

# The Manufacture of Nitric Acid

## THE ROLE OF PLATINUM ALLOY GAUZES IN THE AMMONIA OXIDATION PROCESS

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*Nitric acid production by the oxidation of ammonia on platinum gauzes constitutes one of the world's major chemical industries. In this article the author outlines some of the principal features of this process, and describes in some detail the chemical reaction taking place at the platinum surface. He also discusses the changes that occur in the gauze leading to metal loss during operation. Handling and repairing the gauzes on a plant site and platinum dust recovery by filters are among other aspects of interest to plant operators with which the author deals.*

Thomas Malthus (1766-1834) maintained that the world's population increases more rapidly than its food supplies, and only disease, war, poverty and vice prevent large-scale starvation. He could not foresee the world of the twentieth century, nor the role to be played by platinum gauzes in producing fixed nitrogen fertilisers without which his gloomy predictions might well be realised.

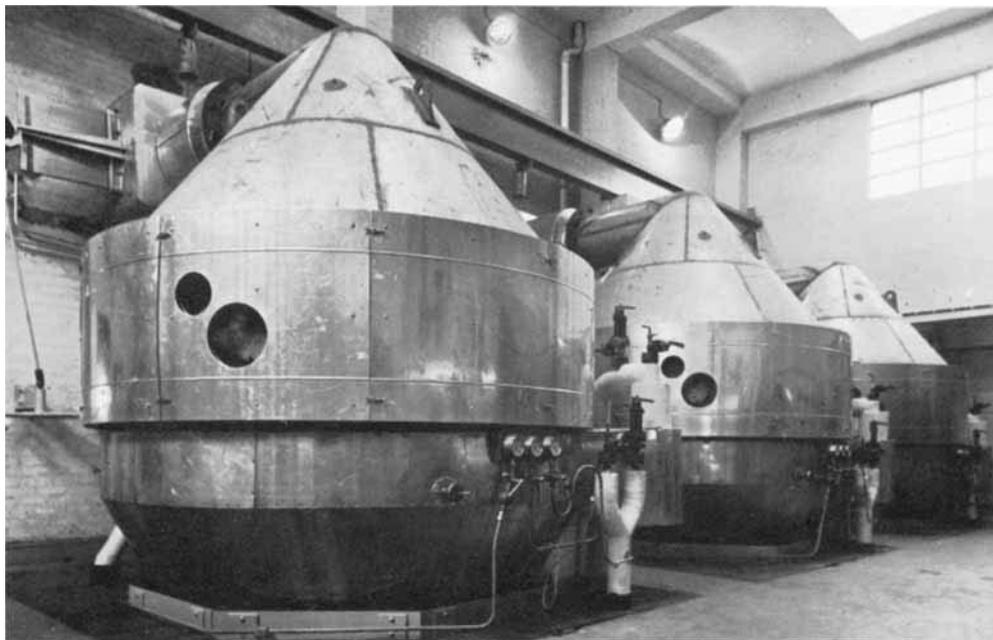
It is now estimated that the total world output of nitric acid has risen from about 18.3 million tonnes (100 per cent  $\text{HNO}_3$ ) in 1962-63 to just under 23.5 million tonnes in 1965-66 (1). At this level of production the world's nitric acid plants are believed to operate at an average of 82 per cent of all available production capacity. The estimated production of the major manufacturing countries is shown in Table I (1). It may also be estimated that this total plant capacity represents a platinum gauze inventory of

around 200,000 oz troy (about 6250 kg), excluding the weight of spare gauzes that most plants hold.

