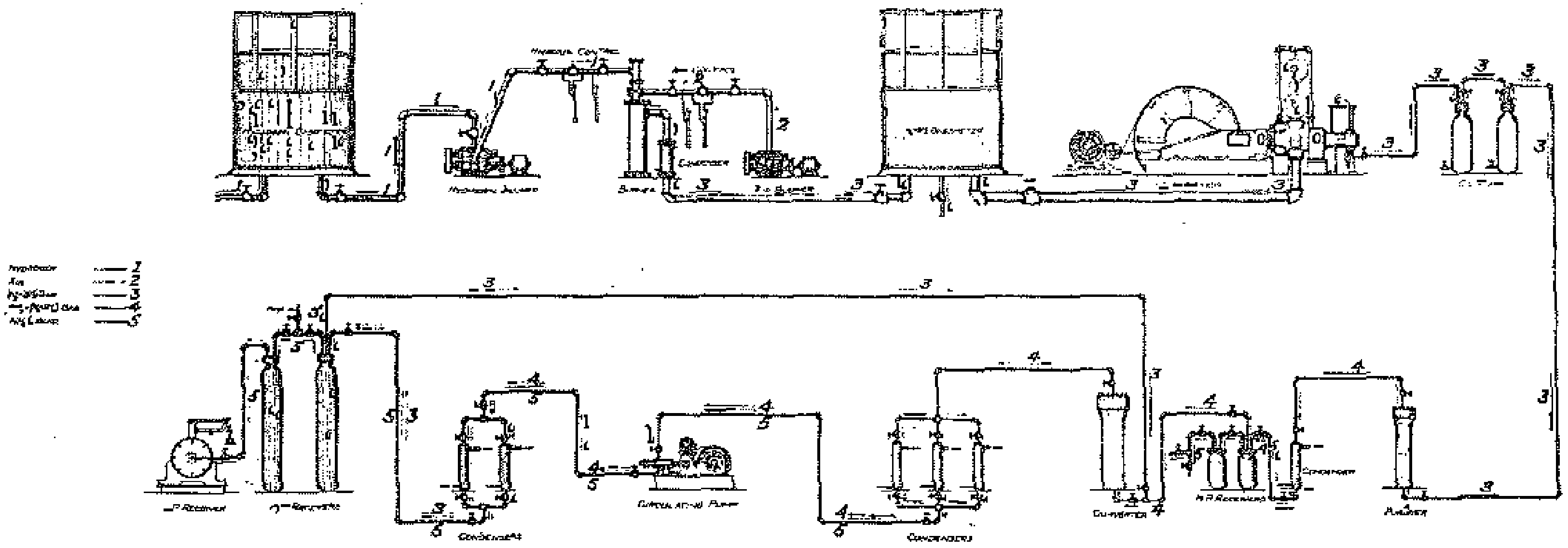
Industrial Chemical Monographs

Fixation of ATMOSPHERIC NITROGEN



FLOW DIAGRAM OF DIRECT SYNTHETIC AMMONIA PROCESS

Industrial Chemical Monographs

Fixation of
ATMOSPHERIC NITROGEN

By

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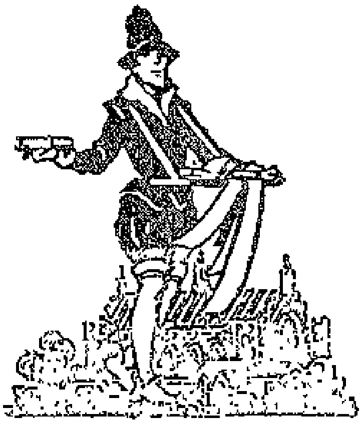

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FOREWORD

ALTHOUGH several books and a large number of pamphlets or articles have been written on various phases of the fixation of atmospheric nitrogen, these have been for the most part written by and for the scientist or technician intimately interested in or associated with the work. From the large number of questions and the nature of the questions asked at the various technical society meetings and from the number of letters which have come to me in my official capacity on the staff of the Fixed Nitrogen Research Laboratory, it was very evident that these books and pamphlets had not served all requirements. It was then in an endeavor to fill a need as was indicated by inquiries both personal and by letter that this small volume was written. This book is not, therefore, intended for the scientist or technician familiar with the subject of the fixation of atmospheric nitrogen, but is intended for the technical man of other walks of life, for the teacher and student, for the business man and the banker. It is hoped that this small contribution will give the general information necessary to influence its reader to become more deeply interested in the subject and seek the other and more technical writings on the subject.

In this volume an attempt was made to show the necessity for nitrogen, and its sources; to give some historical facts leading up to the present industry; to give a general description, neither wholly chemical nor wholly engineering, of the

CHAPTER I

NITROGEN

NITROGEN, the supply of which in utilizable forms is now engaging the attention of all of the important and progressive countries of the world, is one of the most plentiful of the elements.

Although the ultimate source of practically all nitrogen is probably the atmosphere, there are today four generally accepted commercial sources, viz., the organics, the deposits of natural nitrates, the deposits of coal and peat, and the atmosphere.

For thousands of years the use of nitrogen compounds was confined to the fertilizing of the land by the return to it of animal and vegetable refuse. Just when such practice was actually started by man is not known. It is reported, however, that as early as the fourth century B.C. the Egyptians utilized camel dung which they dug from the Libyan Desert near the temple of their god "Ammon." It is supposed that a salt comparable with our present "sal ammoniac" was also produced from this material. In addition to such manures, the organic nitrogen materials of today include dried blood and tankage from the slaughter house, cottonseed meal from the oil mills, fish scrap, leather scrap, waste products of the cocoa factory, and other similar materials.

The use of inorganic nitrogen started with the discovery of the natural saltpeter deposits of India and for years a lively trade in this material with the other countries of the world was enjoyed. With the discovery of black powder, the manufacture of which depended upon potassium nitrate, these Indian deposits immediately assumed a position of even greater importance. The nations of the world were now dependent upon India for the material necessary for national defense and preservation.

The demand for nitrogen compounds rapidly increased with this introduction of military explosives and finally led in 1830 to the discovery of the vast deposits of sodium nitrate in Chile. Although these Chilean deposits almost immediately assumed a position of importance it was with the discovery of a method of manufacturing nitric acid, the basis of our present smokeless powder and high explosives, from this sodium nitrate that their real value was recognized. Chile for years was almost the sole source of supply of the world's inorganic nitrogen demands for both peace and war.

Toward the end of the nineteenth century, another source of available inorganic nitrogen was introduced with the bringing into operation of by-product coke ovens. Coking coals contain combined nitrogen in varying quantities up to about 40 pounds per ton. In producing coke in the beehive type of oven all this nitrogen, as well as many other valuable constituents of the coal, are lost. In the by-product ovens, however, a part of this nitrogen is driven off during the coking process and 4 to 5 pounds per ton of coal coked are recovered as ammonia.

Although it was long known that the atmosphere everywhere about us was composed of nearly 80 per cent nitrogen, this vast and inexhaustible source of supply was not utilized until the beginning of this twentieth century. Without this source of supply the World War would never have continued for four years. Germany, because of an insufficient supply of explosives, would undoubtedly have been forced to abandon hostilities at an early period. Yet even though her fleet was held inactive she taught the world a valuable lesson. At the very outset of the war, Germany with but a few converted freight and passage ships, prevented the exportation of nitrate from Chile for several months. This blockade was so complete as to cause a very alarming situation before it was broken. It demonstrated the possible helplessness of a nation relying for its national defense, in fact for its preservation, on a foreign source of supply for its inorganic nitrogen. In time of war greatly increased quantities of nitrogen are necessary not only for explosives but for agriculture as well. The armies in the field must be well fed while the health and hence contentment of the people at home is also of paramount importance. Just as an army cannot be expected to fight effectively on an empty stomach, so a hungry nation cannot be expected to support its armies. If the nitrogen supply is sufficient so that the armies are victorious, but insufficient to provide also for the needs of the remaining populace, then the cause will undoubtedly meet defeat from within.

It is very evident that the consumption of war-time agricultural nitrogen should be at least equivalent to, and if at all possible, greater than the peace-time consumption. Nitrogen for explosives must be additional. If the nitrogen is imported from a foreign source of supply, the necessity for increased transporting capacity for this war demand occurs at the time when the country can least afford to divert additional bottoms to this purpose. If a blockade of this foreign source of supply — such as was successfully maintained by Germany for a period at the beginning of the World War and was maintained against Germany during the whole war — is effected, and the country is dependent upon this source, then that country is almost inevitably doomed to defeat through lack of munitions or starvation, or both.

By increasing the consumption of agricultural nitrogen, larger yields per acre may be expected. This will result in either a greater total production or an equivalent production from smaller acreage, and hence with less labor. Such increased use of nitrogen might be a remedy for some peace-time as well as war-time agricultural difficulties.

It is quite generally believed that Germany declared war in 1914 only after assuring herself that she had a suitable source of fixed nitrogen within her own borders. The rate of consumption of nitrogen in explosives during this war was undoubtedly far beyond the expectations of any individual or nation. In order to meet this demand it was necessary, even with the enormous expansion of the rather young atmospheric nitrogen fixation industry, to stint agriculture. How great an effect this had on the eventual result is rather difficult to appraise, but there is no doubt that the people of several of the warring nations suffered materially and still show the effects of malnutrition.

Although agriculture in peace time and agriculture and military explosives in times of war are the large consumers of nitrogen, it is being used in rapidly increasing quantities in many industries. Agriculture is responsible for approximately 80 per cent of the world's inorganic consumption. In the United States, as much as 40 per cent of the consumption is in chemical industries, the remainder going to agriculture.

Explosives are no longer to be associated only with war. The use of peace-time explosives has grown tremendously until today there is consumed in such pursuits as mining, quarrying, road building and the clearing of land for cultivation, about 500,000,000 pounds annually of high explosives. The chemical uses of nitrogen, largely in the form of nitric acid, are in the manufacture of photographic films, artificial leather, artificial silk, imitation ivory and dyes. In the form of ammonia, nitrogen is used in the refrigeration industry for the manufacture of artificial ice and in the operation of cold-storage plants; it has a wide domestic use as household ammonia, and is used in the manufacture of soda ash, one of our most important staple chemicals.

The provision of an adequate supply of such a vital material must receive the greatest consideration of the various nations of the world, both individually and collectively. Four sources of supply were mentioned earlier and as it has been shown that an unlimited supply is vitally necessary, it will be well to consider the extent of these sources.

Since soil nitrogen, or what may be considered the natural nitrogen of the soil, is almost wholly confined to the surface portion and since the unweathered, underlying rock is devoid of nitrogen, it is evidently of atmospheric origin. The accumulations of soil nitrogen are the results of residues of many generations of plants. This natural combined nitrogen is largely a constituent of organic matter and as such is unavailable for plant use. It must be converted into simple water-soluble compounds. The decomposition of such organic materials results in the conversion of the combined nitrogen to ammonia. This ammonia is then oxidized by the soil bacteria to nitrites, which are further oxidized to nitrates, which are quickly taken up by the growing plant. Such accumulations of the soil nitrogen cannot be considered as a source of our future supply of nitrogen.

The fixation of nitrogen is also accomplished by the bacteria within the tubercles of the plants. Professor Haber once remarked that the fixation of nitrogen in the future for soil fertilization use would not be through great industrial plants, but rather through plant and soil bacteria. Soil conditions readily influence nitrogen fixation by leguminous vegetation, particularly the supply of lime, and organic matter and the aeration of the soil. Tests have shown that 100 to 200 pounds of nitrogen can be gathered in a good crop of leguminous plants per acre. At the present time, however, this method of nitrogen fixation cannot be depended upon to supply our nitrogen demands.

While the natural manures are widely used as fertilizer, yet their availability is practically limited to this use. Such manures are a by-product and the supply cannot be increased at will. The same is true of fish scrap, dried blood, tankage, cottonseed meal, cocoa waste, etc. Approximately 70 per cent of the combined tonnage of these materials is used for cattle feed, while the remainder is consumed in mixed fertilizers. Such materials cannot then be considered as a primary source of supply of nitrogen, but must be supplemental to some other source.

In 1898, the world was rather rudely awakened by a statement by Sir William Crookes, an eminent authority, to the effect that the world was facing ultimate starvation because of its dependence upon the natural niter beds of Chile for its nitrogen supply. While later investigations have given assurance that the exhaustion of these deposits would probably have been further distant than was feared from Sir William's statement, yet his warning was well founded and timely.

At this time it appears certain that Chile could supply the total demands of the world for at least 100 years into the future. It is inevitable that exhaustion must occur, however, and wisdom was shown in anticipating this condition and guarding against its consequences. Although the 2240 square miles of nitrate-bearing ground which has been examined and proven is but 3 per cent of the total nitrate area, yet there is no assurance that the remaining 97 per cent is of proportionately equal value. It might be assumed that the more likely areas have been worked first. On the other hand, future working of this area might show these unexplored regions to be vastly more valuable than the present workings.

There is still an economic question to be considered. The world, in consuming some 2,000,000 tons of Chile nitrate, has contributed to that country's support through the export tax nearly $25,000,000 for the year 1926. Of this amount, the consumer in the United States paid approximately $12,000,000. If nitrogen equivalent to that supplied by this material could be secured within the borders of the United States, even though at the same cost to the consumer as Chile nitrate, *the country as a whole would benefit* to the extent of $12,000,000, the tax which would have been paid to Chile. If, on the other hand, production costs are such as to permit reduction in cost to the consumer, the dual benefit can be immediately seen.

This source of supply in Chile, while of great extent and sufficient for a long period of continued exploitation, is also of limited value both because of eventual exhaustion and also because of the possibility of a nation being shut off from this supply when it is most needed.

The third source of supply, coal by-products, is also limited. While coal, unlike sodium nitrate, is common in large deposits to many parts of the world, its by-products cannot be relied upon to furnish a nation's inorganic nitrogen. The nitrogen from this source must be a by-product and hence its production will not be dependent upon the demand for nitrogen but rather upon the demand for coke. An increased demand for nitrogen might be met by a decreased supply from this source because of conditions which might have affected the coke market which in turn depends upon the iron and steel industries.

These three sources of supply then must be considered as wholly inadequate. No nation can today afford to place entire dependence upon any one, or even all of these three combined. These sources must be considered as supplemental to some other principal source. This principal source is the atmosphere.

The fourth source of supply, the atmosphere, must then be the answer to the important question of an unlimited supply. No nation is more advantageously situated as regards this source than any other. It forms, as was previously stated, nearly 80 per cent of the air we breathe. Over every square mile of the earth there is some 20,000,000 tons. In fact, the atmosphere furnishes an inexhaustible supply. It is apparent then that difficulties which prevented its use were present and were only recently overcome.

Nitrogen is one of the more remarkable of all of the ninety elements so far discovered. In the free form as it occurs in the atmosphere it can be utilized neither by the bodily mechanism nor in explosives or fertilizers. In the free state it is a comparatively inert gas, but once it enters into combination it displays the greatest activity both in the organic and inorganic fields. Owing to the slight affinity between nitrogen and the other elements with which it enters into combination, many of its compounds are unstable and can be decomposed with the almost instantaneous evolution of heat and gas. Because of this slight affinity, military explosives almost without exception are nitrogen compounds.

In order to render this free nitrogen available for use other than as a diluent for the oxygen of the air, it must be combined with other elements. In this form it is known as fixed nitrogen. The nitrogen of the organics, of Chile nitrate, and of by-product coke oven ammonia is already fixed. In these cases the fixation has been accomplished by slow natural processes. In the rapid fixation processes now employed, the natural independence of the element has been overcome by the ingenuity of man. If oxidized and absorbed in water, it is fixed as nitric acid. This is the Arc Process for atmospheric nitrogen fixation. Calcium carbide at red heat will absorb free nitrogen as a sponge will water, thus fixing the nitrogen in the form of calcium cyanamide by the Cyanamide Process. Nitrogen will combine directly with hydrogen under certain conditions, resulting in the fixing of the nitrogen in the form of ammonia, according to the Direct Synthetic Ammonia Process.

Nitrogen fixed in these forms can be readily converted to other materials. Practically all modern explosives are made by treating various substances with nitric acid; for instance, smokeless powder from cotton and nitric acid; nitroglycerin, the basis of dynamite, from glycerin and nitric acid; picric acid from carbolic acid and nitric acid; trinitrotoluene — T.N.T. — from toluol and nitric acid; fulminate of mercury from mercury and nitric acid; and ammonium nitrate from ammonia and nitric acid. Calcium cyanamide gives up its nitrogen in the form of ammonia when treated with steam in an autoclave. Ammonia may be oxidized and absorbed in water to form nitric acid. It may also be used to neutralize sulphuric acid to form ammonium sulphate; or phosphoric acid to form ammonium phosphate, or carbonic acid to form urea, or nitric acid to form ammonium nitrate.

