

Pollution from Nitric Acid Plants

PURIFICATION OF TAIL GAS USING PLATINUM CATALYSTS

By R. A. Searles

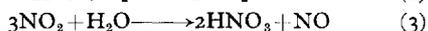
Johnson Matthey Chemicals Limited, London

The tail gas stream from ammonia oxidation plants for the production of nitric acid contains nitrogen oxides, which present a pollution problem. These pollutants can be eliminated successfully by reduction with a fuel gas over Honeycat platinum on ceramic honeycomb catalyst, which has been developed and is produced by Matthey Bishop Inc. and Johnson Matthey Chemicals Limited. Such Honeycat installations in nitric acid plants are becoming numerous and widespread.

The production of nitric acid by the oxidation of ammonia is an important industrial process throughout the world. Nitric acid is used in the manufacture of many products, notably fertilisers, explosives and nylon. While these products may be instrumental in improving the standard of life, nitric acid production can give rise to serious pollution problems. One way in which this problem can be minimised involves platinum metal catalysts, as described in this article.

Production of Nitric Acid

A typical nitric acid plant flow diagram is shown in Fig. 1. The first part of the nitric acid process involves the reaction of ammonia and air under pressure on a rhodium-platinum gauze to give nitric oxide. (Equation 1). After the process gases have been cooled in a series of heat exchangers, boilers and steam super-heaters, they pass into an oxidising absorption tower where with air and water they react to form nitrogen dioxide and subsequently nitric acid. (Equations 2, 3.)



The residual nitric oxide in equation 3 is in practice reoxidised to nitrogen dioxide for further conversion to nitric acid.

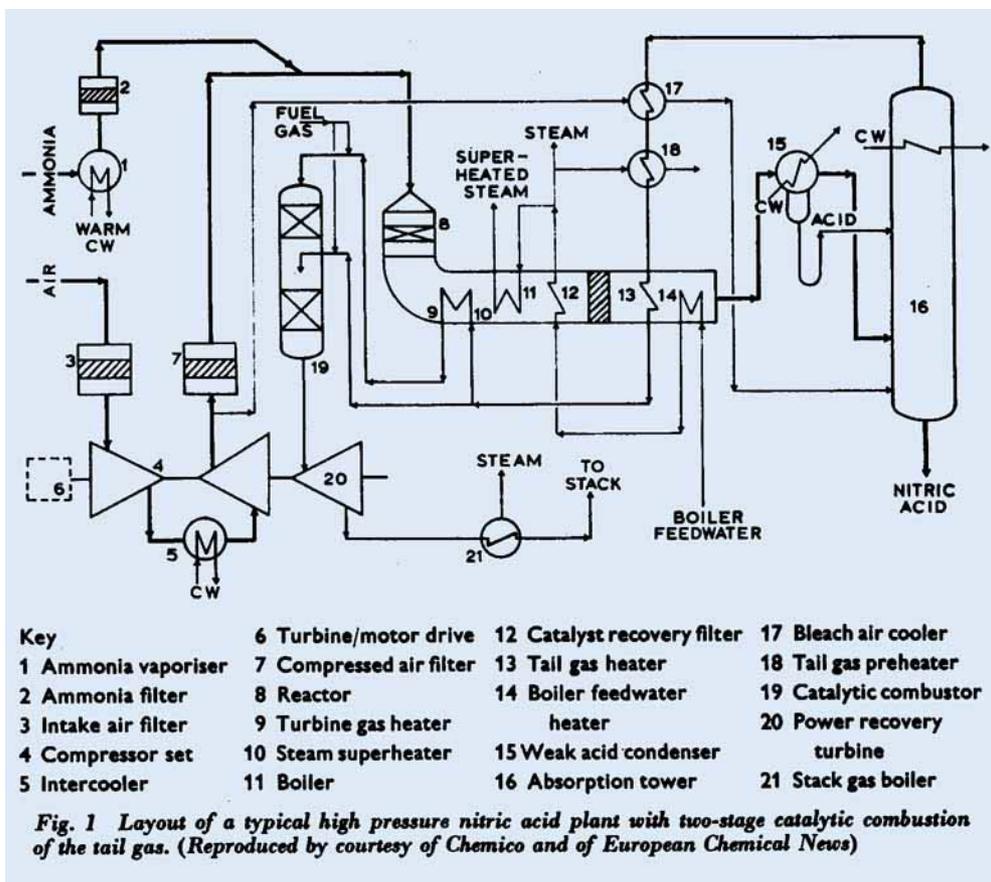
There is an economic limit to the size of the absorption tower that is practicable and the absorption efficiency achieved is generally in the range 98.2 to 99.3 per cent (1). It is the residual concentrations of nitrogen dioxide and nitric oxide (commonly shortened to NO_x) that give rise to the pollution problem.

