

# The Development of the Modern Ammonia Oxidation Process

## INFLUENCE OF ECONOMIC AND TECHNICAL FACTORS IN NITRIC ACID MANUFACTURE

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*By the end of the first world war the manufacture of nitric acid by ammonia oxidation over a platinum catalyst was a technically established process. The rapid increase in production of synthetic ammonia enabled this method to become the principal source of industrial nitric acid, and further development of the process in terms both of technical progress and in the size of unit plant has been determined by economic factors.*

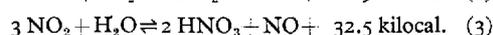
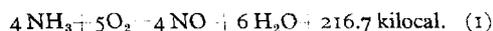
During the past forty years the ammonia oxidation process has been the only process of economic importance for the production of nitric acid. During this period as the demand for nitric acid has increased there has been progressive development of the process both technically and in the size of unit plants.

Nitric acid is required by industry in two forms; either as "weak nitric acid" of 50 to 60 per cent  $\text{HNO}_3$  or as "concentrated nitric acid" of 95 per cent  $\text{HNO}_3$  or greater. The ammonia oxidation process as originally developed produced weak acid, which was often nearer 40 than 50 per cent  $\text{HNO}_3$ . This acid is quite satisfactory for the production of inorganic nitrates but for organic nitrations the explosives and dyestuffs industries needed concentrated acid. The weak acid is concentrated by distillation with a water carrier, such as sulphuric acid, which must subsequently be reconcentrated. In the 1920s a large proportion of the total acid was required in the concentrated form. This proportion has slowly decreased and the present popularity of fertilisers containing nitrate nitrogen means that most of the nitric acid is required in the dilute form.

Because of the high costs of concentration early attempts to improve the ammonia oxidation process were aimed at making more concentrated acid and, if possible, really concentrated acid.

### Effect of Pressure

The reactions involved in the manufacture of nitric acid from ammonia may be summarised as:



As indicated the absorption reaction is reversible and a state of equilibrium can exist between the gas and liquid compositions. This can be expressed as:

$$\frac{(P_{\text{NO}_2})^3 (P_{\text{H}_2\text{O}})}{(P_{\text{HNO}_3})^2 (P_{\text{NO}})} = \text{constant} \quad (4)$$

Absorption proceeds at a rate which is related to the extent to which the system departs from equilibrium. Consideration of equation (4) shows that two of the factors relate to the gas composition and two to the acid composition. To obtain a high strength acid the

ratio  $(P_{\text{NO}_2})^3 : P_{\text{NO}}$  must be high. This can be achieved by increasing the proportion of the total nitrous gas present as  $\text{NO}_2$  (high state of oxidation) or by increasing the total pressure. There is in fact much more scope for gain by increase of pressure and most of the development work for high strength acid was along this line.

The vapour pressure of nitric acid is such that it is not difficult to obtain about 60 per cent  $\text{HNO}_3$  by increasing the working pressure of the absorption system. However, very large and uneconomic increases in pressure are necessary to get significantly above 60 per cent  $\text{HNO}_3$ .

A second very important effect of increased pressure is a marked reduction of the volume required for the absorption system. This more than offsets the other effects of increased pressure so that a high pressure plant has a lower capital cost than a low pressure plant.

