

The Ammonia Oxidation Process for Nitric Acid Manufacture

EARLY DEVELOPMENTS WITH PLATINUM CATALYSTS

By L. B. Hunt, M.Sc., Ph.D.

It is little more than fifty years since the first manufacture of nitric acid by the oxidation of ammonia over a platinum catalyst. Ostwald's original industrial plant had an output of some 100 tons of acid a year; today the world capacity for nitric acid manufacture by this process is about ten million tons a year. This article traces the beginnings and early developments of the process until it became commercially established.

During the latter years of the nineteenth century discussion began to arise among men of science who were interested in the broader issues of their subject on what later became known as "The Nitrogen Problem". Typical of the expositions which now and then reached even the public press was the Presidential Address given by Sir William Crookes to the British Association for the Advancement of Science at its Bristol meeting in September 1898. Crookes was concerned to show that at the prevailing rate of increase of population the world's supplies of wheat would soon prove insufficient, and that the land would not continue to produce the same yield year after year unless adequate quantities of nitrogenous manure were ploughed back. He appealed to the chemist to help remove the fear of famine by establishing a means of fixing atmospheric nitrogen, since the only available source—Chile saltpetre—might be exhausted in a comparatively short period of years.

The Fixation of Nitrogen

This problem, of obtaining from the unlimited supplies of uncombined nitrogen in the atmosphere those compounds—principally ammonia and nitric acid—required for agricultural needs, was soon intensified by



Wilhelm Ostwald

Professor of Chemistry at the University of Leipzig and recipient of the Nobel Prize in Chemistry. Ostwald's response to the needs of his country for an independent source of nitric acid played the major part in the development of this industry

the realisation in a number of European countries that a precisely similar need for assured supplies of nitric acid existed in the manufacture of explosives, and that in the event of war the Chile nitrates might well prove to be inaccessible to one side or the other.



Frédéric Kuhlmann

Many years before Ostwald's time, Kuhlmann had demonstrated the possibility of obtaining nitric acid by the oxidation of ammonia over a platinum catalyst

This is not to say that such thoughts inspired governmental action in any part of Europe; they were, in fact, confined to but a handful of scientists who could foresee their countries' long-term needs. One such man was Professor Pfeffer, the famous botanist, who in 1901 expressed his concern about the need for supplies of fixed nitrogen to his colleague in the University of Leipzig, Professor Wilhelm Ostwald. At this time Ostwald had occupied the Chair of Chemistry at Leipzig for some fourteen years and had built up a school of physical chemistry, devoting much of his energy to investigating the effects of catalysts on chemical reactions. His response to Pfeffer's representations was immediate; it was obviously his duty as a chemist to play his part in making his country independent of Chile saltpetre, and in obtaining nitric acid from other sources.

Two possible lines of investigation presented themselves. Either free nitrogen and oxygen from the air could be combined, or ammonia, then readily available from the

gas industry, could be oxidised to give nitric acid. As it seemed more simple to re-combine nitrogen which was already fixed than to fix free nitrogen, Ostwald decided to give his attention to the oxidation of ammonia.

This reaction was not unknown, and in fact had been proved possible on a laboratory scale. As long ago as 1789 the Rev. Isaac Milner, F.R.S., President of Queens' College and first Jacksonian Professor of Natural Philosophy in the University of Cambridge, had presented a paper to the Royal Society entitled "On the Production of Nitrous Acid and Nitrous Air". In this Milner described a series of experiments in which he had passed "volatile alkali" (ammonia) over "calx of manganese" contained in a gun-barrel heated to redness. The product was found to be "highly nitrous", and the presence of "nitrous air" was confirmed by the appearance of red fumes on mixing with the atmosphere or with "dephlogisticated air". Milner continued:

"I have since frequently repeated this experiment, and have always in some degree succeeded. Much depends on the kind of manganese employed, much on the heat of the furnace, and much on the patience of the operator; as these are varied, there will be great variations of the products. . . . In general, I made use of clean gun-barrels with which no previous experiments had been made. The manganese was used in rough powder; for when it is too finely powdered, the tube is choked and the air cannot pass."

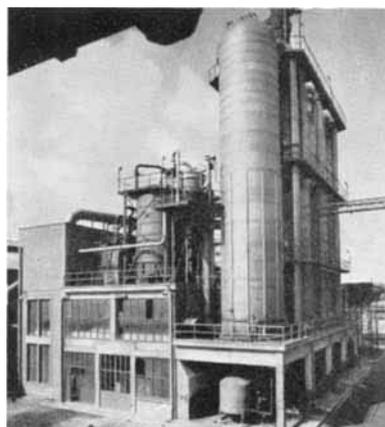
Kuhlmann and his Patent

More fundamental and extensive work had been carried out by Frédéric Kuhlmann, the founder of the great chemical enterprise Etablissements Kuhlmann. Born at Colmar in 1803, Kuhlmann had been a student of Vauquelin and had been nominated by him to the newly-formed Chair of Industrial Chemistry at the University of Lille at the early age of 21.