Pollution by Nitrogen Oxides

Nitrogen dioxide is a red-brown acidic gas with a pungent odour; nitric oxide is colourless and odourless but is oxidised by the oxygen in air to nitrogen dioxide. The toxic effects of nitrogen dioxide are well documented (2). For example, exposure of man to nitrogen dioxide at levels of 300 parts per million (p.p.m.) may cause fatal broncho-pneumonia. Long-term exposure to plants at levels of below 1 p.p.m. can cause leaf damage and decreased fruit yield.

The effluent gas from a typical nitric acid plant of 350 tons/day capacity has a volume of about 20,000 standard cubic feet/minute (34,000 normal cubic metres/hour) with a typical composition in the following range:

NO, NO ₂ (NO _x)	: 0.08–0.30 per cent
Oxygen	: 2–3 per cent
Nitrogen, water	: Balance



Expressed in terms of weight the total NO_x emissions would be over five tons/day (3).

Removal of Nitrogen Oxides

After the gases have left the absorption tower they possess considerable energy, still being at the plant pressure, which may be up to eight atmospheres. This energy is recovered on passing through an expansion turbine; the rotational energy recovered is normally used to drive the plant's compressor.

There are several methods by which the concentration of nitrogen oxides in the tail gas can be reduced to more acceptable levels.

Absorption

By increasing the size of the plant's absorption tower its efficiency may be increased.

This is generally a high capital outlay, particularly for an existing plant, and this outlay is not compensated for by the small increase in nitric acid production that results.

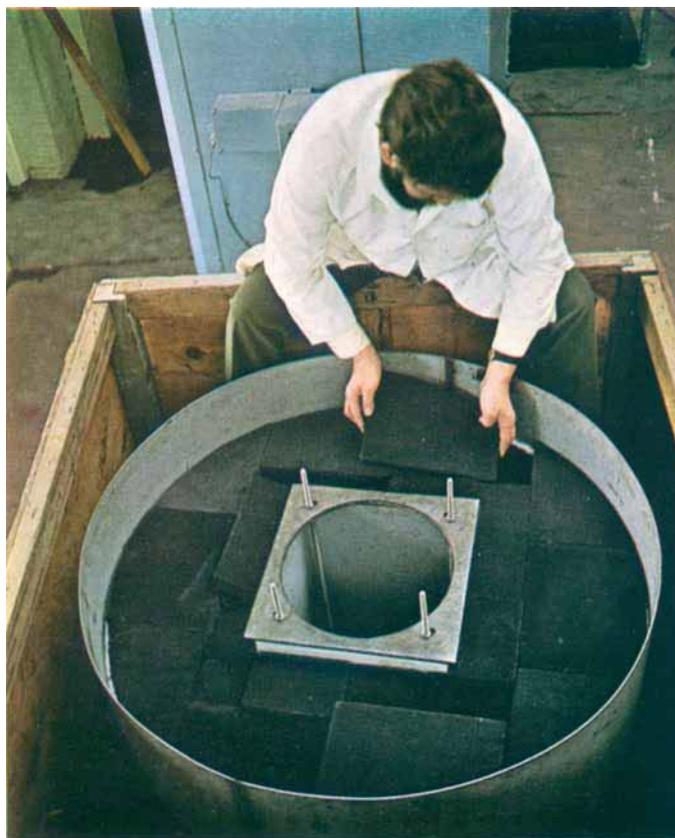
Adsorption

An adsorption system using molecular sieve principles may be installed to recover the nitrogen oxide emissions and to regenerate additional nitric acid. Although impressive claims have been made for these processes, there are to the author's knowledge no commercial plants operating at the present time.

