Platinum Catalysts for the Control of Air Pollution

A TAIL GAS REDUCTION SYSTEM FOR NITRIC ACID PLANTS

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The problems of air pollution are increasingly the subject of public attention. Pressures, and ultimately legislation by governments, will undoubtedly result in a rapid increase in demand for effective low-cost catalytic pollution control systems. Although some catalytic systems have existed for several years, more severe restrictions on permissible atmospheric pollutants in the future will require new equipment and techniques to meet them.

Until recently most air pollution problems were solved by direct flame combustion methods in specially designed reaction chambers. Although catalytic oxidation has long been well recognised as an effective technique, the high pressure drop through dense beds of granular or pelleted catalysts has limited the development of commercially acceptable systems.

This situation has recently changed as a result of the introduction of a new group of ceramic catalyst supports in the form of a honeycomb-like structure. One major advantage of this open type of substrate is its exceptionally low pressure drop. This is an important operating advantage, resulting in lower power and/or compression costs.

Fig. 1 shows a comparison of pressure drop through a commercially available $\frac{1}{8}$ inch cell size honeycomb material known as Torvex, produced by du Pont, with the drop through a bed of standard $\frac{1}{8}$ inch pellets. For a gas flow of 10 s.c.f.m. per square inch of reactor bed, the honeycomb shows a pressure drop of only one inch of water per inch of bed

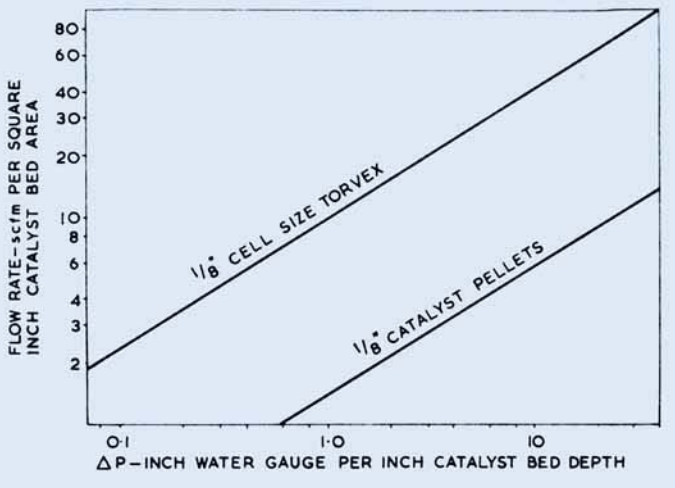
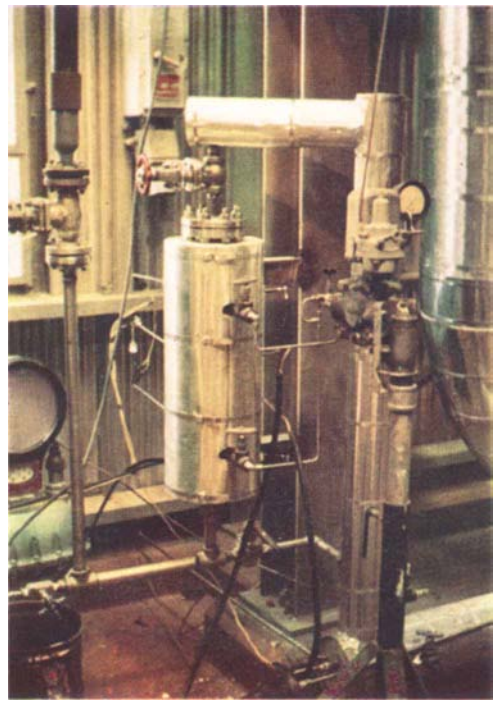


Fig. 1 Comparison of pressure drops across pelleted and Torvex catalyst beds; gas flows at atmospheric pressure

(Torvex is a du Pont registered trade mark for their ceramic honeycomb)

Fig. 2 The pilot plant reactor in which the Matthey Bishop tail gas reduction catalyst was developed



depth, compared with 24 inches of water through the pellet bed.

Other important advantages for honeycomb catalysts include more uniform gas distribution, greater structural strength, no attrition or loss of fines, and no channelling or hot spots. When platinum is used as the catalytic metal, a honeycomb catalyst structure is particularly attractive since there is no loss in effective area such as is found in pellet beds. From the standpoint of system design, the rigid structure also provides greater process flexibility. Horizontal as well as vertical reactors may thus be used.

The development of this unique honeycomb material indeed represents a significant breakthrough in the field of industrial catalysis.

Platinum Honeycomb Catalysts

Matthey Bishop has recently developed a series of metallised ceramic honeycomb catalysts for use in a wide variety of atmospheric pollution control systems and other chemical process applications. Because of its unrivalled resistance to oxidation at high temperatures and to corrosive chemical attack, as well as its unique catalytic properties, platinum is the preferred catalytic metal. Palladium has also been used for certain air pollution applications but, although it is catalytically highly active, it oxidises too readily at high temperatures and is susceptible to poisoning by sulphur.