He knew from the work of Lavoisier that ammonia was composed of nitrogen and hydrogen, and that nitric acid was composed of these two elements together with oxygen. He was also familiar with the early discoveries in catalysis made by Humphry and Edmund

A Prophecy and its Fulfilment

"If in fact the transformation of ammonia to nitric acid in the presence of platinum and air is not economical, the time may come when this process will constitute a profitable industry." So wrote Frédéric Kuhlmann in 1838. Today the great chemical firm that he founded, Etablissements Kuhlmann, is among the leading producers of nitric acid by the oxidation of ammonia in their plant at La Madeleine-lez-Lille.



Davy and by Döbereiner, as well as with the work of Dulong and Thenard, reported in 1823, on the catalytic activity of the platinum metals in bringing about the combination of oxygen and hydrogen. He was also greatly interested in the part played by nitrogen products in agriculture (and in fact in later years carried out investigations on the use of ammonium salts as fertilisers on his own estate).

With this as his background, Kuhlmann went to work vigorously on the nitric acid problem, and found that by passing a mixture of ammonia and air over platinum sponge heated to about 300°C in a glass tube he obtained nitric acid. He filed a patent application for this invention in 1838.

At this time saltpetre was readily and cheaply available, and the new process could not offer any commercial advantage, but in the course of a paper given to the Société des Sciences de Lille in the same year, Kuhlmann made these prophetic remarks:

"If in fact the transformation of ammonia to nitric acid in the presence of platinum and air is not economical, the time may come when this process will constitute a profitable industry, and it may be said with assurance that the facts presented here should serve to allay completely any fears felt by the government on the difficulty of obtaining saltpetre in sufficient quantities in the event of war."

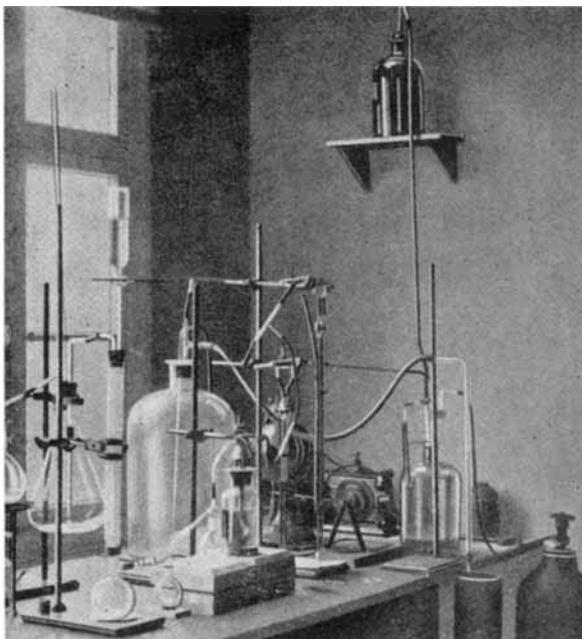
Today the great chemical firm that he founded

is among the leaders in the large-scale production of nitric acid by the oxidation of ammonia over a platinum gauze catalyst.

Ostwald's Experimental Work

To return to Ostwald, it was clear to him that the theoretical basis of the ammonia oxidation reaction would have to be elucidated before it could be developed on a large scale, and experiments were begun by Dr. Eberhard Brauer, at that time Ostwald's private assistant. The first experiments were made using a clean glass tube only a few millimetres in diameter containing platinised asbestos. Ammonia and air were passed over the catalyst in known quantities and with known velocities, and it was at once clear that the conversion to nitric acid was practicable and relatively simple to carry out, although some difficulties lay in the absorption of the reaction products. The historic apparatus used at this stage is shown overpage.

The first experiments using platinised asbestos gave only small yields and a platinum-lined tube proved little better. A new reaction tube was therefore made, consisting of a glass tube 2 mm in diameter in which was coiled a strip of platinum about 20 cm long. The whole tube was heated to redness, and the first experiment gave a conversion of more



The apparatus in which Ostwald and Brauer first investigated the ammonia oxidation process

Ostwald and Brauer, and here a pilot plant was developed. By 1904 the three converters illustrated below had been built and operated, and it was decided to erect a larger-scale plant at the Gewerkschaft des Steinkohlenbirgwerks Lothringen at Gerthe, near Bochum, to produce 300 kg per day of nitric acid.

