High Pressure Ammonia Oxidation

AN EXPERIMENTAL PLANT FOR EVALUATING PLATINUM CATALYST SYSTEMS FOR THE NITRIC ACID INDUSTRY

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The principles of the design and operation of a new variable high pressure, large diameter experimental ammonia oxidation test facility built by Johnson Matthey Metals Limited are described. The layout and arrangement of the plant are illustrated in some detail and examples of its use with platinum catalysts are given. The design of the plant is such that the operating conditions of any current, or likely future, commercial undertaking can be reproduced.

The nitrogen cycle established by the natural world which enables plants to grow is extensively supplemented nowadays by man-made fertilisers. The tangible benefits of additional fertilisers are high crop yields and the delay of Thos. Malthus's gloomy prediction of a world with a population too big to feed. Since early times attempts to rejuvenate the soil's supply of essential minerals have been made, but it was not until the end of the nineteenth century, at the peak of the great European Chemical Industry era, that bulk production of manufactured nitrates was established. In 1908 Ostwald and Brauer first operated the platinum catalysed ammonia oxidation process on a commercial scale in Germany, the method which eventually rendered other inorganic methods of nitrate production obsolete. Their work has been reported in this journal previously (1). Development of the process was spurred on during the following few years due to the wartime blockade of the Chilean nitrate route which interrupted the supply of nitrates for explosives and fertilisers. Since that time the industry has grown to become one of the largest tonnage output processes in the world, estimated to be approximately 60×10^6 tonnes of nitrogen per year (2).

At the heart of the modern process is a chemical reactor, containing a platinum based catalyst and associated catchment gauzes, which allows the ammonia oxidation process to take place readily at an efficient and economic rate. About 70 per cent of the nitric acid produced is used in the manufacture of nitrate fertilisers; the remainder being utilised in the production of nitrogen containing products, such as explosives, plastics and dyestuffs. The reaction is considered by chemists to be a three-stage process involving initially the "burning of ammonia gas with air" over the platinum based catalyst to form nitric oxide, followed by the oxidation and the absorption of this gas in water to form nitric acid. The oxidation reaction with air is complex but can be summarised in the equation:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O + 906.7 \text{ kJ}$$

This gaseous reaction, which gives acceptable yields at temperatures between 750 and 950°C, has been found to be sensitive to a number of variables. Other than temperature and pressure, product yield is influenced by the nature and distribution of the catalyst material and the cleanliness and throughput rate of the reacting gases.

To aid the study of such phenomena an experimental plant representative of today's high pressure, high output manufacturing process has been constructed at Wembley. This plant is superior to installations reported on previously (3) because of its larger catalyst reactor size and its higher operational pressure range. A view of

Fig. 1 The exterior portions of the experimental plant, showing in the bottom left hand corner the bunded ammonia cylinder, with exterior control gear and nitrogen gas store to the centre and right, respectively. The shelter behind the blue cooling tower houses the air compressor, and the large tank in the centre receives acid from the absorption towers. The left hand and central towers extending above the adjacent laboratory handle the acid absorption stages, the third being the tail gas scrubber

the external features of the new plant is shown above in Figure 1, and a diagrammatic layout of the major components is given in Figure 2.

Plant Design

The design is modelled on conventional nitric acid manufacturing plant, with the exception of the reactor section which is specifically made to be adaptable to suit experimental variation, including simulation of different commercial operations.

The operational pressure range is between 1 and 12 bar (15 to 180 psig), with gas preheat capability of between ambient and 375°C. Various catalyst diameters up to 100 mm (4 in) are allowed for with an ability for a "deep bed" arrangement up to 150 mm (6 in) to be accommodated. Gas flow is upwards with gauze ammonia loadings of up to 200 TPD (tonnes per day per m² catalyst projected area) in the

high pressure range, and continuous runs of at least seven days can be made. Longer runs are possible if allowance is made to refill from bulk ammonia storage located on site. The preheater and reactor sections, shown in Figure 3, are housed separately in a ventilated room adjacent to a laboratory area where the system control panel is located; a part can be seen in Figure 4. Controllers, readouts and sample ports sited on the panel allow catalyst activity measurements to be made comfortably and safely in the laboratory. Detailed descriptions of the various parts of the plant are as follows.