### Early Lines of Development

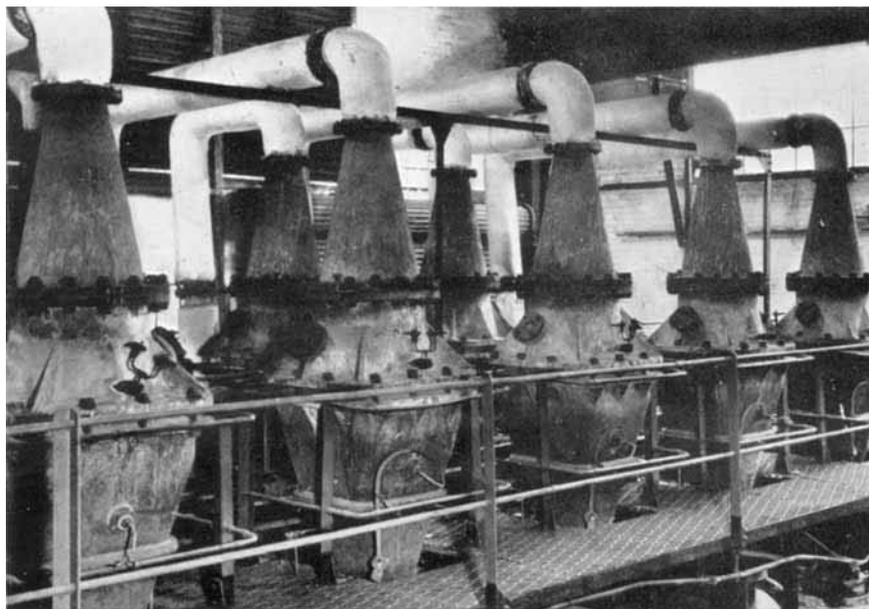
Plants were produced by E. I. du Pont de Nemours and Co. working at 8 atmospheres absolute and by G. Fauser working at 5 atmo-

spheres absolute. The plants differed in that the du Pont plant oxidised the ammonia under pressure while the Fauser plant carried out this stage at atmospheric pressure. These plants produced acid of about 60 per cent  $\text{HNO}_3$  compared to the 40 to 50 per cent of earlier plants.

A different approach was used by the Bamag Company which oxidised the ammonia with oxygen, thus obtaining a very concentrated nitrous gas. By the use of refrigeration a large proportion of the nitrous gas was recovered as liquid  $\text{N}_2\text{O}_4$ . This was reacted in autoclaves under pressure with oxygen and dilute nitric acid to form 98 per cent  $\text{HNO}_3$ .

### Most Economic Pressure

As the emphasis has swung more to low cost weak nitric acid with relatively small premiums for acid concentration, the attractiveness of the high pressure plants has fallen because of their high operating costs. The most economically attractive working pressure is currently about 3 atmospheres absolute and development is concentrated on the efficient utilisation of the considerable heat of reaction.

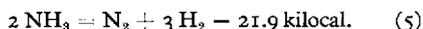


*The original atmospheric pressure ammonia oxidation converters installed at Billingham in the 1920s, employing twenty-inch diameter platinum gauzes with downward flow*

There remains the basic question exemplified by the two original pressure plant designs of whether or not to pressurise the ammonia oxidation step of the process.

### Ammonia Oxidation

The all-important first step in the conversion of ammonia to nitric acid is the oxidation of the ammonia to nitric oxide over a catalyst as set out earlier as reaction (1). The normal working temperature of the platinum or platinum alloy catalyst is 800 to 900°C and the temperature rise due to reaction with the ammonia concentrations normally employed ranges from 600 to 700°C. It is therefore necessary to heat the gases before they reach the catalyst and this involves the risk of thermal decomposition of ammonia:

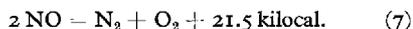


The homogeneous rate of decomposition is negligible under normal nitric acid plant conditions. However, the reaction is catalysed by many materials particularly when an oxide film is present.