The manufacture of nitrogen fertilisers represents by far the largest proportion of the use of nitric acid. These fertilisers, generally with high nitrogen contents, provide the active nitrogen in the form of ammonium nitrate or as nitrophosphate formed by the action of nitric acid on phosphate rock. For these processes "weak" nitric acid (55 to 65 per cent  $\text{HNO}_3$ ) is usually employed. Certain territories, such as Japan, are exceptions to this generalisation, since nitrate fertilisers for domestic agriculture may not be suitable there, and consumption of the acid by the explosive and chemical industries is thus more important. In the U.S.A., about 65 per cent of the nitric acid produced is consumed in the manufacture of fertilisers, for example, ammonium nitrate, and an additional 4 to 5 per cent is used for products such as potassium nitrate and nitrophosphates. The remainder

**Table I**  
**The World's Output of Nitric Acid (1)**  
(Millions of tonnes 100 per cent  $\text{HNO}_3$ )

	1962-63	1965-66
U.S.A.	3.4	4.7
U.S.S.R.	2.5	3.7
West Germany	2.2	2.55
France	1.73	2.2
Italy	1.05	1.3
Norway	1.0	1.25
Netherlands	0.7	0.95
United Kingdom	0.6	0.90
Rest of the world	5.12	5.85
	<hr/> 18.30	<hr/> 23.40



*Fig. 1 Three ammonia converters installed in a modern nitric acid plant operated by Imperial Chemical Industries Limited. Each converter has three rhodium-platinum catalyst gauzes, 114 inches in diameter, woven by Johnson Matthey & Co Limited.*

(about 30 per cent) is used by the explosives, plastics and chemical industries. Table II shows an estimated breakdown of the world's use of nitric acid (1).

In 1962-63 nitric acid represented about 25 per cent of the world's fixed nitrogen production, but this proportion had dropped to an estimated 22.5 per cent by 1965-66. This decline is probably temporary, and is largely attributed to the sustained expansion of fertilisers obtained directly from ammonia, in particular urea and complex fertilisers based on ammonium phosphate. Low-cost ammonia from very large modern plants employing new processes based on hydrogen obtained from petroleum fractions (output about 1000 tonnes per day), together with increasingly large nitric acid plant facilities (about 500 tonnes per day), can be expected to effect substantial reductions in nitric acid production costs. Such reductions may have significant effects on potential applications in which price considerations have limited or prohibited the use of nitric acid until now.

**Table II**  
**The World's Usage of Nitric Acid (1)**

	Millions of Tonnes 100 per cent HNO <sub>3</sub>	
	1962-63	1965-66
Fertiliser production	14.6 (80%)	18.9 (81%)
Explosives, plastics and chemical industries	3.7 (20%)	4.5 (19%)

One such sector is the manufacture of nitro-phosphate-type fertilisers.

With a world population that is expected to be about 7000 million by the end of this century, and with two-thirds of them undernourished by even the most frugal standards, the outlook for nitrogen fertiliser production seems assured, and nitrate fertilisers based on nitric acid are likely to play a very major role in fulfilling total fertiliser demand.

### **The Nitric Acid Process**

The foundation of the modern nitric acid process was laid by Kuhlmann in 1838 when he filed a patent for the catalytic oxidation of

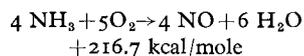
ammonia over platinum sponge, although Milner had earlier oxidised this gas to nitric oxide over manganese dioxide in 1789. Pilot plant scale experiments were carried out by Ostwald and Brauer in the period 1901 to 1904, and the first plant to produce 300 kg of nitric acid per day was commissioned at Gerthe, near Bochum, in 1906. A tenfold increase in production was achieved by 1908. These early plants used crimped platinum strips wound into a coil, but in 1909 Kaiser filed a patent for the use of platinum in the form of a gauze woven of wire 0.06 mm diameter with 1050 apertures/cm<sup>2</sup>, and such gauzes are still used today. The contribution of Ostwald and his co-workers to the development of the nitric acid process, and the trials that led to the establishment of this new technology, have been described elsewhere (2, 3).