CHAPTER II

ATMOSPHERIC NITROGEN FIXATION

THE chemist has known for many years how to convert the inert free nitrogen of the atmosphere into compounds of nitrogen in his laboratory. As early as 1774 Priestly isolated ammonia, which in 1777 was shown by Scheele to contain nitrogen. Further work by Berthelot showed it to be composed of one volume of nitrogen to three volumes of hydrogen. In 1781, Cavendish noted the formation of nitric acid when hydrogen was burned in air and in 1800 Sir Humphrey Davy made nitric oxide by passing air over a wire heated by an electric current. In 1865 Deville passed a nitrogen-hydrogen mixture through a porcelain tube and found that ammonia was produced when the tube was heated to about 1300° C. Although these and other reactions of nitrogen were known, the reluctance of this element to enter into combination limited progress for years to the experimental laboratory. The quantities of product obtained in this early work were distressingly small.

The warning of Sir William Crookes in 1898, however, gave impetus to the work looking toward commercial fixation of the nitrogen of the atmosphere. In 1902, the application on an industrial scale of the combined results of experiment and theory was attempted. In that year, the Atmospheric Products Company was organized with a capital of $1,000,000. This company took over the process and equipment patents of two Americans, C. S. Bradley and

R. Lovejoy, and erected a large works at Niagara Falls, New York. The industrial fixation of atmospheric nitrogen thus had its birth in the United States.

The process of Bradley and Lovejoy effects the direct combination of the nitrogen and oxygen of the air to form nitric oxide. By further oxidation and absorption of the oxides by water, nitric acid of approximately 35 per cent concentration is formed. This method of fixation is known as the arc process.

Although this first plant might well be called a technical success, it was not an economical success and closed down in 1904, after less than two years of operation. The yield of 948 pounds of nitric acid per kilowatt year of power employed proved insufficient and the equipment besides being costly was rather fragile, requiring frequent repairs.

The commercial possibilities for the direct oxidation of the nitrogen of the atmosphere for the production of nitric acid had been demonstrated. Here was a possible means of avoiding the serious situation indicated by Sir William Crookes. Even before the plant at Niagara Falls had discontinued operations, a furnace was developed in Norway by Prof. Christian Birkeland and Engineer Samuel Eyde, which proved to be both a mechanical and economical success. Experiments with this furnace using 3 horsepower were carried on early in 1903, and in October of that year a small commercial plant employing 150 horsepower was started in operation at Ankerlökken, near Oslo. This plant proved so successful that the following year a plant of 1,000 horsepower capacity was erected near Arendal.

In 1905, the present works at Notodden were started into operation with a capacity of 2,500 horsepower. Subsequent enlargements brought the capacity of this plant to 40,000 horsepower in 1907, 55,000 in 1911, and 60,000 in 1919. In 1911, the operating company, the Norwegian Hydro-Electric Nitrogen Company (Norsk Hydro) started a second works at Rjukan, for a consumption of 130,000 horsepower and added a second unit of similar size in 1915. The Notodden and Rjukan plants are still in operation with a combined consumption of 320,000 horsepower, and an output of 38,000 tons of nitrogen fixed per year.

Other arc process furnaces developed and put into commercial operation are those of Schönherr, Moscicki, Pauling, Guye, and Wielgolaski. The installations other than those at Notodden and Rjukan have been relatively small, so that the total installed capacity is approximately 45,000 tons of nitrogen per year.

Two further attempts have been made to establish the arc process in the United States. In 1913, the Southern Electro-Chemical Company, a subsidiary of the Southern Power Company, incorporated under the laws of the State of New York, erected a plant at Nitrolee, South Carolina. This plant employed the Pauling furnace and was equipped for nitric acid concentration and ammonium nitrate production. The plant as enlarged in 1915 was of a capacity to utilize some 7,000 electrical horsepower. Its total consumption for the month of March 1915, the best period of operation, was at the rate of less than half that amount, however.

During this month, the equivalent of 42.5 tons of 100 per cent nitric acid was produced, while 32 tons was concentrated, 20.5 tons packed and sold and 10 tons consumed in ammonium nitrate manufacture. The manufacturing cost, $90 per ton of concentrated acid exclusive of capital charges, and reckoning power at \$10 per horsepower year was high. This power rate of \$10 per horsepower year was far below the prevailing rate for that locality. The consumption of over three horsepower years per ton of nitric acid was too high, and rendered operation uneconomical, so that the plant was closed down early in 1916, and operation has never been resumed.

In the following year, the third attempt at establishing the arc process in this country was made, and the first permanent plant for the fixation of atmospheric nitrogen in the United States was started. This plant, erected and operated by the American Nitrogen Products Company, was of about one ton of nitrogen per day capacity and was located at Le Grande, Washington. After enjoying nearly ten years of operation, the plant was destroyed by fire in the spring of 1927, and it is believed it will not be rebuilt.

The search for means of fixing nitrogen in the form of alkali cyanides for gold extraction led to the work of Frank and Caro, two eminent German chemists, during the close of the nineteenth century. The patents granted these investigators in 1895–98 formed the basis of a process for the fixation of atmospheric nitrogen known as the cyanamide process, in which calcium carbide is produced through the reaction between lime and coke in an electric furnace. By the interaction of calcium carbide and pure nitrogen at a red heat, the nitrogen is fixed in the form of calcium cyanamide.

The first commercial plant utilizing this process was put into operation at Westeregeln near Magdeburg, Germany, in 1905. This plant was not a commercial success and was abandoned in 1908. Some 800 tons of cyanamide had been produced the first year. A second and successful plant was started into operation in 1905, at Piano d'Orta, Italy. The initial capacity of this Italian plant was 4,000 tons of cyanamide per year. From this small beginning, the industry enjoyed a rather rapid growth to its peak in 1918 of 35 plants of a rated capacity of 350,000 tons of nitrogen per year. A large part of this capacity was erected for the war emergency, so that after the war there followed a curtailment of production and even a dismantling of some plants.

The first cyanamide plant erected on this continent and in fact the first successful plant for the fixation of atmospheric nitrogen was that of the American Cyanamid Company at Niagara Falls, Canada. This company was incorporated in 1907 under the laws of the State of Maine and in 1909 started into operation a plant for the annual production of 5,000 tons of cyanamide. Subsequent enlargements and improvements have increased the capacity to 120,000 tons of cyanamide per year, equivalent to 25,000 tons of nitrogen.

When in 1917, due to the urgency caused by war, it became apparent that a large and positive source of fixed nitrogen must be provided in the United States, it was decided after careful consideration to erect a plant of the cyanamide process. This plant of a rated capacity of 40,000 tons of nitrogen per year, the largest cyanamide plant in the world, was erected at Muscle Shoals, Alabama. It is known as U. S. Nitrate Plant No. 2, and except for a two months' test run it has never operated.

Although attempts to produce ammonia directly from nitrogen and hydrogen date back to 1807, commercial interest was not aroused until after the publication by Prof. Fritz Haber of a series of papers on this subject in 1905 and 1906. The Badische Anilin Und Soda Fabrik, in 1910, took an active interest in the possibilities of this method for the commercial fixation of atmospheric nitrogen and in 1913 started in successful operation a plant of a capacity of 7,000 tons of nitrogen per year. From this start, world capacity of direct synthetic ammonia process plants has rapidly increased to an operating and under-construction capacity today of 979,000 tons of nitrogen per year. This is more than double the installed capacity of the cyanamide and arc processes combined.

The World War proved a great stimulus to the atmospheric nitrogen industry. At the close of the year 1913, or just prior to the outbreak of the war, there were in operation seven arc plants of a capacity of 20,000 tons of nitrogen per year, 15 cyanamide plants of a capacity of 66,000 tons of nitrogen and one direct synthetic ammonia plant of a capacity of 7,000 tons of nitrogen per year. Five years later, the close of the year 1918, there were operating or building and later put into operation, 12 arc plants of a capacity of 40,000 tons of nitrogen, 35 cyanamide plants of a capacity of 350,000 tons, and three direct synthetic ammonia plants of 330,000 tons.

The period following the war has apparently favored the direct synthetic ammonia process. The capacities in tons of nitrogen installed and building for the various processes at this time are: arc, 5 plants of 44,750 tons; cyanamide, 28 plants of 315,500 tons; direct synthetic ammonia, 51 plants of 979,000 tons.

The first plant of this process erected in the United States was the U. S. Nitrate Plant No. 1 at Sheffield, Alabama. The imminence of war led to the passage in Congress of Section 124 of the National Defense Act of June 3, 1916. This section made $20,000,000 available to the

President for an investigation of the various methods for the production of "nitrate and other products for munitions of war and useful in the manufacture of fertilizers."

There followed the appointment of a committee of scientists and engineers of the National Academy of Sciences in co-operation with the American Chemical Society at the request of the Secretary of War. In addition, two investigators were sent abroad to study and report on conditions in Europe. In the meantime the General Chemical Company had worked up and patented a modification of the direct synthetic ammonia process as operated in Germany, and made preparations for the erection of a plant. This plant of 7.5 tons of ammonia per day capacity was to be erected at Shadyside, New York.

The result of the various investigations made for the Government was the recommendation that the War Department take over the process of the General Chemical Company and erect a pilot plant to test the process. Accordingly, U. S. Nitrate Plant No. 1 was erected at Sheffield, Ala. This plant of a capacity of 30 tons of ammonia, including the 7.5 ton unit which was to have been erected at Shadyside, was never completed. Only one unit of 7.5 tons of ammonia per day capacity was ready for trial operation prior to the signing of the armistice. Continuous operation of this unit was never realized, and only a small amount of ammonia was produced.

In addition to these three processes, a great amount of investigational work was done on other processes, and a large number of methods have been proposed from time to time for the commercial fixation of nitrogen. Very few of these have appeared to present promising possibilities. It must be remembered, however, that unforeseen developments in our knowledge, or changes in the industrial situation due to new demands or supplies, may in the future make possible the commercial success of processes at present entirely impracticable.

In the cyanide process a mixture of sodium carbonate and coke with iron in small quantities is heated in a stream of pure nitrogen to a temperature of approximately 1000° C. This operation results in the formation of sodium cyanide, which may be decomposed with steam to yield ammonia.

The commercial development of this sodium cyanide process was undertaken in the United States by the Nitrogen Products Company according to the patents of Prof. J. E. Bucher. Experimental plants were erected at Saltville, Virginia and Greene, Rhode Island, while in 1918 the Government undertook the erection of United States Chemical Plant No. 4 at Saltville, Virginia, for the production of 10 tons of sodium cyanide per day by this process. Operation of this plant started in September of that year, resulting in a production of some four tons of sodium cyanide. As operating costs proved to be too high to render the plant commercially practicable for the production of either cyanide or ammonia, operation was discontinued in December, and the plant was later disposed of through salvage.

Of the various nitride processes, perhaps the one best developed is that for making aluminum nitride from crude aluminum oxide (bauxite), coke and nitrogen, heated in an electric furnace to a temperature of about 1800° C. The aluminum nitride may be decomposed with steam or dilute caustic solution to yield ammonia and regenerate the alumina.

Various small scale experimental plants of this process have been constructed and operated in France, Germany and the United States. The chief difficulty in all cases is in securing economically the high temperatures necessary for the reaction, and in obtaining materials of construction capable of resisting these temperatures in continuous operation.

The explosion, or Hausser, process depends for the fixation of nitrogen upon the fact that by exploding a mixture of combustible gas with air or oxygen under proper conditions high enough temperatures can be reached to bring about the combination of a small amount of the nitrogen and oxygen present. By this means it is attempted to bring about the same direct combination of nitrogen and oxygen that occurs in the arc process without its enormous expenditure of electrical energy.

Experimental plants in which operations have been conducted in stationary bombs with mechanically operated valves have been run at Heeringen and Neuremberg, Germany. The mechanical strains to which the apparatus is subjected limit the developments. In its present state of development this process cannot compete successfully with other processes for the fixation of atmospheric nitrogen.

Of these processes, the arc process requires the greatest expenditure of electrical energy, the cyanamide and nitride processes rank next, while the direct synthetic ammonia, cyanide and Hausser processes require only small amounts or none at all.

It is interesting to note that commercial development of the three processes now in commercial operation stands in approximately inverse proportion to the unit power consumption of each. For instance, only six per cent of the atmospheric nitrogen fixed during 1926 was fixed by the arc process, which requires the expenditure of 61,000 kilowatt hours per ton. The cyanamide process requires an average of 14,000 (some plants as low as 12,000) kilowatt hours, or less than one-fourth that of the arc process, and was accountable for 24 per cent of the year's production. The remaining 70 per cent production was by means of the direct synthetic ammonia process, with an average power consumption of 4,000 kilowatt hours per ton of nitrogen fixed.

The 6 per cent of nitrogen produced by the arc process consumed 37 per cent of the total power used in fixing nitrogen, the 24 per cent by the cyanamide process consumed 35 per cent, while the 70 per cent by the direct synthetic ammonia process consumed only 28 per cent of the total power.

The average power consumption at this time for the three fixation processes combined is 10,000 kilowatt hours per ton of nitrogen as compared with 70,000 kilowatt hours per ton 25 years ago. The total power consumption now, however, is at the rate of 7,000,000,000 kilowatt hours per year, as compared with less than 1,000,000 then.

CHAPTER III

THE ARC PROCESS

THE commercial development of the arc process was the result of the attempts of man to emulate nature. It is estimated that through the lightning discharge of electrical storms 100,000,000 tons of nitrogen are fixed annually and carried to the earth's surface by the precipitation of rain, snow and hail. Unfortunately this fixed nitrogen is not returned to the earth at the time and place most convenient to man and he must resort to methods more under his control.

In the commercial operation of this process, air is passed rapidly through a zone of exceedingly high temperature produced in an electric arc furnace. The heat of the gases containing the nitric oxide produced is recovered in waste-heat boilers, while the nitrogen dioxide formed on cooling the nitric oxide in the presence of the accompanying oxygen is absorbed in water, producing dilute nitric acid. This is the direct product of the arc process.

The fundamental chemical reaction involved is expressed by the equation

$$N_2 + O_2 \rightleftharpoons 2\ NO - 43{,}200 \text{ gram calories.}$$

From this equation it can be calculated that the chemical energy absorbed in fixing one ton of nitrogen is the equivalent of but 1,630 kilowatt hours of electrical energy. This chemical energy equivalent, however, represents less than 3 per cent of the total electrical energy requirements, 61,000 kilowatt hours per ton nitrogen fixed. Over 97 per cent of the total energy expended is wasted so far as actual nitric oxide formation is concerned, and is necessary for preparing and maintaining conditions favorable to the formation of the oxide.

Nitric oxide exists in equilibrium quantities with heated air. For instance, the equilibrium amount at 2300° C is 2 per cent, while at 3300° C it is 6 per cent by volume. As there naturally is a heat gradient of decreasing intensity away from the center of the arc but a relatively small quantity of the air attains a temperature of as high as 3300° C. Yet even though it were assumed that all the air passed through the furnace attained this temperature, still the great excess of total applied energy for heating over the chemical energy received in return can be readily realized. Actually the gases leaving the arc furnace contain an average of 1.2 per cent of nitric oxide. It is therefore necessary to handle 175 tons of this gas mixture per ton of nitrogen fixed as nitric acid. As there is a temperature gradient between the arc filament and the surrounding gas, it is obvious that this gradient should be as steep as possible. In addition to the saving of electrical energy which would otherwise be used for heating the gas if the gradient were flatter, the cooler gas surrounding the arc assists materially in reducing the temperature of the nitric oxide containing gases as they leave the arc filament.

A factor working against an efficient utilization of the energy input is the rapid decomposition of nitric oxide at high temperatures. Although means have been devised to effect rapid cooling of the gases, yet it is believed that considerable decomposition actually takes place. It is by means of the operation of cooling the gases that some of the seemingly wasted energy input is recovered. The gases leaving the furnace at approximately 1100° C are passed directly to waste heat boilers where the heat given up in a drop of temperature to 350° C and further drop to 200° C in economizers is utilized for the generation of steam. This steam besides being used for purposes of solutions and evaporations is used for the operation of turbo-generators for the generation or regeneration of electrical energy. Although decomposition of the oxide takes place at these lower temperatures, the rate of such decomposition is extremely slow.

The oxidation of nitric oxide represented by the equation

$$2\ NO + O_2 \rightleftharpoons 2\ NO_2 + 27{,}800 \text{ gram calories}$$

proceeds very slowly, so that the velocity of the gas must be low while the oxidation chambers must be very large.