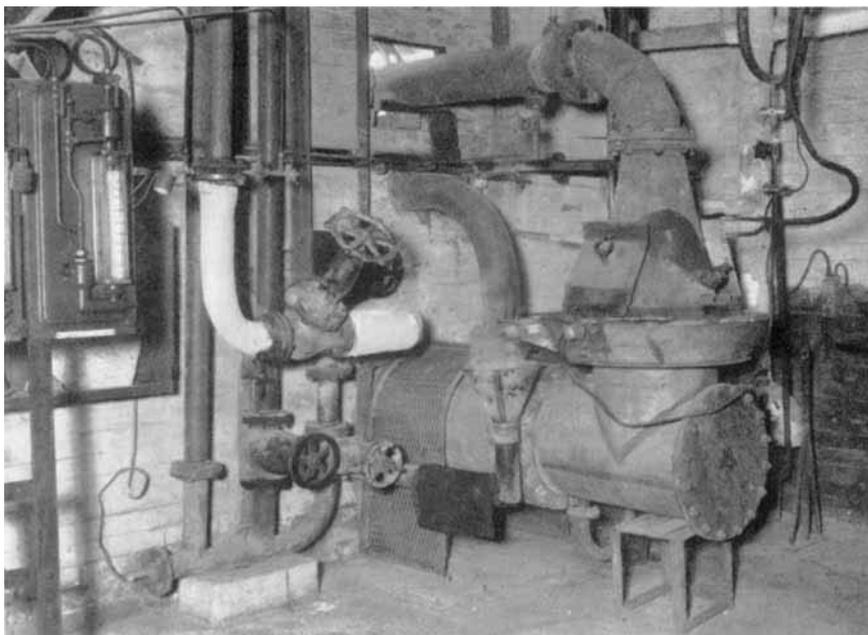
Ammonia is oxidised to NO on the platinum catalyst with remarkable facility and it appears that every ammonia molecule which strikes the catalyst is oxidised. However, the catalyst can be loaded to the point where ammonia breaks through and this will then react in the gas phase with the nitric oxide:



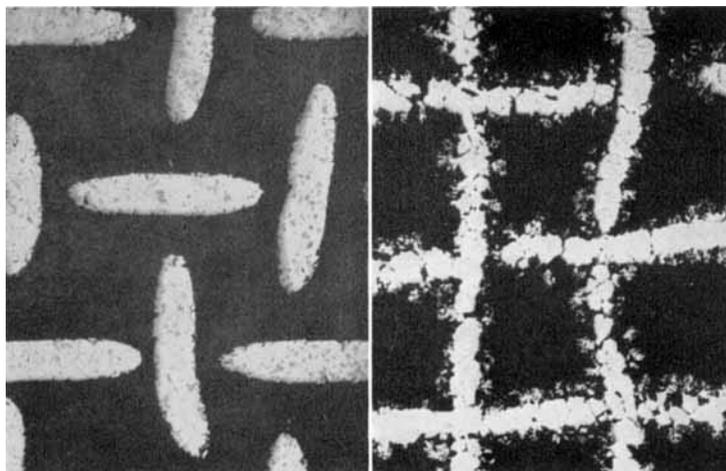
If on the other hand the catalyst is very lightly loaded the nitric oxide may be decomposed by the catalyst:



Since the efficiency can be reduced by both high loading and low loading there must be an optimum loading. In practice the optimum is broad and over an appreciable range of loadings the conversion is constant. The optimum loading is affected by many factors, the most striking effects being produced by catalyst temperature and gas pressure. Owing to the increased chance of an ammonia molecule colliding with the catalyst the



*Conversion at high pressure in a down flow converter using a thick pad of sixteen-inch hexagonal rhodium-platinum alloy gauzes*



Photomicrographs ( $\times 100$ ) of catalyst gauzes. Left, a fairly new catalyst; right, a well-used catalyst

optimum loading increases with both catalyst temperature and gas pressure. As ammonia is a major cost item in the production of nitric acid, converters are normally designed for and operated at the optimum efficiency.