Until the early 1920s ammonia was obtained from gas works liquors and the impurities it contained — mainly sulphur and arsenic — resulted in comparatively short catalyst lives. The really large-scale production of nitric acid had to await two other major technological developments: the availability of cheap, high-purity synthetic ammonia from the Haber process, and stainless steel as a material of construction for efficient absorption systems working under pressure. The contribution the latter development has made to plant design may be judged by the fact that in 1919 a U.S.A. plant to produce 280 tonnes per day of nitric acid required 24 atmospheric pressure acid absorption towers, each 35 ft square and 60 ft high — a total volume of 1.63 million cubic feet, not counting 12 large oxidation towers (4).

The modern nitric acid process proceeds essentially in three stages:

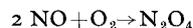
- 1 Liquefied ammonia is vapourised and pre-heated before being mixed with pre-heated air. The mixture at about 300°C, and usually containing 10.5 to 12 volume per cent of ammonia, is passed downwards through a pad of platinum alloy gauzes in a converter. Nitric oxide is

formed as a result of an extremely rapid, highly exothermic reaction at the platinum surface in accordance with the overall equation



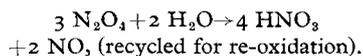
This reaction will be discussed in fuller detail in a later section.

- 2 The nitric oxide that is produced at the platinum gauze is oxidised further by means of secondary air reacting homogeneously in the gas phase in accordance with the overall equation



Formation of dinitrogen tetroxide proceeds via an intermediate nitrogen dioxide, NO<sub>2</sub>. The nitric oxide oxidation reaction has a negative temperature coefficient, hence low temperatures favour high yields. Elevated pressures also raise the yields of the tetroxide, making possible the production of higher strengths of acid.

- 3 Dinitrogen tetroxide is absorbed in water with the formation of nitric acid in accordance with the simplified equation



The absorption proceeds at greater rates, and with higher efficiencies, at elevated pressures and low temperatures.

In a modern plant the heat liberated by the ammonia oxidation reaction is usually recovered, enabling the plant to be self-supporting for its power requirements once the reaction has reached optimum conditions and capacity working is attained.

### Modern Proprietary Processes

There is no universally optimum overall design of a nitric acid plant; conditions of pressure, temperature, flow rate and other factors for each stage in the process may be varied to suit particular local requirements and situations. At least fifteen proprietary nitric acid processes are available now; the choice presented to operators is wide, and the selection of the "best" process to suit a given

**Table III**  
**Effect of Major Process Variables on Nitric Acid Manufacture (7)**

Process Change	Oxidation of NH <sub>3</sub>	Oxidation of NO	Absorption of NO <sub>2</sub>
Increased temperature	Greater yield	Lower yield	Reduced absorption, lower HNO <sub>3</sub> strength
Increased pressure	Oxidation rate slightly reduced. Weight of NH <sub>3</sub> oxidised increased per unit time	Increased yield	Improved absorption, greater HNO <sub>3</sub> strength
Increased flow rate	Optimum operating temperature increased. Weight of NH <sub>3</sub> oxidised increased. NO yield improved	Reduced secondary reactions. More turbulence and increased yield	Minor improvements only, as absorption mostly controlled by gas composition and reaction rates

requirement involves the evaluation of numerous technical and economic factors (5, 6).

The principal design variables for the ammonia oxidation and subsequent stages of the plant are temperature, pressure and gas flow rate. Their main effects in these sections are shown in Table III (7). Since the oxidation of nitric oxide and the absorption stages are always carried out at pressures in the range 4 to 9 atmospheres, plants are generally described by the pressures within the ammonia oxidation converter: low, or atmospheric, medium (3 to 5 atmospheres) or high (5 to 9 atmospheres). Ammonia oxidation at low pressures results in higher conversion efficiencies and lower platinum metal losses compared with medium or high pressure oxidation. Longer operating periods between shut-downs for gauze maintenance are also possible, but such converters are bulkier, more expensive and require costly hot-gas compressors to raise the gas pressure after oxidation to that required in the subsequent stages.