The oxide leaving the economizers at about 200° C is further cooled in cooling towers to about 50° C before it enters the series of towers of the absorption system, since the completeness of the absorption decreases rapidly with increasing temperature. In the first tower of the system, the oxygen of the accompanying air reacts with the nitric oxide to form nitrogen dioxide. The gases pass in series through the following towers of the absorption system where they are brought into intimate contact with water by which the nitrogen dioxide is absorbed forming nitric acid. This reaction occurs according to the equation:

$$3\ NO_2 + H_2O \rightleftharpoons 2\ HNO_3 + NO$$

which is shown in one step although actually taking place in two.

It will be noted that nitric oxide is again liberated by this absorption operation. In fact, one third of the oxidized nitric oxide reacting with water in the absorption system reverts to nitric oxide which must be reoxidized. The reoxidation of this nitric oxide, like the original oxidation, is a slow process. Because of this the absorption towers must be very large in order to permit time for the liberated gas to be oxidized and reoxidized until it is eventually practically completely absorbed. The resulting product is a nitric acid of 30 per cent strength.

In commercial operation, only about 80 per cent of the nitrogen oxides are obtained in the form of nitric acid, since it is not practicable to obtain better absorption. Some 17 per cent of these oxides then are absorbed in subsequent alkaline towers over which flows a solution of soda ash. The absorption of the nitrogen oxides by this alkaline solution results in the production of sodium nitrite or a mixture of sodium nitrite and sodium nitrate, depending upon such conditions of operation as temperature and degree of oxidation of the nitric oxide. The equations for these two reactions are, respectively:

$$NO + NO_2 + 2\ NaOH = 2\ NaNO_2 + H_2O, \text{ and}$$

$$2\ NO_2 + 2\ NaOH = NaNO_2 + NaNO_3 + H_2O.$$

Even with these alkaline towers, complete absorption of the nitrogen oxides is not achieved and some 3 per cent escapes to the atmosphere. If sodium nitrite rather than nitric acid is desired, alkaline towers alone should be used for the absorption of the nitrogen oxides.

Although five different arc furnaces were mentioned in a previous chapter as having been used in commercial operation, only three of these have enjoyed large-scale operation. These are the Birkeland-Eyde, the Schönherr, and the Pauling furnaces.

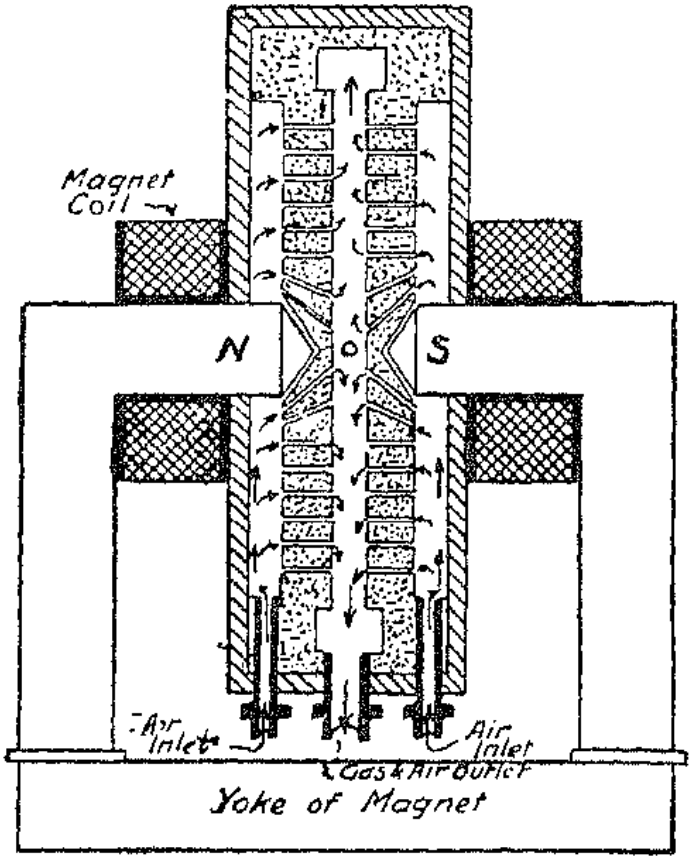
In the Birkeland-Eyde furnace, advantage is taken of the phenomenon of the deflection of an arc by means of a magnetic field at right angles to it in order to spread the arc through the gas. The Schönherr furnace is built upon an altogether different principle, the object here being to secure a steady and very long slender arc. The Pauling furnace more nearly resembles the Birkeland-Eyde, in that it operates on the principle of a spread arc. In this furnace, however, this spread of the arc is obtained by a blast of air directed against it.

The Birkeland-Eyde and the Schönherr furnaces both are in operation at the Rjukan plant of the Norsk Hydro Company. This plant is really the only large installation of the arc process. Its rated capacity of approximately 30,000 tons of nitrogen per year represents over 70 per cent of the world capacity.

This plant is in two units, of equal size, Plant I, completed in 1912, and Plant II, completed in 1916. Each plant is served by an individual hydro-electric power station of 140,000 electrical horsepower capacity. The water for Power House I is brought to the turbines from a lake high up in the mountains and three miles distant from the power house, through a number of steel tubes or conduits in parallel. The spent water from this station is then led through a rock tunnel cut in the mountain, a distance of 3½ miles to Power House II. In addition to the hydro-electric generating equipment, each power station operates three steam driven turbo-generators of a rated capacity of 13,000 electrical horsepower each. The steam for these generators is supplied by the waste heat boilers for cooling the nitrogen oxide containing gases leaving the arc furnace.

In the arc furnace room of Plant I there are installed 120

Schönherr furnaces of 1,000 kilowatts capacity each, and six of the earlier Birkeland-Eyde type of 3,500 kilowatts capacity each. At Plant II are 36 Birkeland-Eyde furnaces. The Schönherr furnaces, to satisfy the demands for the long slender arc, are 30 inches in diameter by 25 feet in length. In the new Birkeland-Eyde furnaces, as of Plant II, an alternating current arc is maintained between water-cooled copper electrodes which are placed between the poles of an electromagnet, so that the direction of the arc is at right angles to that of constant magnetic field. This furnace is inclosed within a steel cylindrical case, 12 feet in diameter by 5 feet between the flat ends. The inner surface of this casing is lined with fire brick leaving a cylindrical space 6 feet in diameter by 6 inches thick in which the arc expands. The



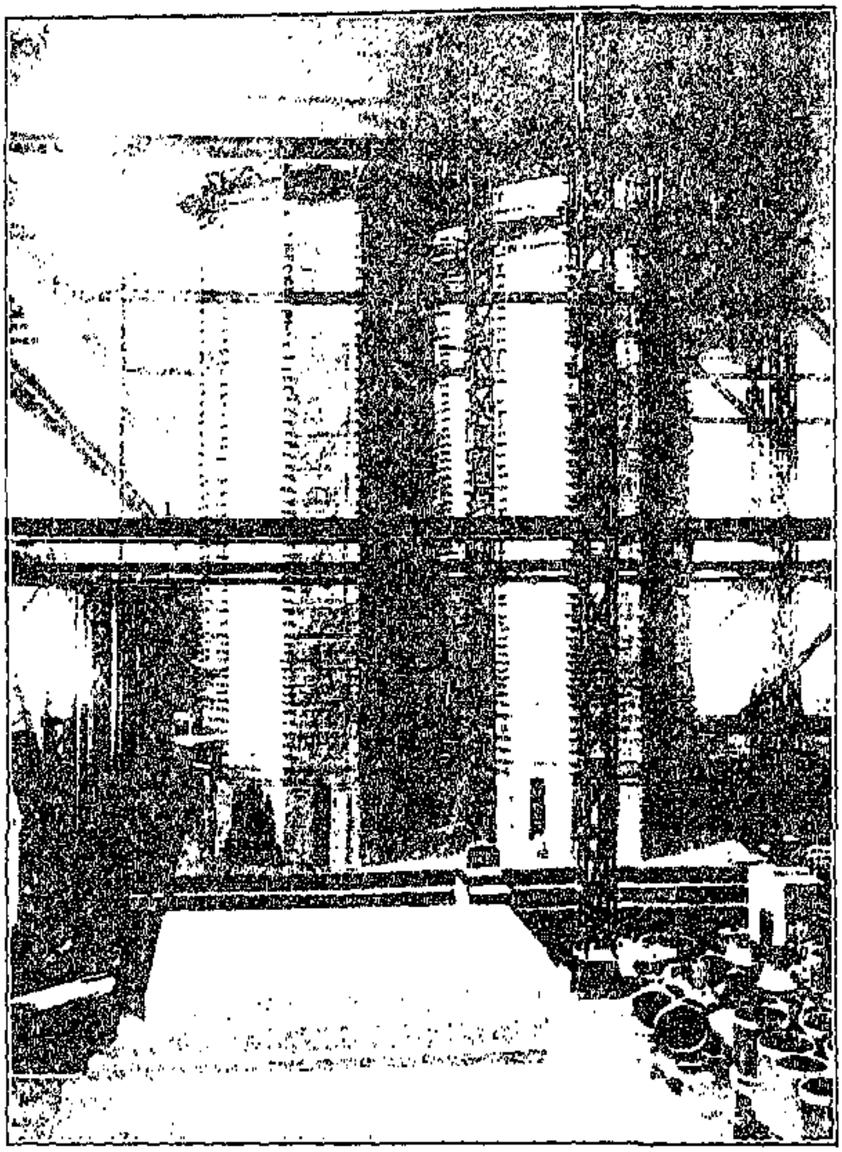
Diagrammatic Sketch of Birkeland Edge Furnace air enters this arc region through perforations in the brick wall and leaves through openings along the circumference of this region. The capacity of these furnaces is 4,000 kw. each.

Although the furnace rooms of the two plants are about a mile apart the absorption buildings are adjacent and in the immediate vicinity of the furnace room of Plant I. This makes it necessary to convey the gases as they leave the economizers of Plant II a distance of nearly a mile. In traveling this distance through 5 aluminum tubes, each 3 feet in diameter, the gases are cooled from 200° C to about 50° C, obviating the necessity of a cooling tower. Further, upon cooling, oxidation of the nitric oxide takes place so that the gases upon reaching the absorption building are drawn directly into the absorption system.

The absorption towers which are of granite are 22 feet in diameter by 70 feet high and are arranged in sets of four each. The furnace gases entering the base of tower No. 4 pass up through this tower to the base of tower No. 3, and so on through this tower and through towers No. 2 and No. 1. From the exit of tower No. 1 the gases pass in series through two alkaline towers from which the unabsorbed nitrogen oxides pass to the atmosphere. The absorbing liquid flows through these towers counter-currently. Water sprayed from the top of tower No. 1 absorbs some of the nitrogen oxides on its descent. The weak nitric acid from the base of this tower is pumped to the top of tower No. 2 and so on, through tower No. 4, where the acid reaches 30 per cent strength.

A product of this plant, but not necessarily a product of the arc process, is calcium nitrate or Norwegian saltpeter. This salt is produced by treating limestone with nitric acid.

A use for some of the steam of the waste heat boilers is presented here for evaporation to concentrate the solution



GRANITE TOWERS AT RJUKAN PLANT FOR ABSORPTION OF NITROGEN OXIDES

to 13 per cent nitrogen. Calcium nitrate is used for fertilizer purposes.

The Pauling furnace is operated in a plant of 1,000 tons of nitrogen annual capacity at Patsch, near Innsbruck, Austria. In this furnace the arc passes between two water-cooled, cast-steel tubular electrodes, which are set perpendicular to each other and in a vertical plane and spaced about two inches apart. The arc has the appearance of a vertical sheet of flame extending between the electrodes. The gas leaving the furnace at 1000° C is cooled in a preheater and in a cooling tower packed with fire brick before the gas reaches the steam boilers. The capacity of the Pauling furnace is 800 kilowatts.

In an operation in which the efficiency of energy utilization is so very low the margin of conceivable improvement is great. Such a condition leads naturally to intensive research and development. The results of these investigations with small-scale furnaces have invariably indicated marked improvements in the efficiency of energy utilization. This increase in efficiency gradually diminishes with an increase in the size of the furnace used, until it has disappeared entirely when a size of furnace which might be considered commercial has been reached.

The use of oxygen-enriched air, to the extent of a 50–50 ratio of nitrogen to oxygen gave some promise of increased yields. In such a system, however, economy in the use of oxygen necessitates the return of the gas to the furnace after the absorption of the oxides. Preheating the air entering the furnace has also been tried but it has been found that any advantage gained through such preheating has been lost through increased decomposition of the nitric oxide. Operation of the arc under a pressure of several atmospheres has not given enough promise of improvement to warrant large-scale experiments.

The possibility at this time for marked improvements in operation efficiency is not hopeful and there are indications of the arc process giving way to the direct synthetic ammonia process.

CHAPTER IV

THE CYANAMIDE PROCESS

IN the cyanamide process gaseous nitrogen is fixed by bringing it into contact with finely powdered calcium carbide heated to 1000° C. This formation of calcium cyanamide is represented by the equation

$$CaC_2 + N_2 = CaCN_2 + C.$$

In producing the two reacting materials, extremes of temperatures are employed. Calcium carbide is produced by means of the intense heat of the electric furnace, while the nitrogen is secured through the fractionation of air which has been liquefied at a temperature of 190° C below zero.

The production of calcium cyanamide involves four steps: (1) The production of lime from limestone; (2) The production of calcium carbide; (3) The production of gaseous nitrogen; and (4) The nitrification of the carbide.

In the first step, crushed limestone is burned in a kiln at a temperature of 1100° C until the carbon dioxide has been driven off. This process is represented by the equation

$$CaCO_3 = CaO + CO_2 - 42{,}900 \text{ gram. calories.}$$

and may be carried out in either a rotary or vertical kiln. In the rotary kiln the limestone rock is fed into one end of the kiln which is so inclined that upon rotation the limestone flows slowly down its length. The fuel, dried and finely pulverized coal for instance, is introduced through a burner at this lower end. The rock is gradually decomposed and the liberated carbon dioxide is carried away with the furnace gases, by means of a stack. The burnt lime is discharged at 1100° C to a cooler from which it is conveyed to storage. In this cooler, which may be a rotary kiln usually of smaller diameter and length, the temperature is reduced to about 200° C. Since for the production of calcium carbide limestone of one inch diameter lump is preferred, there is a large quantity of fines, perhaps as much as 25 per cent of the total. These fines are waste so far as the cyanamide process is concerned, but may have a value as agricultural or building lime.

The production of calcium carbide is the power consuming operation of the cyanamide process. The carbide is formed by fusing a charge of a mixture of lime and carbon in the ratio of approximately 1,000 pounds of carbon to 600 pounds of coke in an electric furnace. The reaction is as expressed by the equation

$$CaO + 3\ C = CaC_2 + CO - 121{,}000 \text{ gram calories.}$$

The carbon may be introduced as anthracite coal, charcoal or coke. The latter has proved preferable, however, and is by far of widest use in this industry. It should be a soft burned rather than metallurgical coke and of about three-fourths inch in size. It should contain at a maximum 6 per cent ash and 0.5 per cent moisture.

The carbon monoxide formed, which amounts to about 735 pounds per ton of crude carbide, is not recovered, although it has a heating value of 4,380 B.T.U. per pound.

The furnaces are usually rectangular in shape, 5 feet or 6 feet deep, with the depth below the operating floor, so that the carbide may be tapped from the furnace at the lower floor. The carbon electrodes, usually two feet square each, are clamped three together in such a way as to give the appearance of one big electrode 2 feet by 6 feet. These electrodes six feet long are suspended above the furnace in such a manner that their depth in the charge is automatically regulated by a solenoid which controls a motor-driven hoist.

After the current to the electrodes has been turned on, the mixed charge of lime and coke is shoveled around the electrodes, the depth of charge being such that the top or visible layer is never thoroughly fused. In the fused state, the lime reacts with the carbon to produce molten carbide. The furnace is tapped at intervals of perhaps 35 minutes by fusing the tap plug with a needlelike carbon electrode. As the carbide issues from the furnace at a temperature of 2200° C, it is run into iron chill cars where it is allowed to cool for from one day to a day and a half.

The material is an 80 per cent to 85 per cent carbide, consuming in production about 3,000 kilowatt hours per ton, equivalent to approximately 3,600 kilowatt hours per ton of 100 per cent carbide, when produced in a furnace approximately 22 feet by 13 feet by 6 feet deep.

The 99.8 per cent pure nitrogen necessary for the nitrification of the carbide is separated from the atmosphere through a liquefaction and distillation process. Either one of two systems is generally used, the Claude or the Linde. The cost of the nitrogen is exceedingly small as compared with its fixation cost. When nitrogen fixation is spoken of, the accent should be on the fixation, rather than the nitrogen from a cost consideration.