### Catalyst Performance

Since the noble metal catalyst is expensive, it is economically attractive to reduce the amount of catalyst employed. This may be done by increasing the throughput and raising the working temperature to maintain the efficiency of conversion of ammonia to nitric oxide. However, the catalyst deteriorates in service and some of the metal is lost from the wire gauzes, which eventually become so weak that they must be removed and the metal recovered. The rates of deterioration and of loss of metal increase very rapidly with temperature and with pressure and make it unattractive to push up the loading and hence the working temperature. When the oxidation of ammonia is carried out under pressure the need to restrict the size of the catalyst chamber and the general effects of pressure favour high catalyst loading and high catalyst temperature. These conditions would have involved unacceptable losses of metal with the original platinum catalyst and were made possible only because of the development of an alloy which suffered much reduced loss of metal. This alloy was chosen out of many

possibilities by Handforth and Tilley, of du Pont de Nemours and Co., in the United States of America, who published their results in 1934 in *Industrial and Engineering Chemistry*, and comprised a 10 per cent rhodium-platinum alloy. Because of its better efficiency, reduced rate of loss and longer life this alloy is now the standard ammonia oxidation catalyst and is used universally in the form of gauze. The gauze is normally of 80 mesh, the wire being about 0.003 inch diameter.

The mechanism by which the catalyst is "lost" is not known. It is a matter of observation that during service the smooth wires of the catalyst develop excrescences and recrystallisation proceeds until the "wire" is a chain of crystals with extremely poor mechanical properties. The excrescences become detached in operation and may be recovered by suitable filters installed after the catalyst.

### Recovery of Catalyst Metal

A process for recovering the metal lost from the catalyst was developed in Germany during the war. The hot gases were passed through a bed of gold-plated ceramic rings and the platinum alloyed with the gold. The coating was subsequently stripped and refined. More recently fibrous filters have been developed in the United States to filter

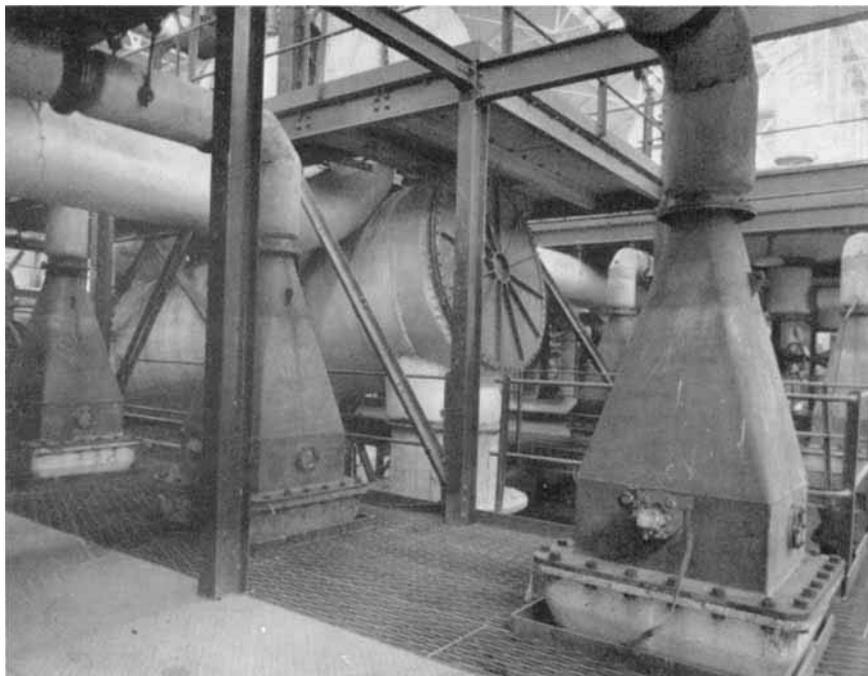
out the particles of platinum from the hot gas stream. Because of the pressure drop introduced into the plant these filters have not been universally adopted.

