, consisting of four chapters, deals with the role of noble metals in medicine. The use of gold therapy for arthritis and platinum-based chemotherapy for cancer is now well known and, although the reviews are well written, the interested reader will probably be aware of this material already, or wish for a more detailed study as provided in numerous other specialised texts. Other chapters in this section deal with the use of osmium compounds in arthritis and ruthenium compounds for cancer therapy.

For those who have considered the role of noble metals in the environment and their interaction with biological systems, this volume should provide something of interest. It offers a guide to some of the less well known literature on this subject matter, much of which was originally published in Russian. C.F.J.B.