Ammonia and Air Supply

Ammonia for the plant is stored in a thick rolled steel shell ammonia cylinder which has a capacity of 1400 kg, sufficient to run the plant continuously for a week at maximum throughput. In order to run the plant at pressures
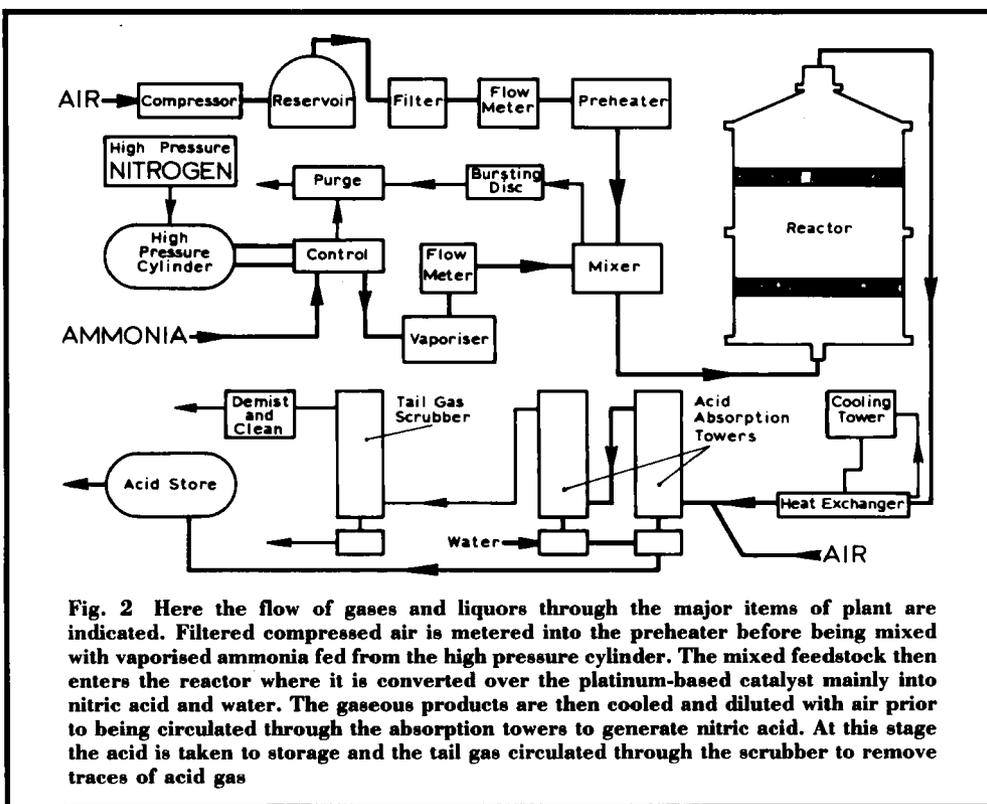
Fig. 2 Here the flow of gases and liquors through the major items of plant are indicated. Filtered compressed air is metered into the preheater before being mixed with vaporised ammonia fed from the high pressure cylinder. The mixed feedstock then enters the reactor where it is converted over the platinum-based catalyst mainly into nitric acid and water. The gaseous products are then cooled and diluted with air prior to being circulated through the absorption towers to generate nitric acid. At this stage the acid is taken to storage and the tail gas circulated through the scrubber to remove traces of acid gas

greater than the vapour pressure of ammonia and to eliminate fluctuations in flow caused by changes in ambient temperature, the cylinder is pressurised with nitrogen to an operating pressure of about 15 bar (225 psig). During use the cylinder pressure is maintained automatically by means of a pressure controlled solenoid valve on the nitrogen supply line. The cylinder is charged with ammonia from a 20 tonne bulk ammonia storage facility located on site.

For health and safety reasons the ammonia cylinder is located within a high retaining wall, with all apparatus controlled from a panel positioned outside.

The content of the cylinder is measured using a load cell situated underneath. The display for this is located on the control panel along with gauges showing supply line pressure, cylinder pressure and nitrogen pressure. The load cell is also connected to alarms in the control room to warn when filling is required and to signal completion of the filling operation. The ammonia supply is transferred to the reactor site in liquid form, where it is vaporised by means of a standard ammonia boiler.