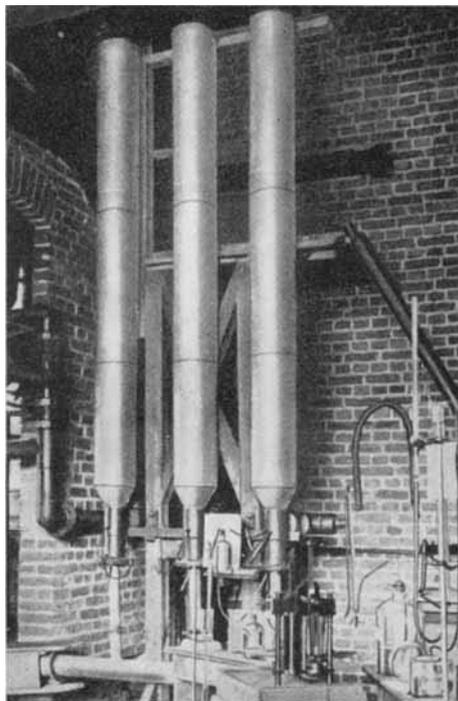
This plant was brought into operation in May 1906 and fully proved the feasibility of the process. A larger-scale plant was then designed and built, and by the end of 1908 was producing some three tons of 53 per cent nitric acid per day.

than 50 per cent. Attempts to increase the yield by reducing the gas velocity or increasing the time of contact gave just the opposite result, while increasing the gas velocity gave a conversion of 85 per cent. Ostwald, after several days brooding on this apparent anomaly, hit on the explanation; the nitrogen oxides formed could decompose to free nitrogen and oxygen if the time of contact between the gases and the catalyst were lengthened. Corroboration of this conclusion lay in the fact that unburnt ammonia was never detected behind the contact zone.

This determined the course of further experiments, which included investigations on the effects of variations in the ammonia : air ratio, in the time of contact and in the temperature of the catalyst. Thus were laid the foundations of a technical process for producing nitric acid from ammonia, but the translation from idea to practice presented many problems before the project was brought to fruition.

A small factory was made available to

The catalyst used at this time consisted of a roll of corrugated platinum strip about 2 cm wide and weighing about 50 g, heated initially by a hydrogen flame. The life of the



The three reactors of the pilot plant built by Ostwald and Brauer in 1904

catalyst was no more than a month or six weeks. The disadvantages of the process included the relatively large amount of platinum required per unit of acid produced, and the uncertainty of temperature control of the catalyst, but improvements were not long wanting.

The Platinum Gauze Catalyst

Dr. Karl Kaiser, of the Technische Hochschule, Charlottenburg, attacked the problem, and filed patents in 1909 covering the pre-heating of the air to 300 or 400°C and the use of a layer, usually four in number, of platinum gauzes. He was the first to employ platinum in the form of gauze, and it is a tribute to his experimental skill that the precise form of gauze he settled on—wire 0.06 millimetre diameter woven to 1050 mesh per square centimetre—is still very largely employed. By 1912 Kaiser had a pilot plant in operation at Spandau, Berlin, but while this was inspected repeatedly by British, French and American industrialists, he failed to interest them in his process, although a plant was erected at Kharkov in Russia.

A little earlier, in 1907, Dr. Nikodem Caro, of the Bayerische Stickstoffwerke A.G., and Adolph Frank, the joint inventors of the cyanamide process, had claimed a method of producing nitric acid from ammonia by means of a catalyst consisting essentially of thorium oxide admixed with small amounts of rare earths such as cerium oxide. This process failed, chiefly because the catalyst sintered and rapidly became impermeable, but further work was carried out by Caro and Frank's son Albert, who was then a chemical engineer at the Bayerische Stickstoffwerke. Several patents were filed during 1914, the process being based upon a single platinum gauze which was electrically heated. Progress was slow for a time, and numerous experimental plants failed, but the outbreak of war gave a much greater urge to the project and by 1916 the picture had changed radically. The Frank and Caro converter had by then been engineered by the Berlin-Anhaltische Maschinenbau

A.G. (BAMAG), who had constructed more than thirty plants, first for the supply of nitric oxide to lead chamber sulphuric acid plants and later for nitric acid production. The single platinum gauze was subsequently replaced by multiple gauzes, and the electrical heating was discontinued. This type of plant supplied all the nitric acid required for explosives in Germany during the later years of the war. The converter had a diameter of 20 inches, the catalyst consisting of a layer of three platinum gauzes woven from 0.006 inch diameter wire of 80 mesh to the linear inch, operating at about 700°C. The three gauzes were spot welded to a platinum grid and retained in place by embedding in asbestos. A much greater catalyst life was obtained in this design of plant, extending to six months provided that conditions were uniform and that the gases were free from impurities that might have a poisoning effect.