The American high pressure plants—all derived from the Du Pont process—operate with a converter pressure around 8 atmospheres and with a gauze pad temperature in the range 900 to 950°C. They also have high

gas flow rates per unit area of gauze, and hence the platinum loss rates are high, in practice running to 250 to 400 mg/ton 100 per cent HNO<sub>3</sub>. Among the European process licensors, Uhde and Stamicarbon also offer high pressure plants with the gauze pad operating at temperatures about 900°C. These, however, have lower gas flow rates and the platinum losses are correspondingly reduced to 180 to 200 mg/ton. Medium pressure converters with gauze temperatures of 845 to 880°C generally experience platinum losses from 85 to 125 mg/ton, while converters operating at atmospheric pressure with gauze temperatures about 800°C have the lowest metal loss rates, around 50 mg/ton (5, 8). It must be mentioned that process licensors' claims for platinum loss rates generally appear to be conservative in the light of actual operating experience.

Table IV summarises the principal features of some commercial nitric acid processes available to operators under licence. It is based on licensors' specifications and is reproduced by courtesy of the Noyes Development Corporation, New York (7).

The cost of producing ammonia has fallen recently following the introduction of new processes for manufacturing low cost hydro-

**Table IV**  
**Principal Features of Some Commercial Nitric Acid Processes**

Name	Approximate operating pressures, atmospheres (abs)			Product acid per cent HNO <sub>3</sub>	Typical requirements per tonne of 100% HNO <sub>3</sub>		Distinctive features
	Combustion	Oxidation	Absorption				
<b>Bamag (Monopressure)</b>	1,4 or 8	1,4 or 8	1,4 or 8	55 to 70	dependent on pressures used		Uses perforated plate towers with cooling water coils on the plates
<b>Bamag (Combination)</b>	1,4 or 8	4 or 8	4 or 8	55 to 70	NH <sub>3</sub> Pt cooling H <sub>2</sub> O pure H <sub>2</sub> O	280 kg 45 mg 170 m <sup>3</sup> 100 kg	Similar to above
<b>Chemico</b>	8 to 9	8 to 9	8 to 9	55 to 65	(steam turbine and plus expander) NH <sub>3</sub> Pt cooling H <sub>2</sub> O pure H <sub>2</sub> O	510°C 287 kg 128 mg 135 m <sup>3</sup> 500 kg	(with steam turbine and 680°C plus expander) 287 kg Pt 128 mg cooling H <sub>2</sub> O 100 m <sup>3</sup> pure H <sub>2</sub> O 540 kg
<b>C &amp; I</b>	8	8	8	55 to 67 plus	NH <sub>3</sub> Pt cooling H <sub>2</sub> O pure H <sub>2</sub> O	292 kg 170 mg 117 m <sup>3</sup> 400 kg	Uses cascade cooling and a single tower for oxidation/absorption/bleaching
<b>Grand Paroisse</b>	3 to 4	7 to 8	7 to 8	56 to 70	NH <sub>3</sub> Pt cooling H <sub>2</sub> O pure H <sub>2</sub> O	282 kg 100 mg 200 m <sup>3</sup> 710 kg	Oxidation towers cooled externally by water. Absorption tower cooled by internal water coils. 5 unit, single shaft, turbo-compressor used
<b>Hercules</b>	8	8	8	57 to 60	NH <sub>3</sub> Pt cooling H <sub>2</sub> O pure H <sub>2</sub> O	285 kg 174 mg 95 m <sup>3</sup> 500 kg	85 to 95 Uses high gas superheat to obtain maximum power recovery. Specially designed water-cooled absorption trays ensure a minimum 99% absorption efficiency
<b>Kuhlmann</b>	1	4	5	55 to 70	NH <sub>3</sub> Pt cooling H <sub>2</sub> O	280 kg 45 mg 150 m <sup>3</sup>	Uses a specially designed tray to induce oxidation and absorption in the liquid phase
<b>Montecatini</b>	4 to 5	4 to 5	4 to 5	53 to 62	NH <sub>3</sub> Pt cooling H <sub>2</sub> O	286 kg 100 mg 100 m <sup>3</sup>	Uses separate oxidation and absorption towers fitted with refrigerated trays
<b>Pechiney-St Gobain</b>	4 to 5	4 to 5	4 to 5	normally up to 60	NH <sub>3</sub> Pt	286 kg 100 mg	Uses specially designed water-cooled trays in oxidation absorption columns
<b>SBA (Société Belge de l'Azote)</b>	1	3 to 5	3 to 5	58 to 70	(for 55% HNO <sub>3</sub> ) NH <sub>3</sub> Pt cooling H <sub>2</sub> O pure H <sub>2</sub> O	281 kg 45 mg 150 m <sup>3</sup> 650 kg	Packed columns for 58% acid. Additional plate-type columns used for 70% acid
<b>SBA</b>	3.3	3 to 5	8	50 to 70	Similar to above		Similar to above. Uses catalytic tail-gas combustion for maximum energy recovery
<b>Stamicarbon</b>	1	5 to 6	5 to 6	50 to 65	NH <sub>3</sub> Pt cooling H <sub>2</sub> O pure H <sub>2</sub> O	285 kg 45 mg 250 m <sup>3</sup> 730 kg	Specially designed plate coolers used in conjunction with packed columns
<b>Uhde (normal strength)</b>	7 to 8	7 to 8	7 to 8	55 to 60	NH <sub>3</sub> Pt cooling H <sub>2</sub> O	285 kg 200 mg 150 m <sup>3</sup>	79% of steam produced used for driving air compressor, 11% for heating tail-gas, 10% as product steam. Bubble tray absorbers used
<b>Uhde (high strength)</b>	(a) 4.5 (b) 1	4 to 5 4 to 5	4 to 5 4 to 5	60 max. 68 min.	NH <sub>3</sub> Pt cooling H <sub>2</sub> O pure H <sub>2</sub> O	283 kg 60 mg 165 m <sup>3</sup> 250 kg	Uses multi-stage, packed oxidation and absorption columns; each stage fitted with own cooler and pump. Figures listed refer to process (a)
<b>Weatherly</b>	9.5	9.0	9.0	55 to 60 (or higher)	NH <sub>3</sub> Pt cooling H <sub>2</sub> O pure H <sub>2</sub> O	284 kg 165 mg 142 m <sup>3</sup> 750 kg	Uses butted heat-exchanger assembly and a single oxidation/absorption/bleaching column fitted with bubble trays