Catalytic Combustion

The catalytic reduction of nitrogen oxides to nitrogen gas takes place on a catalyst such as platinum or palladium on a ceramic honey-

Fig. 2 A cylindrical tail gas reactor unit for a nitric acid plant being loaded with Honeycat platinum on ceramic honeycomb catalyst at the works of Johnson Matthey Chemicals Limited



comb support or alumina pellets or nickel-chromium alloy ribbon. This method involves an increase in the capital cost of the plant but recent estimates (1) show that for a 450 ton/day plant the cost for lowering the NO_x outlet concentration to 300 p.p.m. would be \$200,000 lower for catalytic combustion than for an increased absorption capacity at higher pressure giving the same efficiency.

Catalytic Reactions

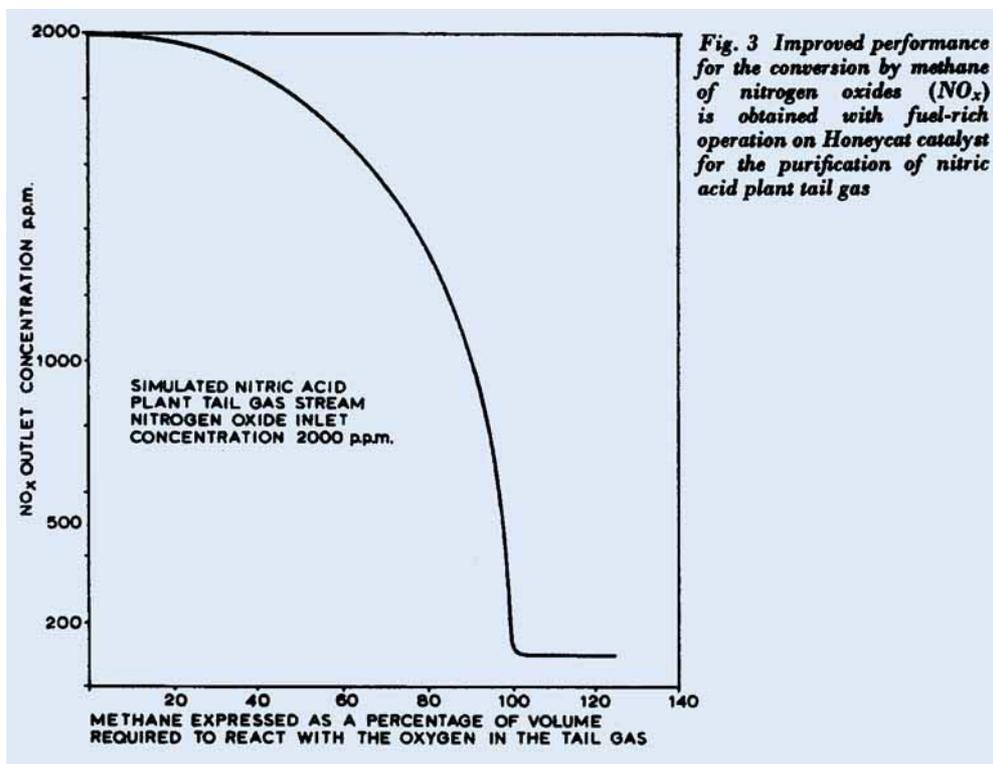
The catalytic method for removing the nitrogen oxides is based on the reaction of NO_x with a fuel to give colourless and harmless nitrogen and water. The reducing fuel chosen is generally determined by availability and price; typical fuels are hydrogen (for example, ammonia synthesis-loop purge gas or refinery off-gas), light naphtha, methane (natural gas), or L.P.G. (butane or propane).

The tail gas from the absorption tower is pre-heated by heat exchange with the hot gases from the rhodium-platinum ammonia-oxidation gauze to a temperature which is dependent on the design of the plant and the fuel used. This is shown in Fig. 1. Minimum inlet temperatures for good conversion efficiency and catalyst life are shown below for commonly used fuels with the Honeycat* catalyst specially developed by the Johnson Matthey Group.

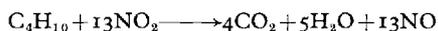
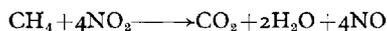
Hydrogen	200°C
Naphtha, L.P.G.	350°C
Natural gas	480°C

The fuel gas is introduced into the gas stream and a homogeneous mixture of tail gas and fuel passed into a reactor containing a bed of catalyst as shown in Fig. 2. Honeycat

*Registered trade mark. Marketed under the name THT in North America by Matthey Bishop Inc.