When air or a gas is compressed the air heats up, due to its compression, necessitating intercoolers and aftercoolers on the compressor. When this air expands, the reverse naturally happens and the expanding air gives up heat or is chilled. Now if the intercoolers on the compressor have cooled the air after compression to the same temperature as it was originally, a cooling effect can be produced. This is the principle of the air liquefier.

In the Linde process the air is compressed to 3,000 pounds and simply expanded, while the cold expanded air passes in heat exchange contiguity with the warmer incoming air, thereby reducing its temperature. In the Claude process the compressed air is expanded in an expansion engine thus obtaining a cooling effect due to external work as well as to the simple expansion or Joule-Thompson effect of the Linde process. Because of this, the air in the Claude process is compressed to only 450 pounds originally, and a shorter time is consumed in reaching the liquefaction temperature.

In the operation of the Claude liquefaction system, air which has been washed in caustic soda towers for the removal of carbon dioxide and passed through separators for the removal of caustic soda spray, is compressed to 450 pounds and cooled in an aftercooler to the temperature of the cooling water, perhaps 20° C. It is then passed through two heat exchangers in series, where its temperature is lowered through exchange of heat with colder outgoing air. Most of the moisture of the air is condensed out here and collected in a purge bottle while any remaining together with any carbon dioxide which may not have been scrubbed out is deposited as a snow on the tubes of the second exchanger. When this snow deposition is great enough to interfere with the free flow of air through it, the flow is automatically changed so that the order of the exchangers is changed. That is, exchanger No. 2 is now No. 1, and receives the air at the cooling water temperature, which is high enough to thaw out the frozen tubes.

From the second exchanger, 80 per cent of the air is expanded in the expansion engine and 20 per cent into the liquefiers. The temperature of the air drops from −108° C at the entrance to the expansion engine to −145° C at the outlet valve. The 20 per cent of the air which entered the liquefier is cooled by gases from the rectifying column to the liquefying temperature. These two parts of air, 80 per cent as a gas and 20 per cent as a liquid, are both admitted to the bottom of the rectifying column which consists of a series of vertical tubes called vaporizer tubes, the lower ends of which are submerged in the liquid. Due to the difference in pressure at the bottom of the rectifying column and the space surrounding the tubes partial vaporization of the liquid takes place causing a liquefaction of the air in the tubes. This liquid from the base of the rectifying column is reintroduced into the column about midway between ends. This liquid is richer in oxygen than the original air. The uncondensed gas rich in nitrogen passes through the condensing coil submerged in the liquid which is cold enough to liquefy the nitrogen. This nearly pure liquid nitrogen is passed to the top of the rectifying column from which nitrogen gas of 99.99 per cent purity comes off at a temperature of −190° C and, after passing back through the liquefier and out through the tubes of the heat exchangers, is available for the nitrification of the carbide.

NOMENCLATURE FOR CLAUDE PROCESS FOR PRODUCTION OF PURE NITROGEN GAS[1]

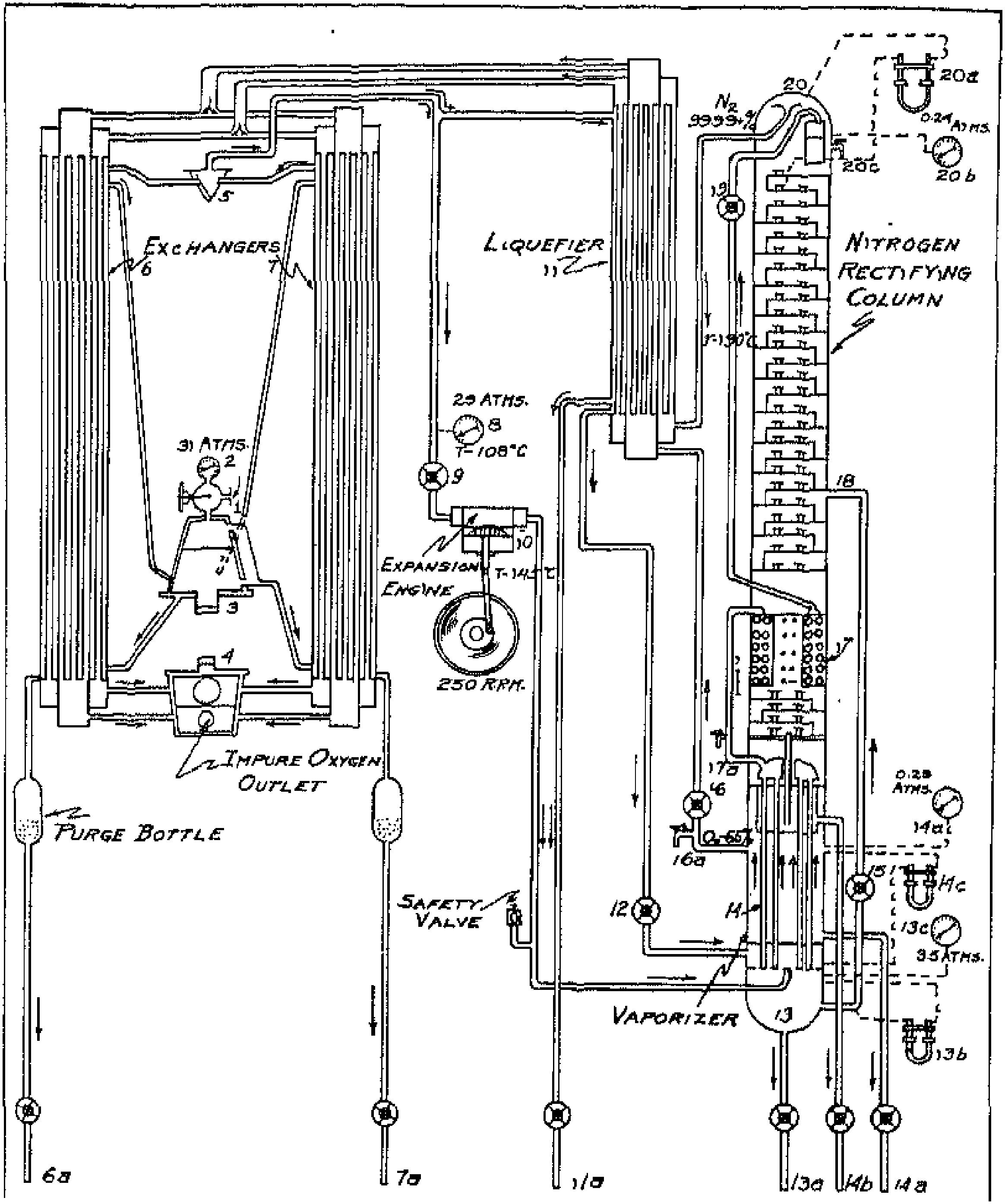
1. Control valve of air entering exchanger.
2. Gauge for the pressure of the compressed air supplied to the apparatus.
3. Valve for inverting the compressed air circulation in the exchanger.

[1] From Fixation and Utilization of Nitrogen, Report #2041.

4. Valve for inverting the oxygen and nitrogen circulation in the exchanger.
5. Valve for inverting the compressed air at the exit from the exchanger.
6. Exchanger for cooling the incoming air.
6a. Drain valve for purge bottle of exchanger.
7. Exchanger for cooling the incoming air.
7a. Drain valve for purge bottle of exchanger.
8. Gauge for the pressure of the compressed air at the expansion engine inlet.
9. Control valve for the expansion engine.
10. Expansion engine for cooling air by external work.
11. Liquefier for liquefaction of air.
11a. Drain valve for the liquefier.
12. Valve for throttling the liquid-air supply to same pressure as engine exhaust.
13. Lowest compartment of rectifying column.
13a. Drain valve for lowest compartment of rectifying column.
13b. Water level for the liquid rich in oxygen.
13c. Gauge for the back pressure in the lowest compartment of rectifying column.
14. Vaporizer tubes for liquefaction of air.
14a. Mercury level of the vaporizer.
14b. Oxygen pressure gauge.
15. Valve for controlling the upflow of the liquid rich in oxygen.
16. Valve for the outlet of the impure oxygen gas.
16a. Cock for sampling waste oxygen.
17. Coil submerged in cooling liquid for liquefaction of nitrogen.
17a. Cock for testing the purity of nitrogen leaving the vaporizer and going to the condensing coil.
18. Inlet to the rectifying column of the liquid rich in oxygen.
19. Valve to control the flow of liquid nitrogen to the top of the column.
20. Top of the rectifying column.
20a. Water level for the liquid poor in oxygen.
20b. Nitrogen pressure gauge.
20c. Cock for the nitrogen test.

Before nitrification the carbide must be finely pulverzied so that at least 85 per cent of it passes through 200 mesh screen. This necessitates a series of grinding operations following the breaking up on the carbide pig. In this pulverized state carbide readily reacts with the moisture of the air to generate acetylene gas which forms explosive mixtures with oxygen. Because of this it is necessary to carry on these grinding and conveying operations in an atmosphere of nitrogen. Frequent analyses are necessary, therefore, to guard against greater concentrations of oxygen and acetylene than 2 per cent and 1 per cent, respectively.

There are two types of nitrifying ovens in operation, a continuous and a discontinuous or batch type. Operation


Exchangers
6
7
5
31 Atms.
2
1
3
4
Impure Oxygen Outlet
Purge Bottle
6a
7a
Liquefier
11
25 Atms.
8
T-108°C
9
Expansion Engine
10
T-145°C
250 RPM.
Safety Valve
11a
N_2 99.99+%
20
20a
0.24 Atms.
20b
20c
19
Nitrogen Rectifying Column
T-190°C
18
17
17a
16
16a
O_2 65%
12
14
0.28 Atms.
14a
15
14c
13c
35 Atms.
Vaporizer
13
13b
13a
14b
14a

of the latter type accounts for at least 95 per cent of the cyanamide output of the world. In operation of the discontinuous type a steel cylinder with perforated walls paper-lined and containing a pasteboard cone to provide an electrode space is filled with the finely ground carbide. This cylinder is contained in a gas-tight cylindrical oven. When the temperature within the oven has reached 1000° C, nitrogen is admitted and the electric current turned off. The reaction is then self-sustaining and continues for between 24 hours and 48 hours, depending upon the size of the oven. The equation for this reaction is

$$CaC_2 + N_2 = CaCN_2 + C + 98{,}430 \text{ gram calories.}$$

The energy consumption for this nitrifying operation is approximately 115 kilowatt hours per ton of nitrogen fixed.

Since the composition of the calcium cyanamide depends upon the quality of the raw materials and methods of operation, it varies with different plants. The composition of the cyanamide produced at U. S. Nitrate Plant No. 2 at Muscle Shoals, Alabama, was as follows:

	Per cent
Calcium Cyanamide	61.2
Calcium Oxide	20.0
Calcium Carbide	1.5
Calcium Sulphide	0.2
Calcium Phosphide	0.04
Free Carbon	12.5
Silica	2.4
Iron and Aluminum Oxides	1.8
Magnesium Oxide	0.2

Upon completion of the nitrifying operation, the cyanamide pig is removed from the furnace, cooled, broken, crushed, and finely ground in a manner and with equipment similar to that used for grinding the carbide.

Since the presence of unnitrified carbide in the cyanamide is objectionable both for the production of ammonia and in fertilizer cyanamide, the finely ground material is sprayed with a limited amount of water in a closed hydrator from which the resulting acetylene gas is carried off.

The principal use for cyanamide is in agriculture as a nitrogenous fertilizer material. For this use however it is generally treated with additional water and briquetted or granulated and sometimes treated with oil to keep down the dustiness.

The product of this process after various stages of treatment is known by various names.

Lime Nitrogen is the crude calcium cyanamide ground to a fine power after removal from the ovens. It is of the composition previously mentioned.

Calcium Cyanamide is the chemical compound as represented by the formula CN.NCa or $CaCN_2$.

Cyanamid is a trade name for the completely hydrated material prepared for use as a fertilizer in the United States. It contains about 45 per cent of calcium cyanamide $CaCN_2$, 27 per cent calcium hydroxide (slaked lime) $Ca(OH)_2$, no carbide and various quantities of other materials which might be called impurities.

Nitrolim is the trade name for the material sold in England for agricultural purposes. It is a lime-nitrogen to which has been added just enough water to destroy the carbide. Practically all free lime is present as calcium oxide.

Kalkstickstoff is the trade name for the material manufactured in Germany for fertilizer use and is similar to nitrolim.

As a fertilizer, cyanamide has several disadvantages. (1) It is a very disagreeable substance with which to work and is somewhat toxic to human beings if the material gets into the skin; (2) It cannot be used in large quantities in mixed fertilizer containing acid phosphate owing to the natural reaction between the acid phosphate and the cyanamide which causes the acid phosphate to revert and also may lead to the formation of the agriculturally undesirable substance, dicyanodiamide; and (3) It has an inherent toxicity to plant growth greater than that of other fertilizer materials. This is particularly noticeable in dry seasons and prevents its use in as large quantities as other forms of nitrogen-containing substances.

Through a process of autoclaving cyanamide may be converted into ammonia. The cyanamide, or lime nitrogen, is introduced into an autoclave with water in the approximate proportions of four parts of cyanamide by weight to five parts of water plus a small amount of strong alkaline liquor, caustic soda, to aid the chemical reaction. The mixture is then treated with steam, and ammonia gas is released according to the equation

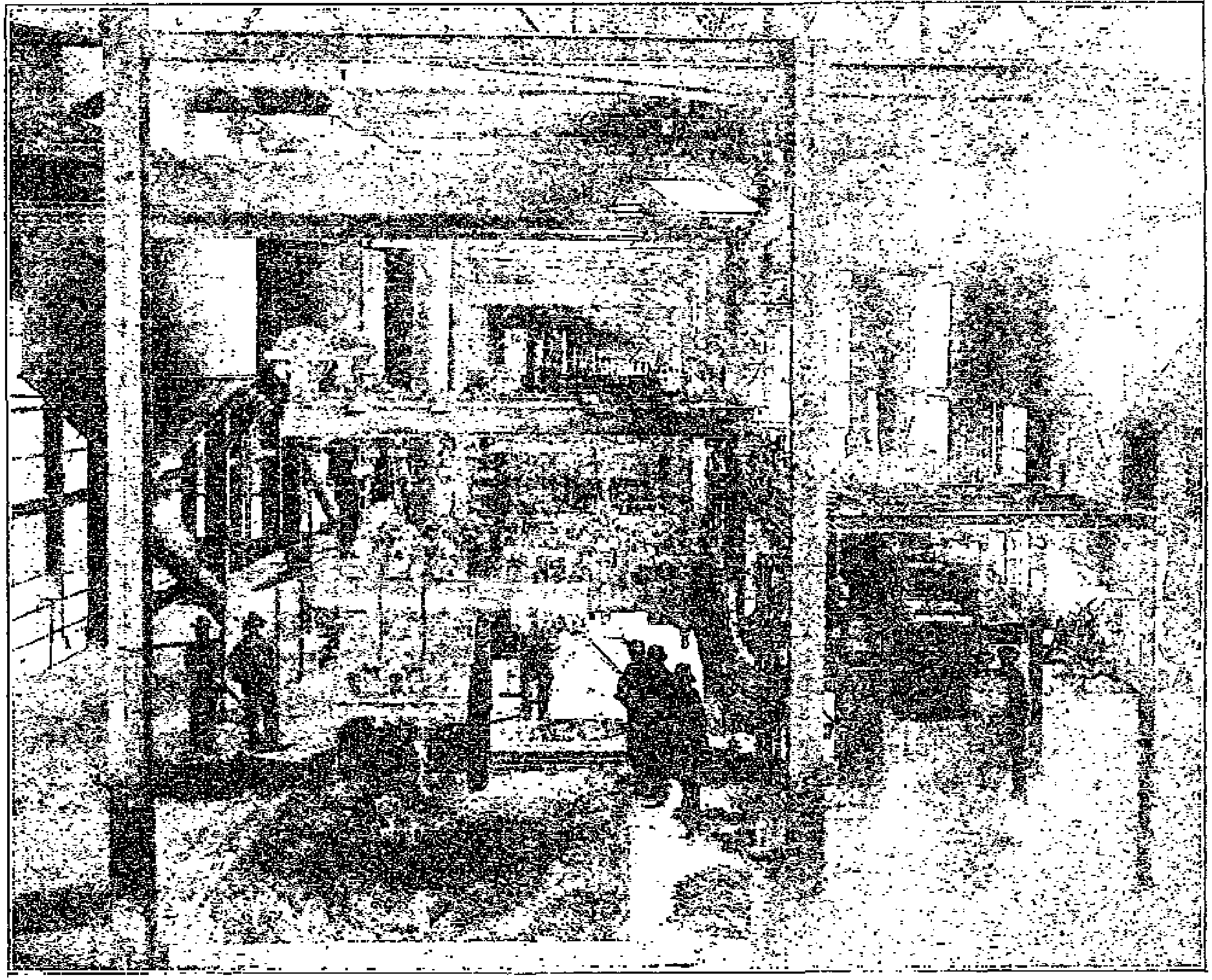
$$CaCN_2 + 3\ H_2O = 2\ NH_3 + CaCO_3.$$

In operation, an autoclave of 6 feet diameter by 21 feet tall is charged with a filtrate liquor of approximately 2 per cent sodium hydroxide (NaOH) to 9 feet depth. This is approximately 19,000 pounds of liquor. To this is added 300 pounds of soda ash to bring the alkaline strength to 3 per cent sodium hydroxide, and 8,000 pounds of cyanamide. The charge is aërated for 15 minutes to eliminate acetylene, phosphine and hydrogen sulphide as completely as possible. The charging door of the autoclave is then closed and the steam turned on to start the reaction. When the pressure within the autoclave rises to 60 pounds as recorded on the gauge the steam is turned off and the reaction continues unaided. The ammonia outlet is then opened and ammonia with large volumes of steam is drawn off continuously for approximately three hours. During this time the pressure remains rather constant, but it finally drops to atmospheric pressure. The outlet valve is then closed and the steam once more turned into the autoclave for about 20 minutes, when the pressure will have reached 120 pounds per square inch within the autoclave. The steam is again shut off and the ammonia discharge opened. The reaction and consequent release of ammonia now continues for an hour and a half. The sludge remaining in the autoclave is discharged to the slurry troughs which feed the filters.