Note: The above table is intended as a general, comparative guide only. It is based on licensors' specifications, and actual plant performances depend on variable and individual plant features such as daily capacities, water temperatures, types of drive and other associated items selected to suit local conditions.

gen from petroleum fractions. With low ammonia costs, the advantages of higher conversion efficiencies achieved by atmospheric pressure converters may no longer outweigh the relatively high capital and operating costs of such mixed-pressure plants. There is a trend in Europe, therefore, to follow American practice and to adopt constant-pressure processes in which the converter and the following sections of the plant operate at the same pressure (usually in the range 3 to 9 atmospheres). The selection of the economically optimum operating pressure depends on a number of factors, for example, ammonia costs, steam credit value and local tax situations (9).

### The Gauze in Operation

The heart of the nitric acid plant is the converter where ammonia is oxidised to nitric oxide. Consisting essentially of a reactor shell wherein the pre-heated ammonia-air mixture generally flows vertically downwards through the gauze pad, it is usually situated immediately on top of the waste heat boiler. A baffle or diffuser system located in the top of the converter ensures that the gas mixture reaching the gauzes is homogeneous, and provides an even gas distribution over the entire gauze surface. This is important in order to avoid "hot spots" with attendant risk of local gauze damage, and becomes more difficult to achieve with increasing converter diameter.