Initial Production in America

At the beginning of the war the United States possessed no source of nitric acid other than Chile saltpetre, and it became distressingly evident that the nation was dependent upon a foreign country in this respect, while the production of nitric acid from this starting-point required large quantities of sulphuric acid, already in short supply.

Cyanamide had been manufactured at Niagara Falls since 1909, and in 1916 the first American plant for the oxidation of ammonia produced from cyanamide was established by the American Cyanamid Company at Warners, New Jersey. The catalyst employed was a single platinum gauze, electrically heated. In the meantime, the Ordnance Department had decided to take action, and Dr. C. L. Parsons, of the Bureau of Mines, was asked to investigate European methods for nitrogen fixation. As a result the American Cyanamid Company was requested, in 1917, to form a subsidiary company, Air Nitrates Corporation, to act as agent for the United States Government for the construction and operation of a plant at

Muscle Shoals, Alabama, to produce 110,000 tons a year of ammonium nitrate. This plant comprised some seven hundred catalyst units each containing a single rectangular platinum gauze woven from 0.003 inch diameter wire, 80 mesh, and heated electrically to 750°C. The total weight of platinum was a little over 300 oz, and the loading ratio about 1 kg per daily ton of ammonia.

A smaller plant was also erected by the government at Sheffield, Alabama, and here a different approach was adopted to the catalyst design, aimed at conserving a greater proportion of the heat of reaction. Four layers of 80 mesh platinum gauze were rolled into a cylinder, which was heated by torch for a short time; on passing the ammonia-air mixture the reaction started at once and then became self-sustaining for many months. This construction was later abandoned, however, on account of the difficulties in installing and operating the gauze cylinder.

Developments in Great Britain

There had been little or no commercial interest in nitrogen fixation in Great Britain before the outbreak of war in 1914, and throughout the war period the supply of nitrogen products for munitions depended almost entirely on Chilean nitrate. Towards the end of the war, ammonium nitrate for the manufacture of Amatol was being prepared at the rate of a million tons per year by the double decomposition of sodium nitrate and ammonium sulphate, a process based on F. A. Freeth's studies of the phase rule.

There were, however, a number of attempts to make nitric acid by the direct oxidation of ammonia, either from gas-liquor or cyanamide. An Ostwald plant was set up at Dagenham Dock by the Nitrogen Products Company in 1916-1917, but never achieved successful operation. The Gas Light and Coke Company developed a plant at Beckton using a pad of three or four flat platinum gauzes as catalyst, and attained an output of a ton of nitric acid per day.

A systematic investigation was undertaken,

at the instigation of the Nitrogen Products Committee, by Professor J. R. Partington and Dr. L. H. Parker, and was carried out in the laboratory of the Munitions Inventions Department. An effective design of converter was evolved, employing either an electrically heated pad with two gauzes or a thicker pad that was self-sustaining in temperature when reaction had been established. Somewhat similar converters were constructed by Brunner Mond & Company and by the United Alkali Company, the latter of a pattern that is still in widespread use in the sulphuric acid chamber plants, constructed of enamelled cast iron with an integral tubular heat exchanger.

Although it came too late to be of service in the war, the decision taken in 1917 to erect a synthetic ammonia plant using the Haber-Bosch process led directly to the building of the Billingham plant by Synthetic Ammonia and Nitrates Ltd. (now Imperial Chemical Industries Ltd.). The ammonia plant first came into operation in December 1923 and the nitric plant—the first successful large-scale plant in this country—during 1927.

Although the process remains unchanged in principle—and even in some details such as the mesh sizes of the gauze pads—the size and complexity of the plant units has been tremendously increased. The first commercial operation at Lothringen Colliery produced 300 kg per day of weak acid. The most recently erected single units, working at a pressure of 120 lb. per sq. in. have an output of 250 tons per day, measured as 100 per cent acid. From the 50 g of corrugated foil in an Ostwald unit, the weight of platinum in a single converter has steadily increased until it may now be 15 kg or more, but the ratio of platinum used per daily ton of ammonia burned has fallen from over a kilogram to 250 g or less.

The next issue of 'Platinum Metals Review' will include an article by Mr. A. W. Holmes, of Imperial Chemical Industries Limited, Billingham, describing the technical and economic factors that have influenced the development of the ammonia oxidation process in more recent years.