### Converter Design

The temperature rise across the catalyst depends primarily on the concentration of ammonia in the gas. Since the temperature for optimum conversion is fixed by the loading of the catalyst, this, in conjunction with the concentration of ammonia in the gas to be converted, fixes the temperature to which the gas must be preheated before it reaches the catalyst. If the ammonia concentration is low then the preheat temperature will be high. In high pressure converters the ammonia concentration in the gas must be kept down to avoid the combustible mixture range and this requires high preheat to obtain the high catalyst temperatures necessary for the high loading. This is in itself an adverse effect since the relatively high surface/volume ratio of high pressure plant favours the crack-

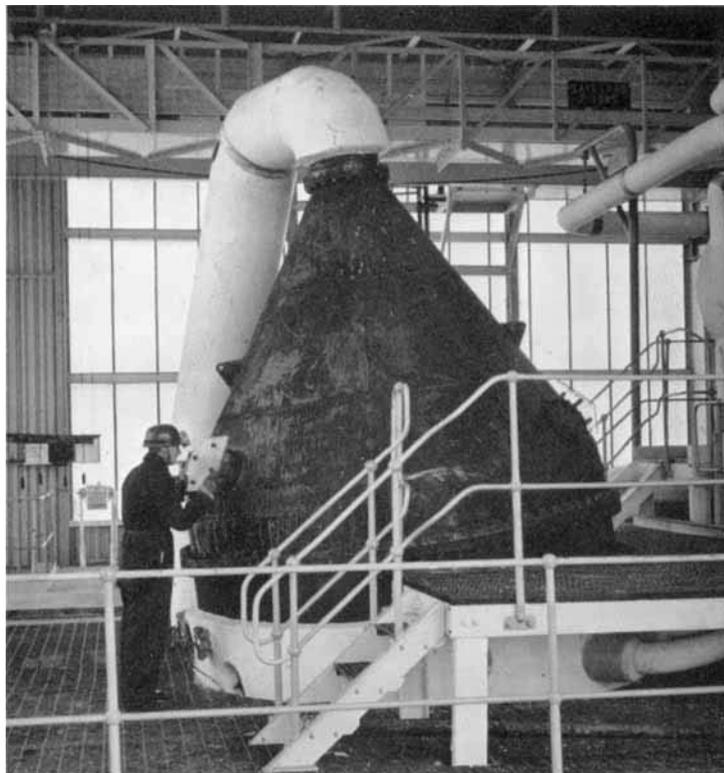
ing of ammonia. The use of suitable materials such as stainless steel, however, enables reasonable efficiencies to be achieved in practice though the efficiency is commonly lower than in low pressure plants and the catalyst loss higher.

Since the catalyst operates at a temperature of 800 to 900°C the rhodium-platinum wire gauze has relatively little mechanical strength and must be supported so that it can sustain the pressure difference due to the flow of gas through the gauze. The difficulty of supporting the catalyst leads initially to two very different solutions. The solution adopted in England was to use a small gauze which was clamped in a joint with limited support against downward flow. The solution on the Continent was to use a very large gauze and to float it on a rising stream of gas. As heat and oxidation resistant materials were developed it became possible to support larger areas of gauze against downward flow and the unit size of gauze in this type of converter increased because of the general advantages



*Medium pressure ammonia oxidation converter of the late 1940s with square gauzes*

*An ammonia oxidation unit in a modern nitric acid plant, employing large circular rhodium-platinum gauze nets for medium pressure conversion*



of a smaller number of units and of less surface area of plant both for cracking of ammonia and for loss of heat. Present-day designs not only enable gauzes of large diameter to be used with adequate support but also permit large converters to be made pressure tight so that the need for atmospheric pressure oxidation of ammonia has been removed. A modern medium pressure converter is illustrated above.

### **Gas Purity**

Owing to the high working temperature the catalyst is not very susceptible to poisoning and this combined with the high purity of ammonia produced in synthesis plants gives a complete absence of trouble due to this cause. However, oxides of iron have a deleterious effect on performance as they catalyse the cracking reaction (5) and any non-volatile non-combustible dust has an adverse effect through blanketing the catalyst. Because of this the gases must be freed from all dust and

scale by filtration before passing to the catalyst. Many types of filter have been used including porous stoneware but the type appears unimportant so long as the dusts normally present in the gases are effectively removed.