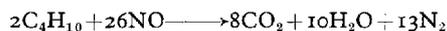
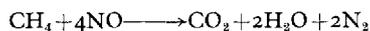
catalyst consists of platinum metals deposited on a ceramic honeycomb. The bed is built up from slabs of the catalyst. The reactions taking place on the catalyst surface can be divided into two groups. The first group of reactions involves the reaction of the fuel with oxygen and nitrogen dioxide, reducing the latter to nitric oxide. These reactions take place first and are sometimes referred to as the *decolorisation* reactions.



In the past, plants have been designed where sufficient fuel is added to raise the temperature of the tail gas and to decolorise the nitrogen oxides. The primary purpose of this operation is to increase the amount of

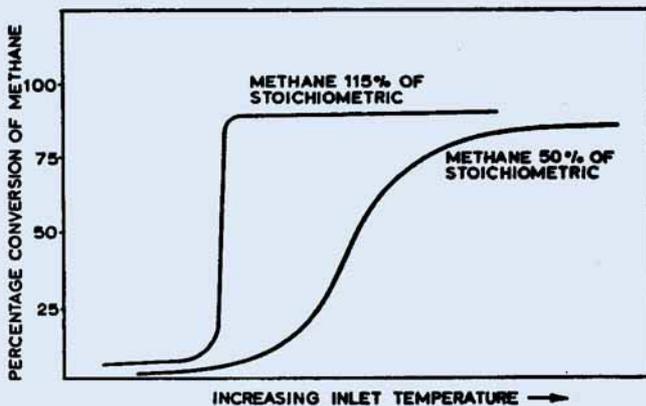
power recovered at the expansion turbine by operation at a higher temperature. Decolorization is a bonus which, while it does not reduce the total acidity of the tail gas, does in fact improve the appearance of the plant and make it a less obvious polluter. However, no new plants are being built with decolorisation and the remainder of this paper will be concerned with total abatement.

The second group of reactions does not commence until reducing conditions have been achieved by all the oxygen in the tail gas being reacted with the fuel. These are sometimes referred to as the *abatement* reactions.



Provided that a sufficient quantity of fuel is provided to react with the oxygen and the nitrogen oxides, the gases leaving the catalyst reactor will contain substantially reduced

Fig. 4 Lower ignition temperature and faster rise to high conversion efficiency are achieved under fuel-rich conditions in the Honeycat unit for the purification of nitric acid plant tail gas



concentrations of nitrogen oxides and oxygen and will consist almost entirely of nitrogen gas and water vapour. Total abatement generally means NO_x removal down to below 200 p.p.m. The advantages of operating a fuel-rich system are lower light-off temperature and higher conversion efficiency when compared to operation under decolorising or oxidising conditions. (Figs. 3 and 4).

The reaction of the fuel gas with the oxygen in the tail gas is, of course, an exothermic reaction and the gas leaves the catalyst at an elevated temperature. This temperature rise is proportional to the oxygen content of the tail gas but varies according to the pressure and temperature of the reaction. As a general rule, however, the following temperature rises can be used for each one per cent of oxygen that is burnt with the named fuel.

- Hydrogen : 160°C
- Methane, naphtha, butane, propane : 130°C

This temperature rise puts a limitation on to the amount of oxygen that can be removed on a single stage. The maximum oxygen content can be calculated by subtracting the inlet temperature required with the chosen fuel from the maximum permissible operating temperature of 750°C and dividing by the temperature rise obtained if one per cent of oxygen were burnt with that fuel. For example, with hydrogen fuel and an inlet temperature of 200°C the maximum

temperature rise allowable is 550°C and the maximum oxygen concentration is 3.4 per cent.

Form of Catalyst

The composition and form of the catalyst used for the above reactions has an important bearing on the flexibility of the operation, the degree of abatement achieved, the efficiency of fuel combustion, and the catalyst life.

The advantages of using ceramic honeycomb supports for platinum metal catalysts for various gas phase reactions, such as odour and NO_x removal, and the treatment of diesel and petrol engine exhausts, have been covered in previous articles in this journal (4-9) and may be summarised as compact process design, high activity, low pressure drop and good catalyst life. These advantages have led to honeycomb-based systems becoming widely accepted, in preference to pelleted or metal ribbon supported systems for the application under discussion.