This ammonia may then be oxidized to nitric acid, which may be neutralized with additional ammonia to form ammonium nitrate. Such is the proposed operation of the U. S. Nitrate Plant No. 2 at Muscle Shoals, Alabama. In order to give a clearer picture of the cyanamide process, there follows an equipment description of this plant, the only cyanamide plant in the United States.

The U. S. Nitrate Plant No. 2 was erected as a war emergency measure for the annual fixation of 40,000 tons of nitrogen in the form of 110,000 tons of ammonium nitrate.

The manufacturing plant occupies an area rectangular in shape 5,310 feet by 2,860 feet with the long dimension running north and south. With the exception of the liquid air production, the sequence of manufacture is from north to south. The raw materials limestone, coal and coke are unloaded from a trestle at the north end of the manufacturing area and started into the process. All materials



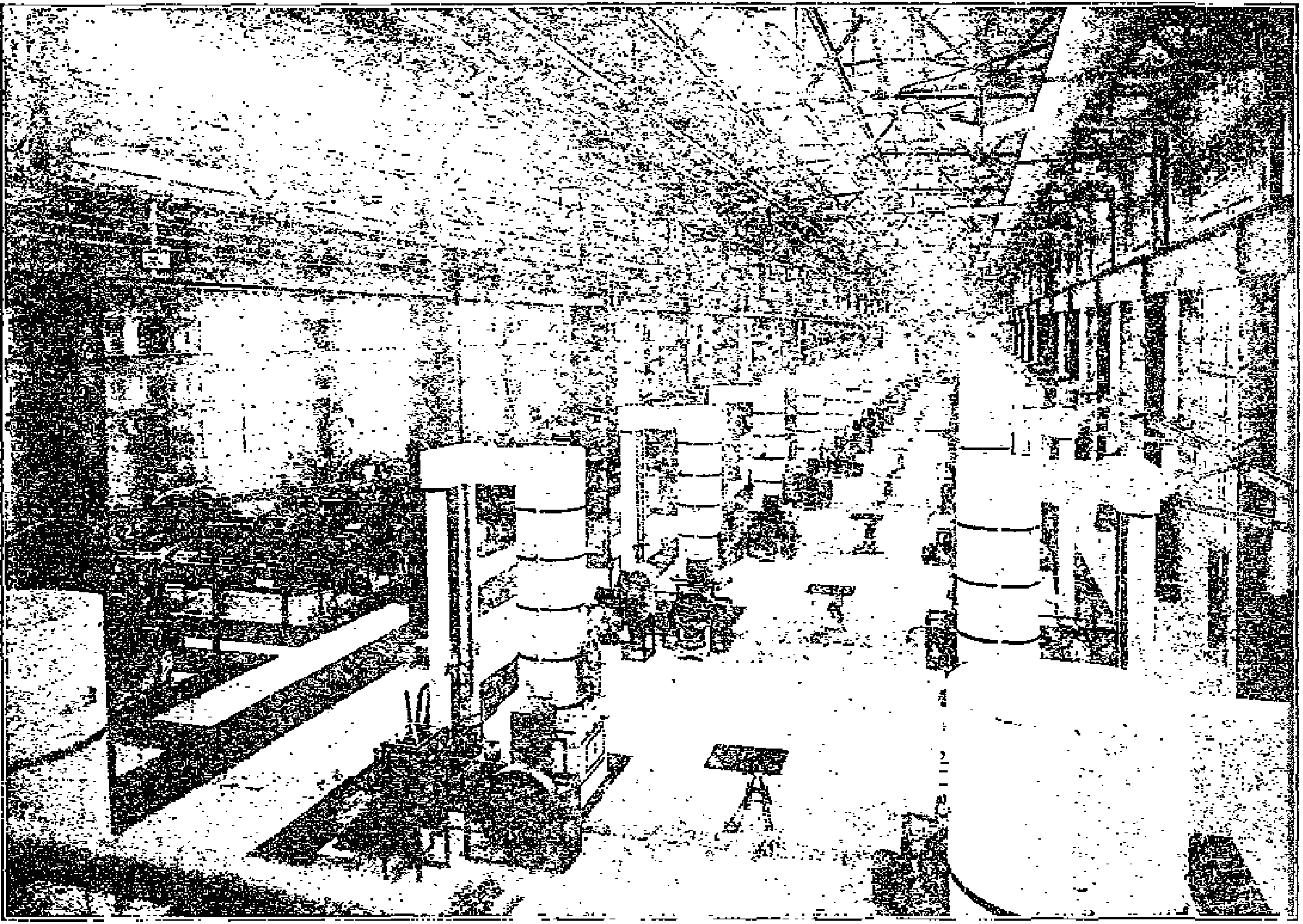
A Calcium Carbide Furnace with Electrodes being removed from the unloading of the raw materials from the cars to the discharge of the finished ammonium nitrate from the grainers are mechanically handled by belt and screw conveyers, bucket elevators, electric traveling cranes and pumps.

The lime-burning plant consists of 7 rotary kilns each 8 feet in diameter by 125 feet long from which the calcined lime is fed to 7 rotary coolers each 5 feet in diameter by 50 feet long. The rated capacity of these is 700 tons of calcined lime per day (24 hours) which is stored in four similar concrete silos of 250 tons capacity. Fuel for the lime kilns is prepared in two Fuller indirect-fired rotary driers, 42 inches by 42 feet, and four Fuller-Lehigh mills. This plant has a rated capacity of 336 tons of dried and pulverized coal per day.

Coke for carbide production is crushed in two crushing units of three sets of double crusher rolls each, and dried in four rotary driers 5½ feet diameter by 40 feet long. This prepared coke is stored in four concrete silos of 160 tons capacity.

Carbide is produced in 12 furnaces 22 feet by 13 feet by 6 feet deep of 60 tons of carbide capacity per day each. Each furnace has three electrodes 16 by 48 by 80 inches each, which weigh together with the cooling head 3,000 pounds. The carbide is crushed and pulverized in three 30 by 42 inch Buchanan jaw crushers, three 10 feet diameter by 48 inch Hardinge ball mills, and three 7 feet diameter by 24 feet Smidth mills.

The liquid air plant of a rated capacity of 12,800,000 cubic feet or 300 tons of nitrogen per 24 hours receives its air through two 36 inch spiral-riveted intake pipes. The air is washed in 8 sets of scrubbers of two to a set. There



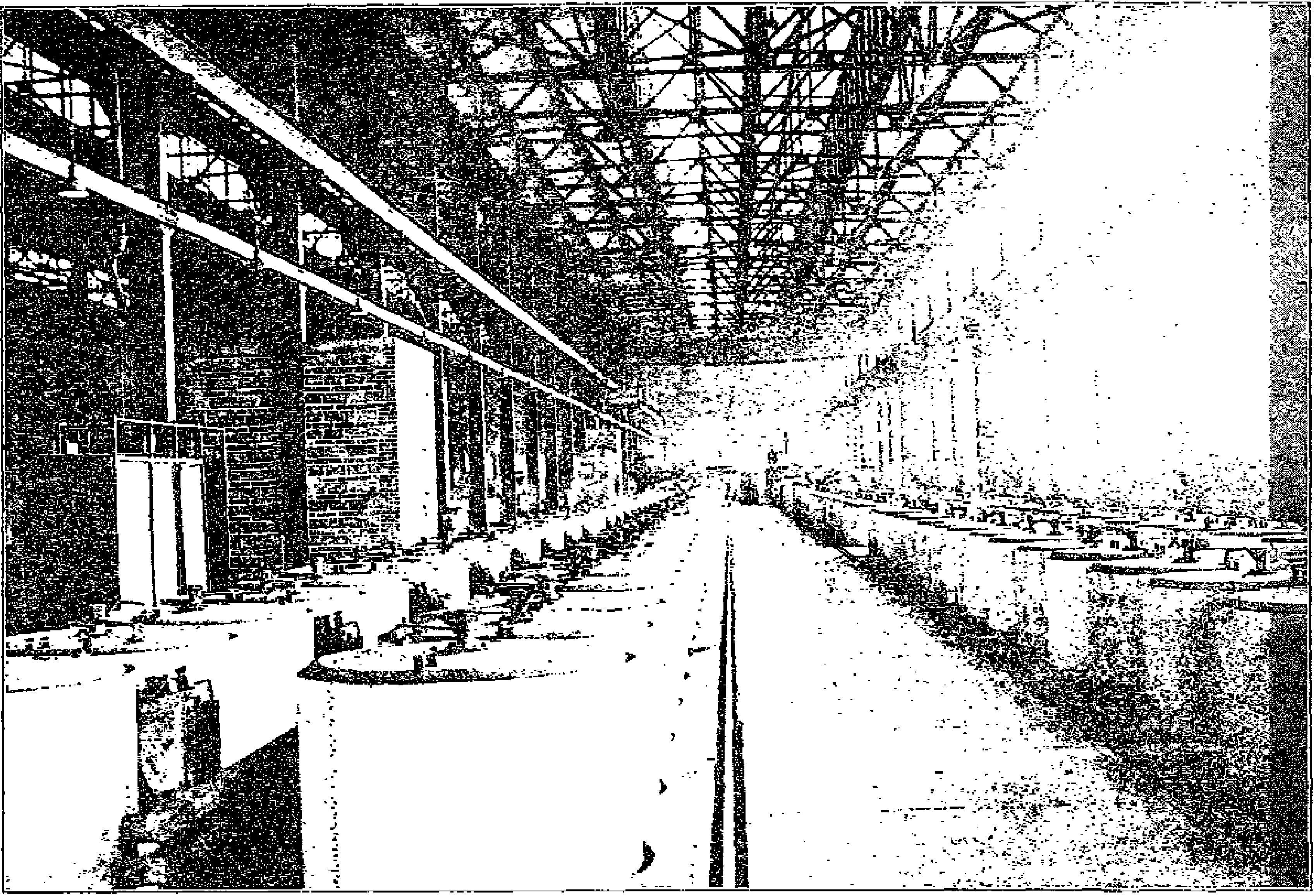
Liquid Air Columns for the Extraction of Nitrogen from the Air are 15 three-stage compressors of about 1,200 cubic feet per minute displacement and a discharge pressure of 600 pounds per square inch. In operation the air is compressed to 450 pounds and is delivered to 30 nitrogen column equipments from which the nitrogen produced is delivered to the cyanamide ovens, one-quarter of a mile to the west, through a 30 inch spiral-riveted pipe.

In the cyanamide plant there are 1,536 nitrifying ovens, each of 2,000 pounds finished product capacity, arranged in 16 rows of 96 ovens each. The maximum rated capacity of this plant is 750 tons of crude calcium cyanamide per 24 hours. The cyanamide ingots after being removed from the ovens by electric cranes are cooled, and then broken by being dropped upon the inclined platform which serves the crushing equipment. After being crushed and pulverized in a plant exactly similar to the carbide crushing plant, the cyanamide is hydrated in three 36 inch by 36 feet long hydrators of a capacity of 2,160 tons of hydrated cyanamide per 24 hours.

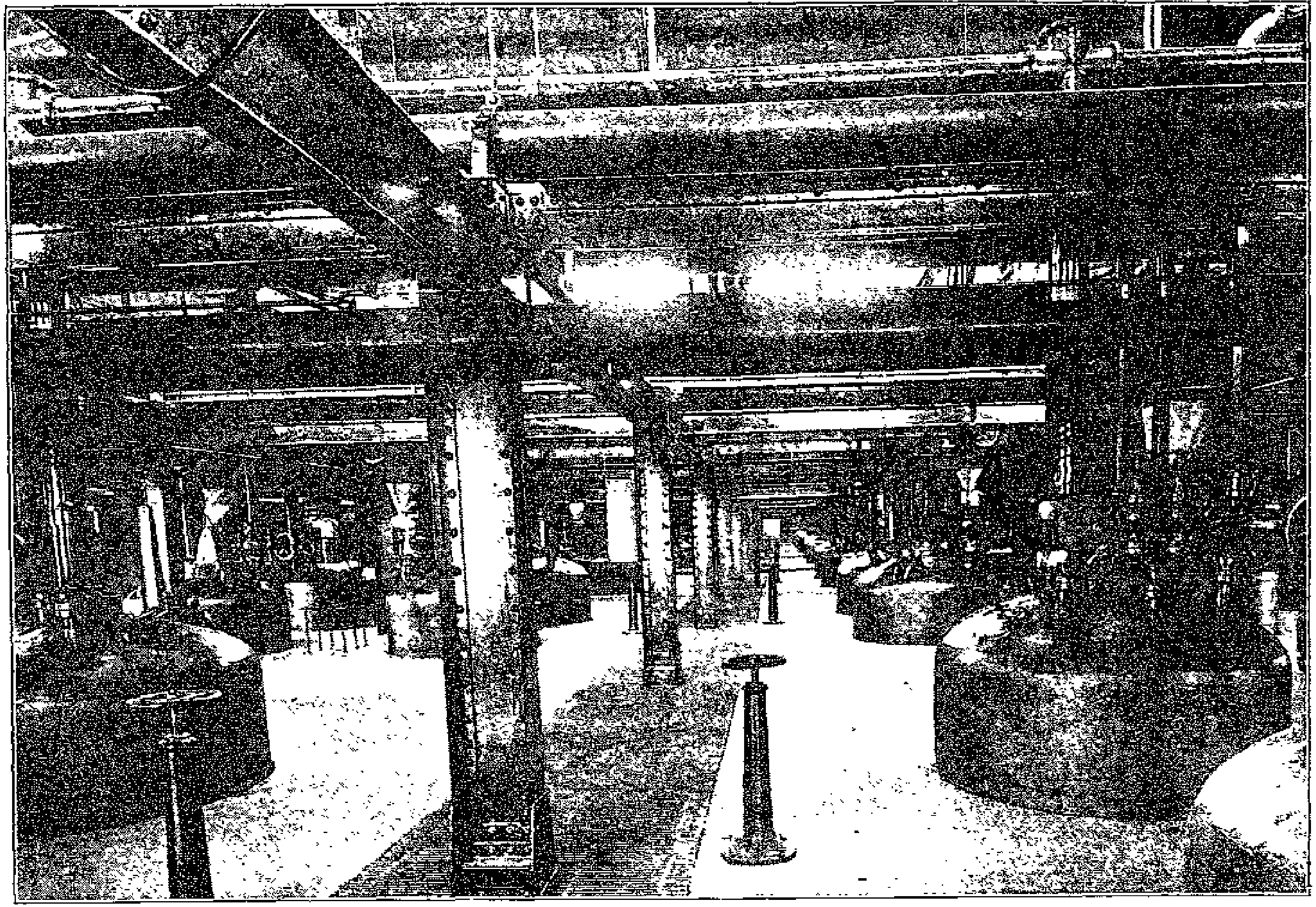
The silo building between the cyanamide plant and the ammonia plant contains nine concrete silos of a capacity of 475 tons of cyanamide each.

The ammonia plant for the autoclaving of cyanamide is of a rated capacity of 166¾ tons of ammonia gas per 24 hours and consists of 56 autoclaves arranged in 14 rows of 4 each. These autoclaves are 6 feet in diameter by 21 feet high and are constructed of welded steel plate of one inch thickness for the side walls and 1¼ inches for the domed tops and bottoms. Each autoclave is fitted with an agitator which revolves at 11½ r.p.m., each set of 4 agitators being driven by one 40-horsepower squirrel-cage induction motor.