Stainless steel or an aluminium-magnesium alloy are used as constructional materials for the ammonia pre-heater, the mixed-gas ducts leading to the converter and the converter hood itself. This is to ensure that ammonia at the pre-heat temperature (250 to 300°C) does not come into contact with surfaces capable of catalysing its decomposition into nitrogen and hydrogen before making contact with the platinum gauzes. Iron oxide—used as an ammonia synthesis catalyst, and equally capable of catalysing the reverse reaction—is particularly liable to cause ammonia losses by pre-decomposition. It should be carefully excluded from the system by avoiding the use of mild steel components liable to rust forma-

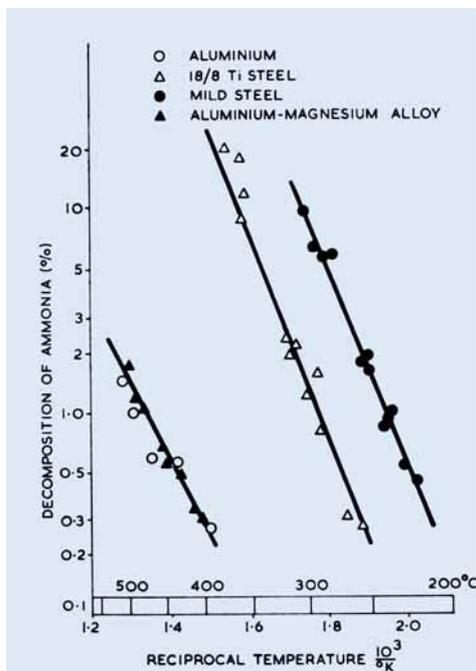


Fig. 2 The rates of decomposition of ammonia on various constructional materials increase sharply with rising temperature. This graph illustrates these rates, using a 10 volume per cent ammonia-air mixture (Spratt).

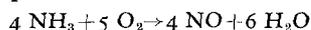
tion. The interior surface of the converter hood is heated by radiation from the gauze pad and external water cooling is required, especially for high pressure converters whose gauzes operate at temperatures up to about 950°C. Fig. 2 illustrates the marked effect of temperature on the decomposition of ammonia on various metal surfaces (10). At normal pre-heat temperatures, ammonia decomposes about 10 times faster on mild steel than on stainless steel. It is estimated that from 1.5 to 3 per cent of the ammonia fed to most plants may be lost by pre-decomposition and thus never reach the platinum gauzes.

### The Ammonia-Air Mixture

The ammonia feedstock is vaporised, superheated and filtered to remove any dust or oil particles before pre-heating. Atmospheric air may be scrubbed with water and is then care-

fully filtered before being pre-heated in a separate heat exchanger. Good mixing of the gases is essential, and for this purpose venturi-type or sparge-type mixers are usually employed.

In certain proportions, ammonia and air form explosive mixtures. At 1 atm. pressure, the lower explosive limit is 13.8 volume per cent  $\text{NH}_3$ , falling to 13.0 and 12.4 volume per cent at 5 and 8 atm. pressures respectively. The stoichiometric composition for the reaction



is 14.2 volume per cent  $\text{NH}_3$ , although a somewhat more important ratio is the kinetic-stoichiometric composition, at which the collision chances for oxygen and ammonia molecules are in the ratio 5/4 : 1. This ratio corresponds to an ammonia concentration of 12.7 volume

per cent in air. In practice, ammonia concentrations in the range 10.5 to 12 volume per cent are used, and in this region it is apparent that there is very little excess oxygen supplied to the reaction system. The variation in the  $\text{NH}_3 : \text{O}_2$  ratio as the reaction proceeds is illustrated in Fig. 3 (11).

### The Reaction at the Gauze

The oxidation of ammonia is a typical example of a very fast heterogeneous reaction with residence times from  $10^{-3}$  to  $10^{-4}$  seconds and hourly space velocities exceeding  $10^6$ . Such conditions entail considerable linear gas velocities, often greater than 20 metres/minute. Since the mean free path of ammonia molecules under the pressure and temperature conditions normally encountered in a converter is of the order of 0.3 micron, compared with a wire diameter around 60 microns and even larger aperture diameters, ammonia mass transfer is not influenced by molecular diffusion limitations. The physical transport of the ammonia molecules to the platinum surface is the rate-determining fac-