The activity of the catalyst is particularly important when methane is used as the reducing fuel because the methane molecule has high stability and is difficult to oxidise. The Honeycat range of catalysts is based on platinum because platinum has high stability coupled with good activity and because under reducing conditions it does not allow carbon formation, which may occur with palladium-based systems. For methane

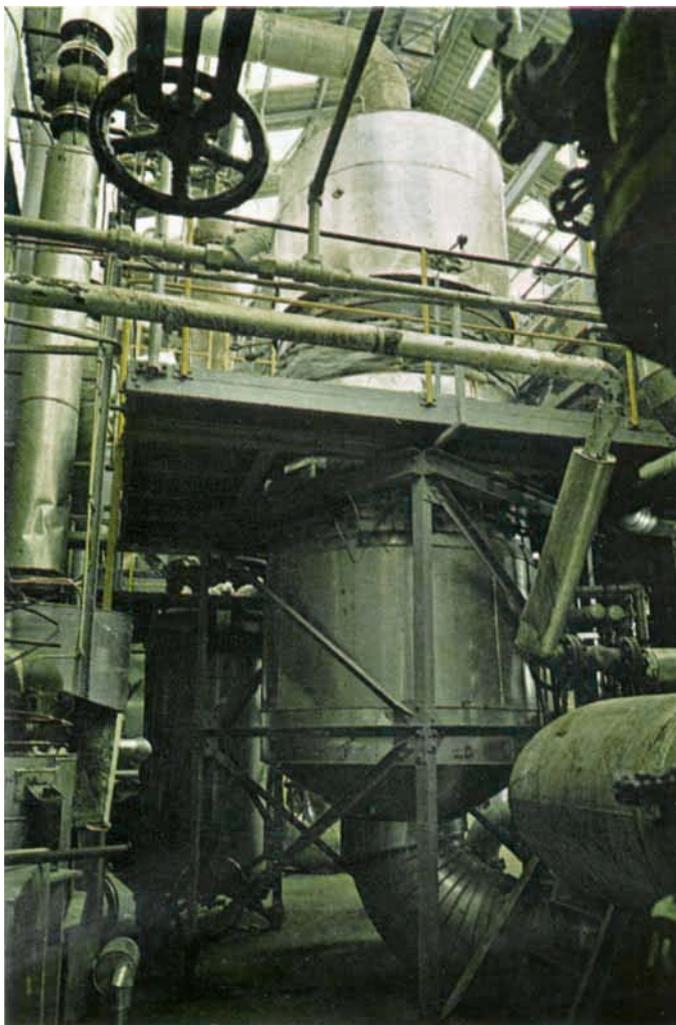


Fig. 5 The nitric acid plant of BASF-Antwerpen in Belgium includes the reactor vessel seen in the centre of this picture. It contains Honeycat catalyst for the reduction of the plant tail gas

combustion an improved version of the Honeycat catalyst has been developed to give higher activity for methane oxidation while retaining the resistance to carbon formation.

Operational Plants

A description of the method of operation of a NO_x abatement system at the plant of BASF-Antwerpen in Belgium will serve to illustrate the principles involved and the advantages to be gained by catalytic abatement. The schematic flow diagram of this 540 ton/day Chemico plant is shown in Fig. 1. In this plant a Chemico Dual Combustion

system is used so that the outlet temperature from the Honeycat catalyst is kept

low enough to enable hot tail gas to pass directly into the expansion turbine for greater power recovery. Figure 5 shows the reactor.

A part of the tail gas is heated to the required inlet temperature of 480°C , mixed with the methane fuel and passed into the first catalyst stage. Reaction takes place on the catalyst and the hot gases leaving the catalyst are then mixed with the other part of the tail gas, which is at a much lower temperature. This quenches the hot tail gas and returns the second stage inlet temperature to the same level as that required by the first stage. By this means the average inlet temperature required is lower than the minimum inlet

Fig. 6 The stack at BASF-Antwerpen shows the effectiveness of the Honeycat system. Without catalytic reduction red-brown emissions would be visible



temperature and a higher percentage of oxygen can be treated without exceeding the maximum operating temperature of the catalyst.

During the first thirteen months operation of the Honeycat catalyst at BASF the average NO_x outlet concentration has been 100 p.p.m. and the maximum has not exceeded 200 p.p.m. During this first year the fuel consumption has not increased and the stack has been colourless (Fig. 6).

Honeycat catalysts have now been installed in nitric acid plants operating in the USA, Canada, Australia and Belgium; some 20 plants are currently operating on purge gas and methane fuels with catalyst lives of up to five years. Further European installations will be made shortly.

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