The Matthey Bishop THT catalysts differ from other commercially available platinum catalysts in two important respects; a highly active platinum is tightly anchored to the ceramic base by a new proprietary technique, while the introduction of a different concept in catalyst packaging not only protects the ceramic structure against breakage but also allows for catalyst interchangeability. Depending on the system requirements two, three or more units may be packaged together to form a bed having any desired pressure drop for a particular catalytic performance that may be needed.

Elimination of Nitrogen Oxide Fumes

In the synthesis of nitric acid a mixture of ammonia and air at high temperature is passed over a platinum gauze catalyst to form nitric oxide (NO). This is followed by oxidation to the dioxide (NO_2) and subsequent absorption of the latter in water to produce aqueous nitric acid. Nitrogen together with small amounts of oxygen and unabsorbed nitric oxides are discharged into the atmosphere as a tail gas. This discharge represents a major source of air pollution. In a typical tail gas, nitrogen oxide concentrations may range from 0.1 to 0.6 per cent by volume. Oxides of nitrogen are also discharged into the atmosphere from some

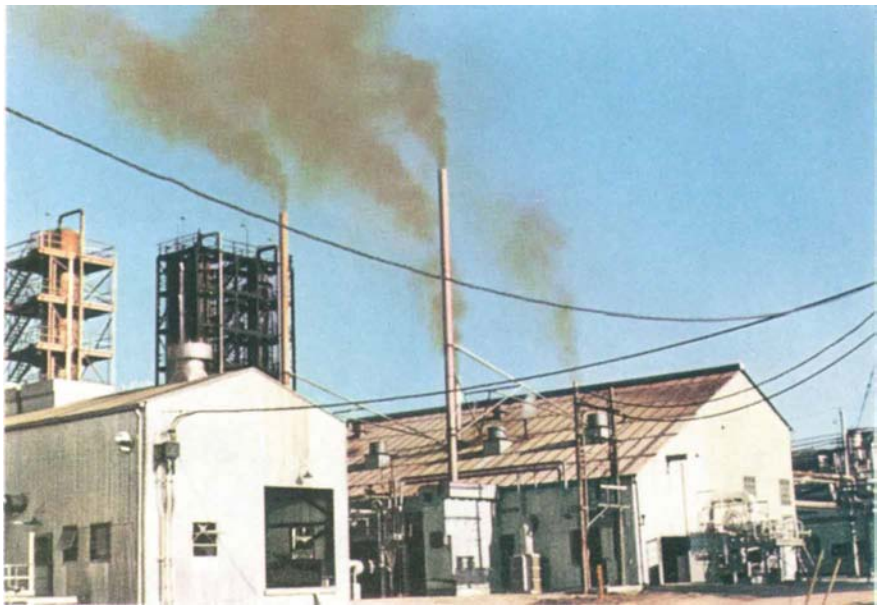


Fig. 3 Four tail gas stacks emitting nitrogen oxide fumes at the Cooperative Farm Chemical Association nitric acid plant at Lawrence, Kansas

chemical operations, from acid concentrators, and from acid storage systems.

Nitric oxide (NO) is a colourless gas, while nitrogen dioxide (NO_2) is intensely reddish brown. Decolourisation of a tail gas occurs when NO_2 is catalytically reduced on a platinum/honeycomb catalyst to NO in the presence of an added fuel (reducing agent) such as hydrogen or methane.

$$NO_2 + H_2 \xrightarrow{\text{Pt-cat.}} NO + H_2O$$

$$4NO_2 + CH_4 \xrightarrow{\text{Pt-cat.}} 4NO + CO_2 + 2H_2O$$

Fume abatement requires conversion of all nitrogen oxides to nitrogen and is achieved when additional fuel is used and the nitrogen oxide concentration is lowered to below 100 p.p.m.

$$2NO_2 + 4H_2 \xrightarrow{\text{Pt-cat.}} N_2 + 4H_2O$$

$$2NO_2 + CH_4 \xrightarrow{\text{Pt-cat.}} N_2 + CO_2 + 2H_2O$$

Although various systems have been devised for controlling nitrogen oxide air pollution, the recently improved technique of catalytic combustion using platinum catalysts on ceramic honeycomb is becoming increasingly popular. Plants equipped with catalytic fume eliminators operate with no visible "plume". In addition, the heat energy generated by the oxidation of the added fuel (hydrogen, carbon monoxide, natural gas or other hydrocarbons) is profitably extracted by high temperature gas turbines or expanders mechanically connected to the air compressor of the ammonia oxidation system. Heat exchangers and waste heat boilers are also used in combination with the expander to augment further the recovery of energy liberated in the catalytic reactors.

In systems where the reactor is placed in front of the expander, the vessel must be designed for operating pressures in the range of 100 p.s.i.g. and for temperatures up to 760°C (1400°F). Catalyst volume is generally based conservatively on an hourly space velocity of 100,000.