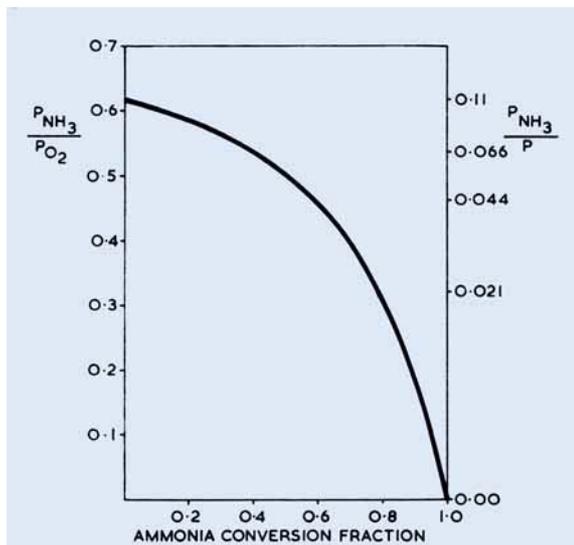
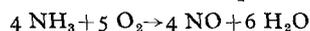


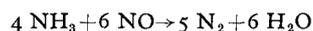
Fig. 3 Graph illustrating the changing ammonia: oxygen ratio as the reaction proceeds on a platinum gauze pad. The initial ammonia concentration was 11.0 volume per cent (Oele)

tor during the greater part of the reaction period.

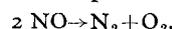
If ammonia and oxygen were allowed to react under equilibrium conditions, nitrogen and water would be the only products. Reaction conditions are such, however, that nearly every molecule that hits the platinum gauze surface is converted to nitric oxide in accordance with the overall equation



If the gas flow rate is too high, some unreacted ammonia passes through the gauze pad, and will then react with nitric oxide (12)



If the rate is too low, some nitric oxide will decompose on the hot platinum surface (13)



Since about 80 to 90 per cent of the reaction is completed on the upper gauze of a 3- to 5-ply pad, or in the top 20 per cent of the layers in a thick pad used in high pressure converters, the gas leaving this zone will contain both ammonia and nitric oxide. In order to reduce to a minimum the reaction between these gases, it is necessary to provide very good

contact between individual gauzes and to avoid any free spaces between them. This is achieved by using gauzes that are perfectly flat and free from folds or buckles that could separate them from each other.

Numerous studies of the kinetics of the principal reaction have been made (14, 15, 16). Among the postulated intermediates are hydroxylamine, nitroxyl, NHO, and the radical NH. It is generally agreed that reaction proceeds between ammonia and an activated oxygen boundary layer that covers most of the platinum surface.

The formation of nitric oxide is favoured by low operating pressures and, since the reaction has a positive temperature coefficient, also by high temperatures. The optimum temperature, moreover, increases with the rate of gas flow.

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*The concluding part of Mr Connor's article, dealing principally with the problem of platinum losses from gauzes during operation and with the production and handling of gauzes, will be published in the April issue of Platinum Metals Review.*

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## Further Increase in Platinum Production at Rustenburg

Any concern felt by users of platinum about the availability of metal to meet their future needs should have been relieved by the announcement recently made by Rustenburg Platinum Mines of their further plans to increase production.

Temporary measures introduced last year to secure a relatively quick increase in output are to be replaced with permanent facilities giving an annual capacity of about 600,000 ounces of platinum by the autumn of this year.

Preliminary work has been started on a further scheme, involving the acceleration of shaft sinking programmes, further extension to the reduction works and smelter plant and the expansion of numerous mining facilities. This, together with the extension of refining plant now being undertaken by Johnson Matthey and by Matte Smelters, will result in a refined platinum capacity of some 750,000 ounces a year. This increased flow of metal, which compares with an output of about 200,000 ounces a year in 1963, will begin to reach users in 1969 and will be fully effective by 1971.

The estimated ore reserves available to Rustenburg are considered to be sufficient to permit production at this rate well beyond the turn of the century.