Steam for the autoclaves and for heating the plant build-



Lime Nitrogen Ovens in which Calcium Carbide is Nitrified



Autoclaves in which Ammonia Gas is produced ings is supplied by a process steam plant of a total boiler capacity at 120 per cent rating of 3,950 horse power.

After leaving the autoclaves the ammonia gas is washed and dried by being passed through a series of mud drums and an installation of 7 ammonia columns each 9 feet in diameter by 19 feet high connected by 14 inch pipe to 7 dephlegmators each 7 feet 2 inches in diameter by 8 feet 3 inches high and 7 condensers similar in size to the dephlegmators. From the condensers, the ammonia gas is stored in two 60,000 cubic feet gas holders.

The slurry from the autoclaves is treated in 4 steel slurry troughs, each of which feed 5 vacuum filters 6 feet in diameter by 3 feet, making one revolution in 4½ minutes and having a capacity of 2½ tons of sludge per hour. From a hopper the sludge is pumped to a waste dump by four 650 g.p.m centrifugal pumps. The filtrate from each set of 10 filters is pumped by three 200 gallons per minute centrifugal pumps to 8 open-top steel storage tanks 13 feet 6 inches in diameter by 12 inches deep from which it is pumped as needed into seven steel filtrate measuring tanks.

The caustic equipment for preparing the autoclave solution consists of one lime-slaking tank, one liquid elevator, three reaction agitators equipped with air lifts and steam coils, three thickener tanks, three diaphragm pumps, one sludge tank, two 15 g.p.m. centrifugal pumps, one solution tank and one 200 gallons per minute centrifugal solution pump.

In the nitric acid plant there are 696 catalyzer units each consisting of a rectangular aluminum tower 14 inches by 28 inches by 5 feet high. A frame near the bottom of the tower holds the 80 mesh platinum gauze, 13 inches by 27 inches, of 0.003 inch diameter wire. The mixture of air and ammonia gas passes down through the tower over the heated platinum gauze and out through a brick flue to the coolers. There are 25 high temperature coolers, 90 inches in diameter by 12 feet long horizontal, steel tubular, marine type boilers covered with an asbestos coating. The 12 low temperature coolers are 25 feet by 36 feet by 7 feet high constructed of chemical brick with 5 passages so arranged that the gas passes the full length of each cooler 5 times. Projecting down into each of these 5 passageways are 4 rows of 35 cooling tubes each (20 rows in all).

The 12 oxidation towers, 15 feet by 31 feet 6 inches, by 15 feet high are similar to the low temperature coolers, except that they do not contain cooling tubes.

There are 24 absorption towers, 31 feet 6 inches, by 34 feet 2 inches, by 60 feet high. Although these towers are built of brick they serve the same purpose as, and are very similar to, the absorption towers previously described for the arc process plant at Rjukan, Norway. These towers are packed with 6 inch and 3 inch vitrified spiral rings. The acid liquor is raised to the tops of the towers by air lifts in acid wells. There are 120 of these acid wells 12 inches in diameter by 96 feet deep. For weighing the acid there are twelve aluminum tanks each 11 feet in diameter by 10 feet deep equipped with Fairbanks beam scales. There are also 12 closed storage tanks each 31 feet diameter by 10 feet high constructed of reinforced concrete of a total capacity of 3,500 tons of 40 per cent acid.

For the production of ammonium nitrate there are 4 absorption towers 6½ feet square by 30 feet high, built of acid brick and filled with spiral tile, 4 coolers, 7½ feet by 13 feet by 8 feet high, 4 neutralizer tanks, 11 feet by 26 feet by 7 feet high; 4 supply tanks 11 feet diameter by 10 feet high; 16 settling tanks each 18 feet in diameter by 6 feet high; 12 Sperry filter presses and 4 filtrate tanks, 18 feet in diameter by 6 feet deep.

The ammonium nitrate liquor is stored in eight steel tanks 20 feet in diameter by 18 feet high and pumped from these to the 12 feet diameter by 12 feet high supply tanks serving each of the 5 evaporating and crystallizing units. Each of these units consists of 10 enameled evaporating pans, 6½ feet by 11 feet and 20 crystallizing pans and grainers 5 feet in diameter by 18 inches deep.

For maintenance purposes there is a fully equipped machine, pipe and carpenter shop, a foundry and blacksmith shop. There is also a water supply system for domestic and fire purposes, consisting of a 60,000,000 gallon capacity reservoir, a settling basin of 300,000 gallon capacity, a filter plant of 1,500,000 gallons per 24 hours capacity, a clear water basin of a capacity of 500,000 gallons, and a pumping station of 44,420 gallons per minute.

To give a somewhat clearer picture of the size of some of the buildings necessary to house the various equipment, it might be mentioned that the carbide furnace building, 90 feet by 1,050 feet by 64 feet high, if placed over the large Union Station in Washington, D. C., would completely envelop it. The cyanamide oven building is 250 feet by 520 feet by 63½ feet high. The liquid air building or nitrogen plant is 100 feet by 575 feet by 52½ feet high, while the cooling and absorption building of the nitric acid group is 200 feet by 600 feet by 90½ feet high and has a ground area 10 per cent in excess of the United States Capitol building. The buildings of the manufacturing area have a ground area of 29 acres.

The cyanamide process is now very well developed and little may be expected by way of improvements. Some economies of electrical energy consumption have been effected by increasing the size of the carbide furnaces and also of the nitrifying ovens. As can be pictured from the description of the U. S. Nitrate Plant No. 2, a cyanamide plant is a collection of previously well known operations, as for instance, lime burning, carbide manufacture, the liquefaction and fractional distillation of air, etc. It is rather natural then that the possibility of improvement of such a process is less than for a new operation such as the direct synthesis of ammonia.

Although over 95 per cent of the cyanamide produced is nitrified in the discontinuous type of oven, several continuous types have been tried. In one type of continuous furnace operated at Knapsack, Germany, carbide is placed in sheet-metal, collapsible boxes of about 3 cubic feet capacity. An iron car on which have been placed 15 of these boxes runs on a track through a tunnel type of nitrifying oven. As a car is admitted to the tunnel a car containing nitrified material is pushed from the other end through heavy iron doors which as far as possible exclude air from the furnace. The oven was heated by producer gas burned under the first third of its length and the nitrogen admitted counter current to the travel of the car. Many mechanical difficulties arose, however, due to the warping of the equipment from the heat of the furnace.

In France at the Marignac plant, a somewhat similar and more successful attempt was made at the operation of a continuous furnace. This furnace was equipped with caisson doors which minimized loss of nitrogen and dilution by air. This oven was heated by carbon pencils which extended from the sides a short distance above the carbide.

The Stockholm Superfosfat Fabrik is operating still a third type of continuous oven in Sweden. The Swedish ovens are cylindrical towers containing shelves so arranged that the carbide charged in at the top moves downward from shelf to shelf counter current to the flow of nitrogen which is admitted at the bottom of the oven. The heat required to start the reaction is furnished by arcs near the top of the furnace. The nitrified carbide is discharged at the lower end. This is the only really continuous oven and is still in operation.

It has been shown how ammonia may be produced from cyanamide. This ammonia may in turn be oxidized to nitric acid or it may be used to neutralize the various acids for the production of the ammoniacal salts. It may be absorbed in water to form aqua ammonia or it may be compressed and liquefied for refrigeration purposes. Cyanamide may also be a source of urea. In burning lime, large volumes of carbon dioxide gas are given off, which gas is utilized in the production of urea from cyanamide. Calcium cyanamide is fed uniformly into water pumped through a circuit with active agitation and the cooled lime kiln gases are blown into this circuit. The circulating liquid dissolves the carbon dioxide out of these gases forming carbonic acid which abstracts the calcium from calcium cyanamide forming *insoluble calcium carbonate and leaving in solution free cy*anamide. A small quantity of sulphuric acid is added to the solution of free cyanamide which after about 12 hours of gentle agitation combines with water forming a 25 per cent solution of urea. This urea solution is then treated with powdered calcium carbonate, converting most of the sulphuric acid to gypsum which is separated out in a filter leaving a clear solution of urea. This clear solution is then evaporated in a vacuum pan in order to evaporate rapidly without using a temperature high enough to decompose the urea. The solution becomes a syrup and is tapped from the evaporator when about 5 per cent of water remains. This concentrated solution of urea may be chilled in a pan forming a slab of urea, or it may be atomized by a blast of cool air, producing the urea in a pellet form. Such urea contains 44 to 45 per cent nitrogen.

Although there is no cyanamide production in the United States, by far the larger production of the American Cyanamid Company's plant at Niagara Falls, Canada, enters this country either as cyanamide or crude cyanide. The cyanamide is consumed directly in mixed fertilizers where it can be used in proportions of only about 60 pounds of cyanamide to a ton of fertilizer, or it is autoclaved at the "Ammo-Phos" Works, Warners, New Jersey, for the production of ammonia for ammonium phosphate. The crude cyanide is used in metallurgy, in the production of hydrocyanic acid for fumigation and the yellow and blue prussiates at the New Jersey plant.

Cyanide is produced by fusing a mixture of cyanamide and sodium chloride in an electric furnace and quickly chilling the molten mass on completion of the reaction. The cyanide is in the form of calcium cyanide, $Ca(CN)_2$, the sodium chloride acting merely as a flux.

CHAPTER V

THE DIRECT SYNTHETIC AMMONIA PROCESS

THE direct synthesis of ammonia from its elements, nitrogen and hydrogen, is expressed by the equation

$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3.$$

This reaction is accompanied by the evolution of 12,000 gram calories of heat per gram mole of ammonia formed, which heat may be utilized in maintaining conditions necessary to continued operation.

Such formation of ammonia, while very direct, is not quite as simple as the equation might indicate. Although ammonia can be synthesized at atmospheric pressure, the yield is so small as to be wholly impracticable. Further, while the percentage of ammonia at equilibrium is greater at the lower temperatures, commercially practicable operation has not been attained at temperatures below about 450° C. In fact, commercial operation is now carried on according to different methods of operation of the process at pressures varying from 100 atmospheres to 900 atmospheres and at temperatures from 450° C to 700° C. Even at these conditions of pressure and temperature, synthesis is practicable only in the presence of a catalyst. In practice a mixture of three parts of hydrogen and one part of nitrogen is compressed and passed over a catalyst at an elevated temperature. The gas coming off the catalyst will then be a mixture of hydrogen, nitrogen and ammonia with the percentage of ammonia in the mixture dependent upon the conditions of operation. As this mixture approaches an equilibrium point, the maximum quantities of ammonia which may be present in the effluent gases of the converter are shown for various conditions of operation in Figure I.[1]

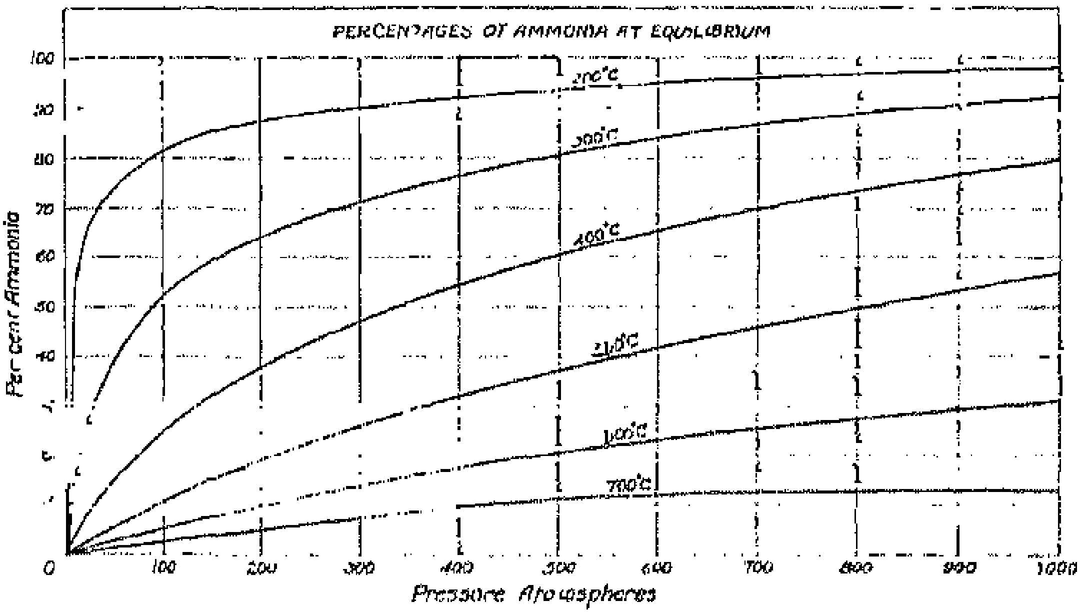


FIG. 1

It will be noticed that a decrease in temperature has even a greater effect than an increase in pressure. For instance at 200 atmospheres and 600° C the equilibrium amount of ammonia is approximately 10 per cent, while at the same pressure but at 400° C, it is nearly 40 per cent. Now, however, if instead of going down in temperature, the pressure is increased to say 900 atmospheres, the ammonia content increases to but 30 per cent. It is evident then that the direction of greatest improvement is in the development of a low temperature catalyst. The consid-

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[1] Larson, "The Ammonia Equilibrium at High Pressures," J. Am. Chem. Soc. 46, 367–72 (1924).

erable effort expended on such an improvement has resulted in the development of a catalyst which operates very satisfactorily at a temperature of from 450° C to 475° C. Continued effort may result in an even lower temperature catalyst but this will present other difficulties. As the temperature decreases the percentage of ammonia increases, and with it the quantity of heat liberated in the reaction, a situation which may well present the problem of taking the heat away fast enough to maintain the lower temperature. However, to overcome this, the pressure might be decreased or the flow of gas over the catalyst increased, either of which or both together would tend to decrease the quantity of ammonia formed per pass, and hence keep the temperature down.

It is readily seen then that the catalyst occupies a most important place in the process. In fact, it has been called the heart of the process and yet very little is known about it. It has been found that iron oxide forms the best catalyst base known at present, but the mechanism of its operation is not known. Practically all of the operations today are by means of an iron base catalyst to which has been added certain substances called promoters which facilitate further the synthesis of ammonia. A catalyst is a material which aids a chemical reaction without itself entering permanently into that reaction and, barring contamination or physical or mechanical destruction, should have indefinite life. As a matter of fact it is known that under certain conditions of operation a catalyst of the promoted iron type has maintained a high efficiency for periods well over a year of continued operation.

According to United States Patent 1,489,497, an active catalyst might be one consisting of 98 per cent of iron, 1 per cent of potassium oxide, and 1 per cent of aluminum oxide. These added promoter materials may be varied, however, from 0.25 per cent to 2 per cent in case of potassium oxide, and from 0.25 per cent to 10 per cent in case of aluminum oxide. In any case the base is the same; that is, iron initially in the form of the oxide.

To quote this patent, such a catalyst may be prepared as follows: " Melt iron in a current of oxygen so that molten iron oxide is formed, or else melt iron oxide. Into this molten iron oxide stir a mixture consisting of approximately 1 per cent of sodium or potassium oxide and approximately 1 per cent of aluminum oxide or silicon dioxide. The total weight of the promoter mixture is thus approximately 2 per cent of the total weight of the mass of the catalyst or catalytic material. It will be understood that these respective proportions may be varied in accordance with the ranges indicated above; but when an iron catalytic agent is employed and ammonia is the product to be obtained, I have found that the proportions just specified give a catalyst or catalytic material that in general produces the most satisfactory result. The mass prepared as stated is allowed to cool and then broken into small pieces."

There are of course other materials which may be used. In some instances a natural magnetite has given good results. In other cases metals other than potassium and aluminum have proved satisfactory as promoters.

As was shown by the equilibrium curves complete conversion of the nitrogen-hydrogen mixture to ammonia cannot be achieved by a single pass of this mixture over the catalyst. In fact, in practical operation the percentage of ammonia formed only approaches these equilibrium amounts. As the rate of gas flow over the catalyst is increased, the percentage of ammonia formed decreases and falls further away from the equilibrium amounts. The percentage of ammonia then is dependent upon the volume of gas per unit volume of catalyst space per hour, or space velocity. For instance, if for every cubic foot of catalyst there is a flow of gas per hour equivalent to 20,000 cubic feet, at normal temperatures and pressures, the space velocity is 20,000.