Air for the plant is taken from the atmosphere and compressed using a two-stage, water cooled, high pressure compressor. This supplies air at 40 bar (600 psig) to a large air reservoir, to which is fitted a pressure switch in order to maintain a pressure of 30 to 33 bar (450 to 500 psig).

The air is then passed through a filter to remove any foreign material before being reduced to the operating pressure by means of a two-stage pressure reduction device. The high initial pressure and the two-stage reduction are employed so that changes in flow due to pressure variation during air compressor cycling are minimised. The ammonia supply, maintained at a temperature of about $150^{\circ}C$ after the vaporiser, is also passed through a

Fig. 3 The insulated gas preheater, mixer and reactor sections are housed inside, adjacent to the analytical laboratory. Meters and check valves are located under the insulated sections while the controllers and sample ports are mounted at the rear of the blue coloured control panel alongside the analysis area

filter and a pressure regulator to reduce its pressure to the desired operating pressure.

Flow Control System

The flowrates and the ratio of the two reactants to the reaction chamber are measured and controlled by means of thermal mass-flow meters located on each line and linked to controllers and flow control valves.

The signal from the air flow meter provides the input to the primary control. The flow-ratio controller provides the set-point signal and receives a process variable signal from the ammonia mass-flow meter. The output is fed to a flow control valve on the ammonia feed line downstream of the flow meter, so that the selected flow-ratio is automatically achieved. The result of this is a dynamic equilibrium of the ammonia and air flows which can thus operate within close limits. This feature is particularly important when the plant is being used experimentally and operating close to the explosion limit of ammonia-air mixtures. Provision exists within the system for manual flow con-trol, and in practice the plant is normally started up in this mode.

This improved flow control system enables a wide range of reactant flowrates to be established quickly and reproducibly and, most
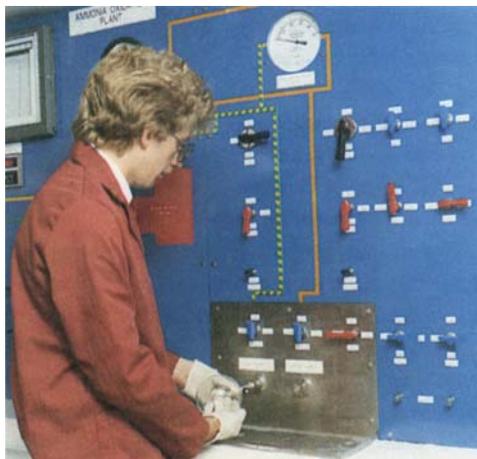

Fig. 4 Here a gaseous sample is being withdrawn from one of the valved outlets sited on the main control panel. The whole experimental operation is monitored from this laboratory

Simulation of Commercial Nitric Acid Plants		
	Medium/high pressure plant	Medium pressure plant
Pressure, atmospheres	7.2	5.2
Preheat temperature, °C	230	150
Ammonia, vol per cent	10.8	10.5
Ammonia loading, tonnes/ m²/day	36	16
Number of gauzes	10	10
Gauze outlet temperature, °C	940	890
Average conversion efficiency, per cent	92–94	93–95
Conversion efficiency obtained on pilot plant, per cent	92.2	93.5

importantly, offers the facility to maintain them within close limits over extended campaigns.

Reactor Assembly

The air is preheated by passing it through two electrically heated sections arranged sequentially, each containing two coiled heating elements. The ammonia is introduced into the air stream after this point by means of a specialised flange designed to create a homogeneous ammonia-air gas mix. Adjacent to this point is a section containing a bursting-disc holder fitted with a 1in reverse type, PTFE coated, nickel disc. The gas stream then passes upwards into the reactor section, illustrated in Figure 3, which has been designed so that the catalyst may be changed between campaigns without difficulty. Catalyst holders able to accommodate gauzes of between 25 mm (1 in) and 100 mm (4 in) diameter and cartridge type catalyst elements up to 150 mm (6 in) deep can be used within the reactor.