Some dust inevitably passes any filter and the catalyst performance deteriorates with time. It is common practice to clean the catalyst periodically by treatment with hot dilute hydrochloric acid. The extent to which this is done is a matter of economics for the used catalyst gauze is brittle and is easily damaged by handling.

### **Heat Economy**

Reference to reactions (1), (2) and (3) will show that 60 per cent of the heat evolved in nitric acid manufacture is evolved in the oxidation of the ammonia to nitric oxide. This heat is available as sensible heat in the gases leaving the catalyst and at a sufficiently high temperature to make recovery worth

while. Some of the sensible heat in the converted gas is used for preheating the gases going to the catalyst but the heat of reaction is available for other purposes. Initially this heat was recovered as steam in waste heat boilers. By the use of economisers the heat recovery can be made effective to about 82 per cent of the heat of oxidation of ammonia but cannot be taken further because of the dewpoint of the converted gases.

When plants are operated under pressure it is possible to recover the heat of reaction as mechanical energy by heating the exhaust gases and using them to drive a turbine. Because of the characteristics of heat engines the amount of energy which can be usefully recovered in this way is limited and for the relatively low pressure plants which are now

favoured the major part of the heat available is recovered as steam with a small part recovered as mechanical energy at a very high conversion efficiency.

The oxidation of nitric oxide to nitrogen dioxide is responsible for about 15 per cent of the total heat evolved in converting ammonia to nitric acid. This heat is usually evolved at low temperature and lost to cooling water because of the negative temperature coefficient of the reaction velocity constant. However, when the process is operated under increased pressure it becomes practicable to raise the working temperature to the point where this heat can be usefully recovered. At the present time this would appear to represent the limit to which the energy of reaction can be recovered.

## Platinum Plating of Zirconium

### PROTECTION FROM CORROSION UNDER IRRADIATION CONDITIONS

Studies on the use of zirconium and its alloys for the construction of spherical shells for a homogeneous reactor at Oak Ridge National Laboratory have shown that these materials corrode slowly in uranyl sulphate solutions of pH 1.7 to 2.5 in the temperature range 250 to 350°C under irradiation conditions. It was thought that a platinum cladding would be sufficiently resistant in these conditions and an investigation was therefore carried out at Battelle Memorial Institute. The results of this study are reported by A. B. Tripler, J. G. Beach and C. L. Faust in the U.S. Atomic Energy Report No. BMI-1097.

Mechanical cladding was temporarily ruled out because of the brittle alloy phase which forms at cladding temperatures and electro-deposition was therefore investigated. It was essential that the deposit should be adherent, continuous and impervious, should resist corrosion under irradiation and should not exceed the thermal neutron capture cross section equivalent to 0.25 inch of zirconium.

A diammino-nitrite bath was used, containing 6 g platinum in 750 ml, with

platinum foil anodes. Preliminary plating tests on nickel showed a continuous D.C. method to give an unsatisfactory deposit. A periodic reverse technique was therefore employed. After establishing optimum conditions of current density and time cycle, dense lustrous deposits were obtained up to 0.0015 inch in thickness.

With a satisfactory method of deposition established, plating of zirconium was undertaken. Studies were made of duplex plates of 0.0005 to 0.00075 inch platinum over 0.001 inch nickel, diffusion bonded to the zirconium, and of deposits of 0.0005 inch platinum directly on to zirconium. Both types were found to be adherent and resistant to corrosion, but microscopic examination showed that the platinum on nickel deposit was much smoother than the direct platinum deposit.

On the basis of these results a procedure involving periodic reverse platinum plating over diffusion bonded nickel was used for the preparation of specimens sent to Oak Ridge for in-pile testing. If necessary, the thickness of platinum could be increased.