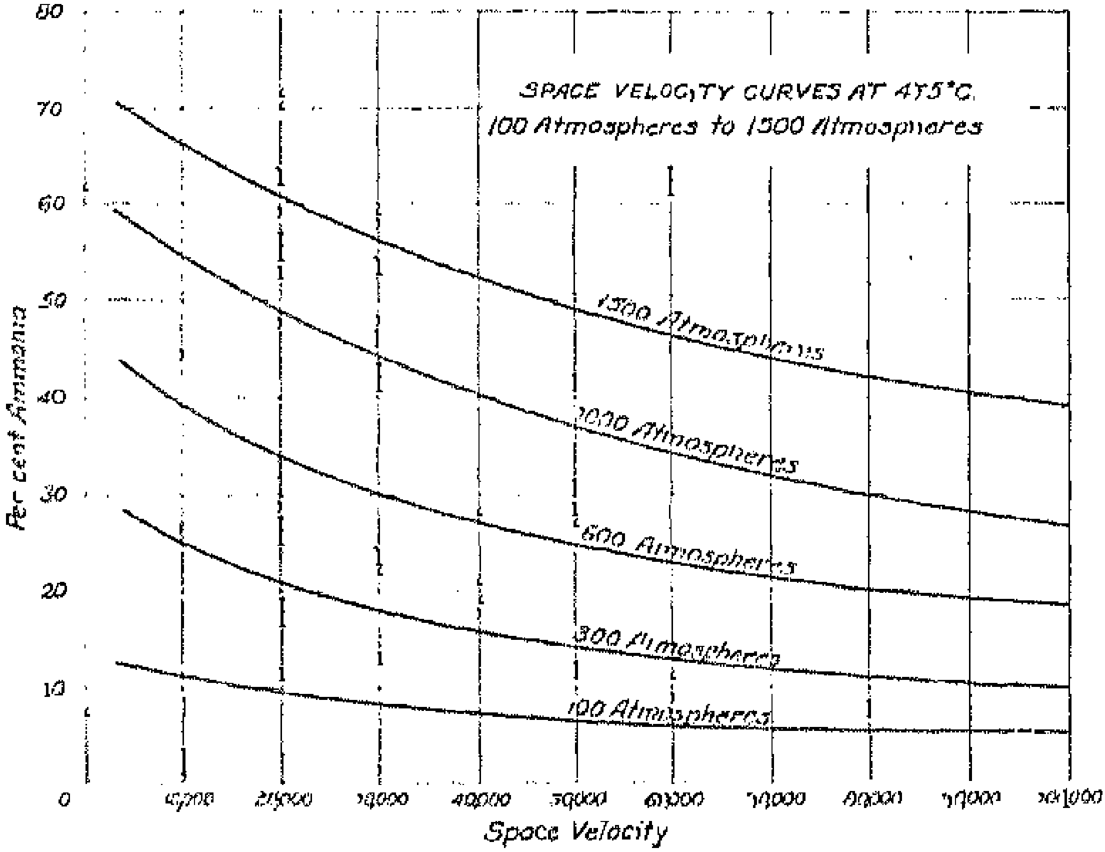

Fig. II

The percentage of ammonia in the effluent gases of a particular catalyst chamber operating at 475° C and at various space velocities for the pressures 100, 300, 600, 1,000 and 1,500 atmospheres was as shown in Figure II. Here again the effect of pressure is shown and in addition there is also shown the effect of volume flow of gas. If the curves were continued up to a zero flow of gas the percentage of ammonia would be practically the equilibrium amounts. It is interesting to note that for 300 atmospheres operation, with a 10,000 space velocity, this catalyst gave about 25 per cent of ammonia in the exit gases. At the same pressure but at 100,000 space velocity, 10 per cent of ammonia was obtained. If one cubic foot of catalyst is considered there is then a flow of 10,000 cubic feet of gas leaving the catalyst per hour, of which 25 per cent or 2,500 cubic feet is ammonia, while in the case of the increased space velocity, of the 100,000 cubic feet of gas leaving the catalyst per hour, 10 per cent or 10,000 cubic feet is ammonia. It is then seen that for this consideration alone there is a decided advantage in working away from equilibrium conditions at least to this extent, rather than towards such conditions.

There is quite a difference of opinion as to the most practicable space velocity. The great majority of the plants now operating are employing a space velocity of 20,000 or less, while the Nitrogen Products Committee of the British Munitions Inventions Department advocated a space velocity of 150,000 or higher. There are many additional considerations to be taken into account, however, in determining upon a space velocity. A low space velocity will require for a certain ammonia production a larger catalyst container than will a higher space velocity. For instance, in the example previously cited, it was found that the hourly conversion of ammonia was four times as great at 100,000 space velocity as at 10,000 space velocity. Obviously then but one-fourth as much catalyst is necessary with the high space velocity as with the low, and hence but a fourth of a cubic foot container is required for the catalyst for 100,000 space velocity as compared with one cubic foot container for the 10,000 space velocity. With the high space velocity, however, different thermal conditions will be present, a circumstance which brings in another point for consideration. The ratio of total gas to ammonia formed in the case of the high space velocity was 100,000 to 10,000 or 10 to 1, while in the other case it was 10,000 to 2,500, or 4 to 1. Thus in the

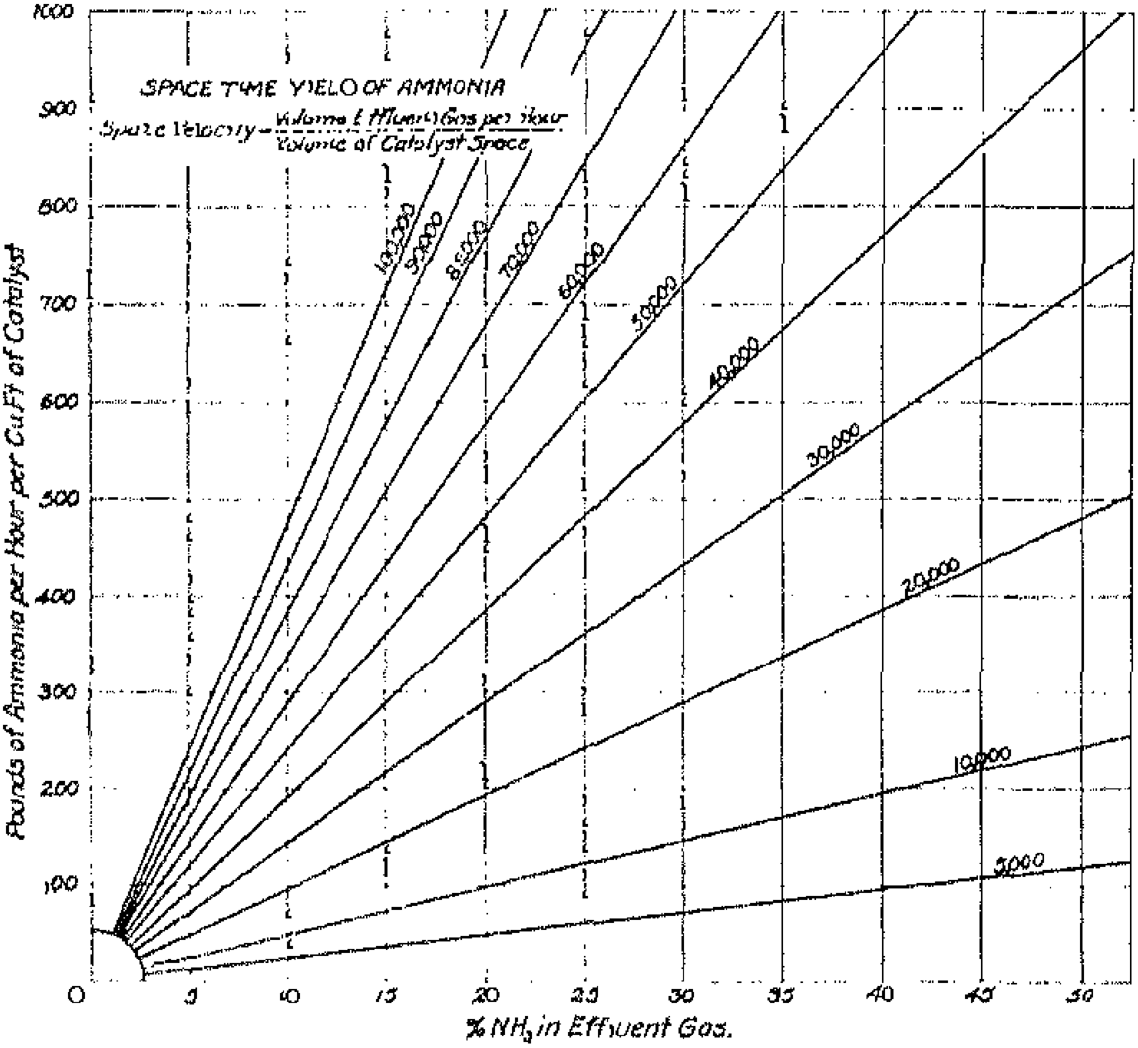

Fig. III

former case there is the heat of formation of one volume of ammonia available to maintain conditions for each ten volumes of gas, while in the latter case this heat of the formation of one volume of ammonia is available for only four volumes.

Figure III is a space time yield diagram based upon the data of Figure II. From such a diagram the operator knowing the per cent of ammonia in the effluent gas and the space velocity can readily determine how much ammonia he should be producing, or knowing the quantity of ammonia being produced and the space velocity, he can determine the per cent of ammonia in the effluent gas. However, by simple analysis he can actually measure the per cent of ammonia in the effluent gas and as he must always have a check on the ammonia production he can easily determine from such a diagram the space velocity or actual flow of gas through the system.

The discussion so far has been of the simple system of passing a compressed mixture of three parts of hydrogen and one of nitrogen over a catalyst at an elevated temperature. As was shown, the gas mixture is not completely converted into ammonia. In fact, only a smaller part is converted. In some actual operations the per cent of ammonia in the effluent gas of the converter is as low as 5 per cent. It can readily be imagined then that the uncombined gases cannot be wasted. They must be returned to the catalyst. This then is a further step in the process which now consists of passing a compressed mixture of 3 parts of hydrogen to 1 part of nitrogen over a catalyst, removing the ammonia formed and returning the uncombined gases to the catalyst for further ammonia formation. In order then that this process may be continuous, a fresh quantity of the mixed gas equivalent to the ammonia removed is added to the system prior to the return of the uncombined gas mixture to the catalyst. As a drop in the pressure of the gas mixture will occur in its passage through the equipment and in the ammonia removal, there is generally inserted in the return system before the converter a circulating pump for the purpose of boosting the pressure up to operating pressure.

This then is the direct synthetic ammonia process for the fixation of atmospheric nitrogen.

Here again the emphasis should be on the fixation rather than on the nitrogen. Securing the free nitrogen is a small part of the cost, while the hydrogen with which the nitrogen is fixed represents approximately 50 per cent of the total cost of the ammonia.

There are today a number of methods of operation of the direct synthetic ammonia process, which of themselves have come to be called processes. In all the various methods nitrogen is fixed with hydrogen as ammonia in the presence of a catalyst. In one method, known as the Claude Process, instead of the uncombined gases being circulated back to the original catalyst after the removal of the contained ammonia, they are passed to another catalyst in series with the first. This is but another method of operating the direct synthetic ammonia process, however, and does not really constitute an individual process for nitrogen fixation any more than do the Casale, Fauser and other methods of operation of this process. Operation, however, might be divided into two general systems, the cyclic, where the uncombined gases following the removal of the contained ammonia are recirculated over the same catalyst; and the series, where these gases pass over a number of catalyst chambers in series with ammonia removal means after each.

There are two means of ammonia removal in commercial practice, absorption and refrigeration. In the first method, water or aqua ammonia is pumped over a tower in which are ascending the gases from the system at the operating pressure. The ammonia gas is scrubbed out of the hydrogen-nitrogen mixture which is returned to the circulatory system while the absorbing liquid is trapped. By regulating the flow of water over the tower, any one of several conditions may be maintained. The quantity of water used in proportion to the ammonia content of the gas may be such that the resulting liquid is a strong aqua ammonia. Increases in the quantity of water used beyond this amount would result in the production of a weaker ammonia liquor while the use of less water would result in free ammonia gas being given off from the solution upon release of pressure. If regulation is so maintained that the quantity of water is such as to carry out complete removal of the ammonia and at the same time to produce a saturated solution at the operating pressure the optimum conditions have been reached, providing ammonia gas is desired. Release of the pressure will free all the ammonia up to the saturation point of the solution at atmospheric pressure. This saturated solution or aqua ammonia may then be pumped over and over again merely absorbing and releasing ammonia. If aqua ammonia is desired as well as ammonia gas, regulation can be such as to have any percentage of the two from all aqua and no gas to all gas and no aqua.

The second method, refrigeration, is in perhaps even wider use than scrubbing, at least from the consideration of the number of plants operating. In this method, the nitrogen-hydrogen-ammonia gas mixture under pressure is cooled, resulting in the liquefaction of a portion of the ammonia, dependent upon the temperature to which the gas mixture is cooled and on the pressure. Figure IV[2] gives the volume percentage of ammonia remaining in the vapor phase in a 3 to 1 mixture of hydrogen and nitrogen saturated with ammonia vapor. If operation is at 300 atmospheres and the cooling medium used chills the gas

[2] Larson and Black. Jour. Am. Chem. Soc. 47, 1015 (1925).

mixture to 15° C, there will remain in the mixture returning to the ammonia converter 5½ per cent of ammonia. The difference between that synthesized and that returned will have been collected as liquid ammonia. If, on the other hand, a cooling medium were used which would reduce the temperature of the gas mixture to say —20° C, there would be only 1½ per cent of ammonia remaining in the gas phase, the difference being collected as liquid ammonia. It is interesting to note the effect of pressure on ammonia removal. At 0° C for instance the ammonia remaining in the vapor phase decreases from 10 per cent at 50 atmospheres pressure to 6 per cent at 100 atmospheres. The advantage obtained by going up to 300 atmospheres, however, is not so marked and at this pressure there remains over 3 per cent of ammonia, while there is 2½ per cent at 600 atmospheres and over 2 per cent at 1,000 atmospheres.

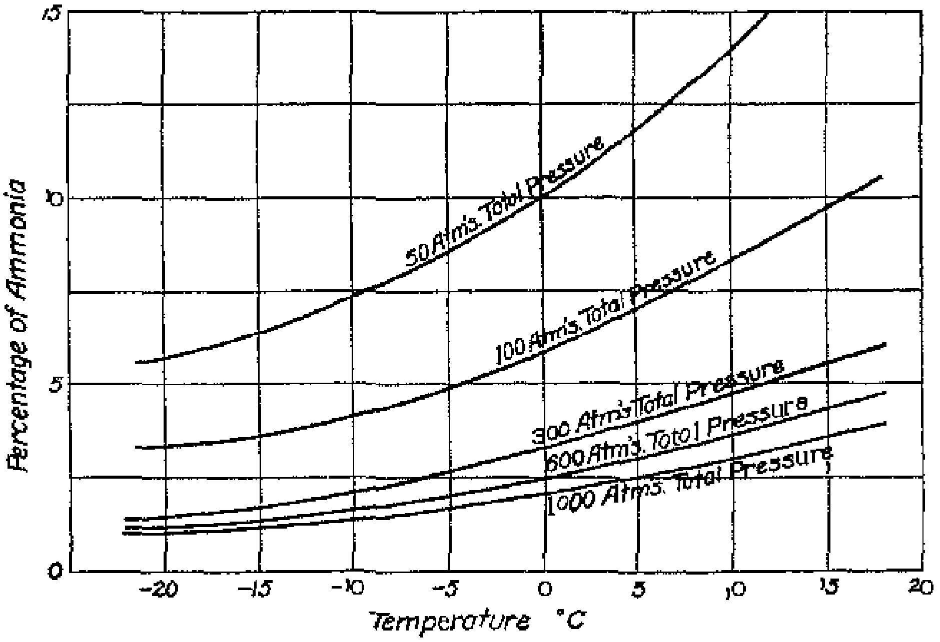

Fig. IV

Before going into the various methods of operation of the direct synthetic ammonia process in any detail, it will be well to consider the sources of nitrogen and hydrogen.

At 20° C and 1 atmosphere, the density of a mixture of one volume of nitrogen and three volumes of hydrogen is 0.02223 pounds per cubic foot. There will then be required per ton of ammonia $\frac{2,000}{0.02223} = 89,970$ cubic feet of the gas mixture. If it is considered that 10 per cent of the gas mixture is lost through leaks and purging, the original volume of the nitrogen-hydrogen mixture for the production of one ton of ammonia will have to be $\frac{89.970}{0.90} =$ 100,000 cubic feet, of which 25 per cent or 25,000 cubic feet is nitrogen and 75 per cent or 75,000 cubic feet is hydrogen.