Thermocouples to monitor the process line temperature, together with pressure switches are located at various points along the reactor and feed lines. These are connected to various recording devices and to alarm sensors which cause the plant to shut itself down in the event of a potentially hazardous situation arising. Thermocouples are also present on either side of the catalyst bed, as are sampling ports so that analysis of the reactant and product gases can

be carried out. These sampling lines are also connected to a differential pressure transducer so enabling the pressure drop across the catalyst bed to be accurately determined.

The pressure drop across the catalyst and the catchment gauzes is an important factor to be considered both from a chemical and an economic viewpoint. In the former case the residence time and reaction path of various reactant and product species is affected, and in the latter case the energy balance is changed. During a production campaign there is a natural increase in pressure drop due to both a metallurgical material restructuring effect and the physical clogging of the gauzes which results from material migration by a catalytic vaporisation-deposition reaction.

Energy balance becomes most important in high pressure plants where the efficiency of heat recovery may be lowered to the detriment of the economics of the whole plant. Figure 4 shows part of the main control panel which contains the pressure drop display and also the sampling section.

Cooling and Absorption Systems

The gases leaving the reactor, at temperatures as high as 960°C, are passed through a specially designed tubular heat exchanger. This consists of an Inconel 825 tube within a stainless steel outer tube fitted with bellows, enabling it to increase in length to take up the

expansion of the Inconel tube. Recirculating water continuously passes through this heat exchanger enabling the product gas to be cooled to below 200°C, after which it is passed through the main flow control and pressure letdown valve. The gas, at about 100°C and just above atmospheric pressure, enters the low pressure oxidation and absorption stages.

Air is added to cool the gas further and promote the oxidation of nitric oxide to nitrogen dioxide. Afterwards the gas enters the first of three, 300 mm (12 in) diameter absorption towers each containing three 1500 mm (5 ft) beds of standard tower packings. Two towers are constructed from 316L stainless steel and handle the acid gas absorption stages. The gas in the first tower is scrubbed by dilute nitric acid produced in the second; giving approximately 30 weight per cent nitric acid which is pumped to a 3500 gallon stainless steel storage vessel before being transferred for use within Johnson Matthey. Water is added to the second tower to maintain the liquid level in the scrubbing system, so producing acid of approximately 10 weight per cent.

The third tower is of similar design to the first two but is constructed from polypropylene. Sodium hydroxide solution is pumped through this tower on a closed circuit system to neutralise any nitrogen oxides remaining in the gas stream before emission to the atmosphere. A demister trap is fitted to the outlet to prevent any sodium hydroxide solution being carried out with the exhaust gas.

Although the absorption processes in the towers are exothermic and favoured by low temperatures, it has only been found necessary to fit a heat exchanger to the recirculatory liquor passing around the first tower. This heat exchanger is water cooled and is fed from a self-contained recirculatory system through an air cooling tower, which also provides water for cooling the water of the plant cooling circuit.

Work Carried Out in the Plant

An example of the capabilities of the ammonia oxidation plant was demonstrated by a simulation of two commercial type operations which use rhodium-platinum alloy gauze. The development of platinum group metal catalyst and catchment systems has been the subject of earlier articles in this journal (4–6). The plants modelled here were a medium pressure and a medium-high pressure installation, each having ten catalyst gauzes woven from 0.076 mm diameter 10 per cent rhodium-platinum wire for a normal campaign. The trials on the test rig were run under the operating conditions of the commercial plants, except that a higher preheat temperature was used to compensate for the greater heat losses experienced on smaller diameter test rigs. These running conditions, together with the results obtained from the investigation, are shown in the Table.

The conversion efficiencies of ammonia to nitric oxide, measured on the pilot plant over 24 to 72 hour campaigns, were obtained by the Gailliard method (7). Within the limits of experimental error, they show close agreement with those normally found on commercial plants.

Other work has included an investigation of the mechanism of reconstruction of catalyst gauzes, reported in this journal recently (8).

A Tool for the Nitric Acid Industry

These examples highlight an important use of the ammonia oxidation test rig. It has also been extensively employed on new catalyst and catchment development as well as for product optimisation. It has become a valuable tool in the development of platinum metal based catalyst and catchment systems for the nitric acid industry.

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