When natural gas is used as a fuel, the temperature rise (ΔT) across a catalytic bed is approximately 130°C (234°F) for every one per cent oxygen consumed. Using the new highly active Matthey Bishop catalyst,

the reduction of nitrogen oxides begins at 370° to 385°C (700° to 725°F) compared with 425° to 480°C (800° to 900°F) for other, older, systems. When hydrogen is employed as the reducing gas the reaction starts at 150°C (300°F) and the temperature rise is somewhat greater, $\Delta T = 150°C$ (270°F). Conservative system design assumes an initial reaction temperature of 454°C (850°F). Since a reactor temperature above 760°C (1400°F) is undesirable, the maximum ΔT across the bed is limited to 300°C (550°F). A system operating on natural gas could therefore burn a maximum of

$$\frac{550}{234} \text{ or } 2.4\% \text{ oxygen per reactor}$$

For higher oxygen contents, two-stage reactors have been used.

For tail gas decolourisation it is generally not necessary to reduce the free oxygen content in the system completely. For total elimination of pollution, however, the amount of fuel used must be in excess of the stoichiometric requirement.

Nitrogen oxide reduction catalysts for the Matthey Bishop system were developed in the pilot unit shown in Fig. 2. Both natural gas and purge gas (approximately 55 per cent H_2) were used as fuels with equal success. Examination of the catalyst after six months of operation showed no sign of deterioration.

The Matthey Bishop Apparatus and Systems Division have already installed the new catalytic tail gas reduction unit in several nitric acid plants having a combined capacity exceeding 1200 tons of acid per day.

The effectiveness of the installation is well illustrated in the photographs. Fig. 3 shows four stacks at the Lawrence, Kansas, plant of Cooperative Farm Chemical Association, each stack handling tail gas from one 120 tons per day nitric acid unit. In Fig. 4, the centre stack has had a Matthey Bishop THT catalyst unit installed and is free from fume. Since this photograph was taken

Fig. 4 After a Matthey Bishop THT catalyst system had been installed at the base of the centre stack this is free from fume. The other three stacks still emitting fume have since been equipped with similar units and are now all completely clear

all four stacks have been equipped with catalyst units and are all completely clear.

Hydrocarbon and Organic Vapour Abatement

Unburned hydrocarbons and carbon monoxide, as well as a wide variety of organic solvents, present even broader air contamination problems than do the nitric acid tail gases. These include the effluents from engines, industrial paint baking ovens, printing presses, wire enamelling, solvent cleaning operations, solvent storage tanks, and from chemical reactions such as the manufacture of ethylene and ethylene oxide.

Miller and Wilhoyte (1) have recently compared the relative effectiveness of platinised spherical pellets, metal foils and ceramic honeycomb. The data reported cover hourly space velocities from 30,000 to 175,000 and temperatures from 150° to 450°C. Toluene and *n*-heptane were used as an experimental pollutants in concentrations up to 10 per cent of that corresponding to the lower explosive limit. This work clearly demonstrates the high catalytic efficiency and low resistance to gas flow of the honeycomb catalysts.

Matthey Bishop THT catalysts were evaluated and have been found to be effective for completely oxidising these organic contaminants. Other solvents such as xylene, methyl ethyl ketone and alcohols are also easily oxidised.

The chemical industry provides a large and diverse market for catalytic atmospheric pollution control systems. The production of floor tiles, asphalt, rubber, petrochemicals, wax, varnish, insecticides, comprise only a few of the industries where odour and smoke abatement problems may be effectively and economically controlled by the use of platinum honeycomb catalysts.

Hydrogen-Oxygen Recombination

In nuclear power installations, intense radiation causes the decomposition of water and the gradual rise in concentration of a hydrogen/oxygen mixture in a closed loop system. Safety considerations require that this should be prevented by continuously passing the gas through a hydrogen-oxygen recombiner. Platinum honeycomb catalyst has been found to be very effective for this conversion. Pellet beds have been used in the past for this purpose but their high pressure drop and the formation of fine dust in the presence of steam make them unattractive by comparison with the new platinum honeycomb catalyst.

Reference

1 A Study of Catalyst Support Systems for Fume Abatement of Hydrocarbon Solvents, M. R. Miller and A. J. Wilhoyte, E. I. du Pont de Nemours & Company Inc., Industrial and Biochemical Department, Wilmington, Delaware

Self-heating in Platinum Resistance Thermometry

Routine measurements of temperatures between −200 and +850°C are carried out with high accuracy using platinum resistance thermometers. However, the measuring current itself causes heating in the platinum element by an amount proportional to the square of the current. Measurements requiring extreme accuracy or those where the measuring current is larger than the usual few milliamperes thus require correction for the self-heating effect.

Dr W. Diehl, of Degussa, Hanau, has now shown (*ETZ-B*, 1967, **19**, (22), 637–640) that the self-heating coefficient can be calculated by applying results of his tests on sealed platinum resistance elements. These tests measured the self-heating effect of such elements in still air, still water and running water. Using a test current of 3 milliamperes, results then were correct to within 0.008 to 0.024°C in still water and to within 0.06 to 0.11°C in still air at 20°C. Self-heating due to other currents can be calculated from the self-heating coefficients in the tables which Dr Diehl has produced.

None the less, for the greatest accuracy, it is recommended that the platinum element should have the lowest possible resistance and that its self-heating coefficient should be determined under conditions similar to those which it will meet in practice.

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