The largest source of hydrogen for the commercial fixation of nitrogen according to the direct synthetic ammonia process is water gas. This gas results from blowing steam over a bed of glowing coke and has the following approximate composition:

H_2	Hydrogen	50 per cent
CO	Carbon monoxide ..	43 per cent
CO_2	Carbon dioxide	4 per cent
N_2	Nitrogen	2 per cent
CH_4, H_2O, H_2S, etc.	....	1 per cent

In the operation of the water gas generator after the bed of glowing coke is partly quenched by the " make " or steam blow, it is revived by an air blow.

Use is made of the carbon monoxide content of the gas to effect the production of additional hydrogen. Water gas as it comes from the gas generator is treated with steam in the presence of a catalyst, usually iron oxide, at atmospheric pressure and at a temperature of about 500° C. The carbon monoxide of the water gas combines with the steam to form hydrogen and carbon dioxide according to the equation

$$CO + H_2O = H_2 + CO_2.$$

This reaction is exothermic, liberating at 500° C approximately 10,000 calories per mol of carbon monoxide reacting, which is sufficient heat to maintain the temperature. From a hundred parts of water gas there is obtained in this way about 90 parts of hydrogen.

The gas as it comes from the carbon monoxide catalyst chamber contains after condensation of the steam about 45 per cent of carbon dioxide and 3 per cent of carbon monoxide, the remaining 52 per cent being hydrogen from which these other gases must be moved. The larger part of the carbon dioxide may be removed by scrubbing with water. This is usually carried out at a pressure of 30 atmospheres or more. The remaining carbon dioxide, two per cent or less, is removed by scrubbing with caustic solution. The traces of carbon monoxide remaining in the gas are removed by scrubbing with a cuprous ammonium formate solution.

The necessary nitrogen for ammonia synthesis may be produced as lean or producer gas, a gas produced by blowing air over glowing coke. This producer gas is of a composition of about

H_2	Hydrogen	10 per cent
N_2	Nitrogen	60 per cent
CO	Carbon monoxide ..	25 per cent
CO_2	CH_4 Carbon dioxide, etc., methane, etc.	5 per cent

In order to obtain the desired mixture of 3 parts of hydrogen and 1 part of nitrogen, approximately two volumes of water gas are mixed with one volume of producer gas. This mixture is deficient in nitrogen, which deficiency is made up by the addition of free nitrogen, procurable through the liquefaction and fractional distillation of air, in order to keep accurate control of the composition of the mixture.

As an alternative to this mixing of the water and producer gases which had been made separately the mixture could be made directly in a water gas generator by admitting air to the glowing coke along with the steam blow. Due to difficulties of this operation, it has not found favor generally.

Another source of hydrogen in which coal plays the principal part is coke oven gas. The gas as it comes from the by-product coke oven is composed of approximately

Hydrogen	55 per cent
Methane	30 per cent
Carbon monoxide	6 per cent
Carbon dioxide	2 per cent
Illuminants	3 per cent

The hydrogen is removed from this mixture by the liquefaction and fractional distillation process.

Although electrolytic hydrogen is ideal for ammonia synthesis because of its purity it accounts for only 15 per cent of the ammonia produced by the direct synthetic ammonia process. The capital cost of a plant for the electrolysis is high, and except for a few especially favorable locations, electrical energy is more valuable for other industries. Although better results are claimed for certain cells, experience shows that the larger installations in this country have consumed

140 kilowatt hours per 1,000 cubic feet of hydrogen. The 5,000 ampere cells, such as are in operation in the United States at 2.24 volts, consume 268.8 kilowatt hours for the production of 1,920 cubic feet of hydrogen per 24 hours each. These cells contain about 150 gallons of water in which is dissolved 435 pounds of 88 to 92 per cent potassium hydroxide. The cells operate on direct current, necessitating in most cases the conversion of alternating current, usually by means of a motor generator set, although rotary converters are sometimes used.

Hydrogen is also obtained as a by-product in a number of electrochemical processes such as the production of caustic and chlorine. Although the total volume of such hydrogen is very large the quantity available at any one location is relatively small, a ten ton per day ammonia unit being the largest plant operating on such waste hydrogen.

The fermentation of corn for the production of "butynol," butyl alcohol, is a further source of hydrogen. The Commercial Solvents Corporation has been wasting over 1,500,000 cubic feet of such hydrogen per day at two plants at Terre Haute, Indiana, and Peoria, Illinois. During the spring of 1927, a direct synthetic ammonia plant of 12 to 15 tons of ammonia per day capacity was started into operation to utilize this otherwise waste hydrogen. This plant was later utilized for the production of synthetic methyl alcohol (methanol), thus utilizing both the previously wasted hydrogen and carbon dioxide.

There are also millions of cubic feet of hydrogen going to waste from natural gas wells. At Monroe, Louisiana, at the carbon black plant of the Thermatomic Carbon Company some 10,000,000 cubic feet of hydrogen containing about 6 per cent of methane is being wasted daily. This source of hydrogen has been investigated by a large number of industrial concerns. There are several objections to this source, however. The removal of the 6 per cent of methane presents a serious problem, while the doubtful life of this supply greatly magnifies the risk of a large investment such as would be necessary for the utilization of all this hydrogen for the production of synthetic ammonia.

Another source of hydrogen of promise is that of the so-called Liljenroth Process. In this process elementary phosphorus is produced in an electric furnace from phosphate rock, silica and coke. A mixture of phosphorus vapor and steam is then passed over a catalyst maintained at about 700° C, producing phosphoric acid and hydrogen.

The principal reactions are represented by the equations:

$$2\ Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C = 6\ CaSiO_3 + 10\ CO + P_4$$

$$P_4 + 16\ H_2O = 4\ H_3PO_4 + 10\ H_2.$$

In carrying out the latter reaction on a commercial scale, difficulty is experienced in preventing the formation of phosphine according to the following equation:

$$P_4 + 12\ H_2O = PH_3 + 3\ H_3PO_4 + 6\ H_2.$$

The importance of such a source of hydrogen for ammonia production lies in the value of phosphoric acid, a plant food, as an ammonia carrier. A plant for the production of phosphorus according to this process is in operation at the cyanamide plant at Piesteritz, Germany. The phosphorus produced is shipped to the Badische Anilin und Soda Fabrik at Merseburg, where it is oxidized with steam to phosphoric acid and hydrogen.

In addition to the producer gas method for nitrogen production, nitrogen may also be separated from the air by the liquefaction-distillation method described in the chapter dealing with the cyanamide process, or hydrogen may be burned in air to combine with the oxygen to form water, leaving the nitrogen. In this latter method, by admitting the hydrogen in sufficient excess of that required to remove the oxygen, the resulting gas mixture may be adjusted to contain three parts of hydrogen to one part of nitrogen.

If the composition of the air is considered as being

Nitrogen	78.14 per cent
Oxygen	20.92 per cent
Argon	0.90 per cent
Others	0.14 per cent
	100.00

there will be required $\frac{25{,}000}{0.7814} = 32{,}000$ cubic feet of air to produce the nitrogen required per ton of ammonia. From this amount of air there will be $32{,}000 \times 0.2092 = 6{,}690$ cubic feet of oxygen to be disposed of, requiring 13,380 cubic feet of hydrogen. The total hydrogen requirements per ton of ammonia for a plant obtaining its nitrogen in this way will be $75{,}000 + 13{,}380 = 88{,}380$ cubic feet measured at 20° C and 1 atmosphere.

The flow diagram shown in the frontispiece and the model of a complete equipment assembly, Figure V, give a clearer picture of the direct synthetic ammonia process in commercial plant operation.

In the model, hydrogen, produced by one of the methods previously mentioned, is brought into the plant by means of main 1. It passes through blowers 2, where its pressure is increased to 2½ pounds per square inch, to burner 3. Air is introduced to the burner 3 through main 4 and blower 5, in which its pressure is raised to 2½ pounds also. In the burner the hydrogen and air mix and come in contact with a spark. Combustion then takes place with the formation of water which is removed in condenser 6, the residual gases passing out to a gasometer through the mixed gas main 7. By proper regulation of the flow of hydrogen and air to the burner, the gas coming off the condenser can be maintained as a 1 to 3 mixture of nitrogen and hydrogen, which is the ratio of these elements in ammonia. 8 is a control board, containing the volume gauges indicating the flow of gas to the burner, and the valves for regulating this flow.

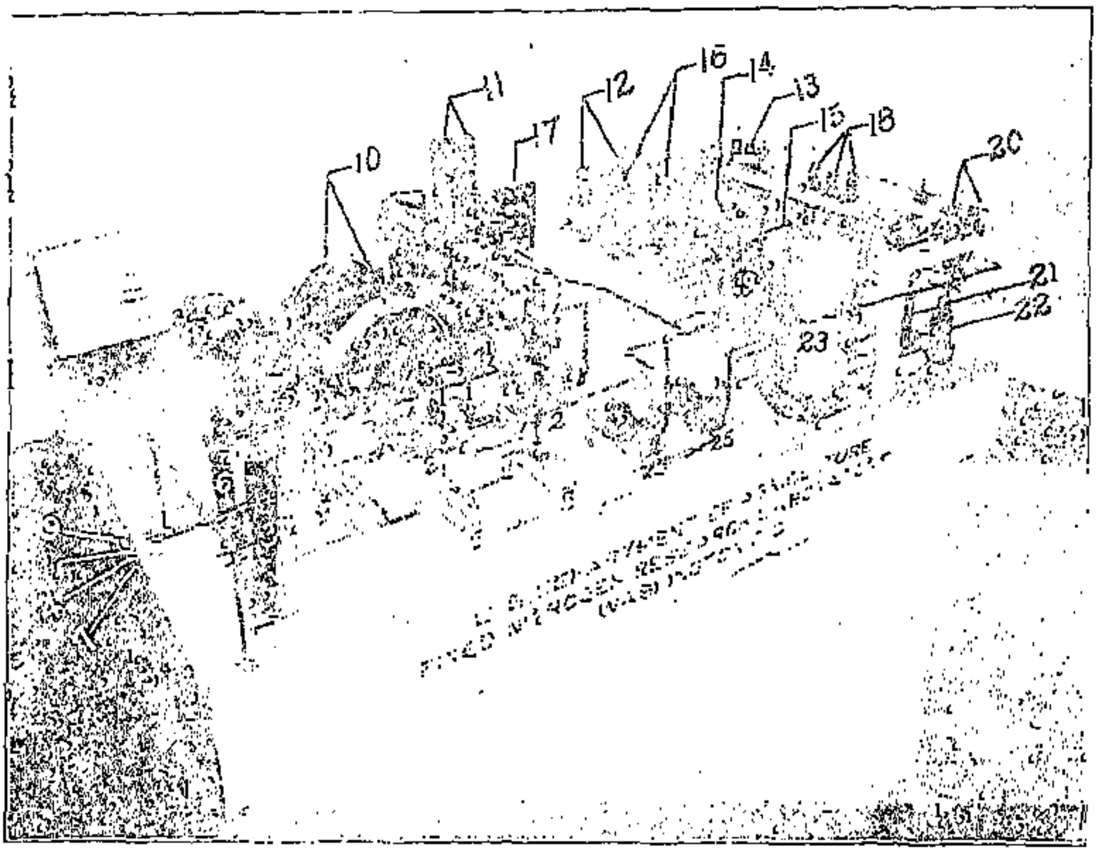

Fig. V

Model of a Direct Synthetic Ammonia Plant

From the gasometer this mixed gas ($N_2 + 3\,H_2$) is drawn through main 9, to the compressors 10, where, in this system, it is compressed to 300 atmospheres. The compressed gas then passes on through oil traps 11 for the removal of compressor lubricant to the purifier 12. This purifier contains a catalyst which while not an efficient ammonia catalyst is not easily poisoned. Only a relatively small percentage of ammonia is formed in this purifier. This is condensed out in the condenser 13 and collected in receiver 14. The ammonia in condensing out of the gas picks up any contained water and water vapors, leaving the residual gas which had been purified of other catalyst poisons in the purifier, pure and dry. When a sufficient quantity of liquid ammonia has been collected in receiver 14, it is unloaded to receiver 15, which when shut off from 14 is subjected only to the vapor pressure of ammonia. It may then be safely unloaded to lower pressure equipment.

From receiver 14 the gas after dropping the liquid ammonia passes through converter 16. In this converter, which contains the ammonia catalyst, synthesis takes place, resulting, at 300 atmospheres and 475° C, in the effluent gases containing 20 per cent of ammonia. 17 is the control panel containing pressure gauges, temperature recorders and purifier and converter control. From the converter the gas mixture ($N_2 + 3H_2 + 20\% \ NH_3$) flows through condensers 18, where a small amount of ammonia is liquefied but not removed. Due to friction in passing through the catalyst mass and subsequent equipment, the gas pressure has dropped and so must be boosted up to the original operating pressure in order that the uncombined gases may be recirculated through the converter. As this gas is at this stage pure and dry, it is desired not to contaminate it by admitting oil or other such lubricant to the circulating or boosting pump. This mixture of ($N_2 + 3 \ H_2 +$ gaseous $NH_3 +$ liquid NH_3) from the condensers 18 is admitted to the cir-

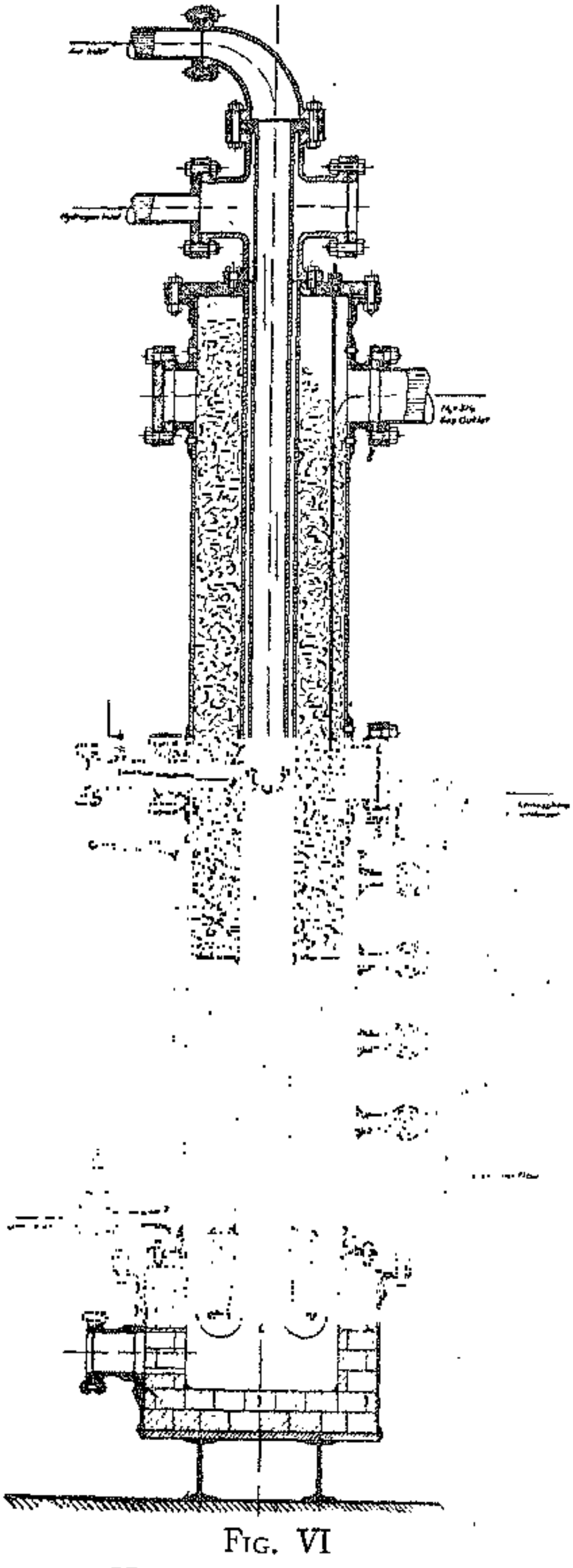

FIG. VI
HYDROGEN-AIR BURNER

culating pump 19, where the liquid ammonia acts as the lubricant. The flow is then through the condensers 20 to receiver 21, where the liquid ammonia is collected while the uncombined gases pass on to meet the make-up gas at the entrance to the converter. From receiver 21, the liquid ammonia is unloaded to receiver 22, from which it is unloaded to the low-pressure storage 23. From this storage, a part of the ammonia goes to accumulator 24, which maintains the level of the ammonia in the condensers 20. The expanded ammonia from the condensers and the surplus ammonia in the storage is then piped off to the ammonia conversion or utilization plant. 25 denotes water pumps for the supply of cooling water to the burner condenser 6, compressors 10 and condensers 13 and 18.

The hydrogen-air burner shown in the model as 3 is shown in cross sectional detail in Figure VI. Hydrogen and air are admitted separately, as shown, and meet at a point about midway of the length of the body of the burner. Here by means of a spark jumping from an extended lead of a spark plug, the hydrogen-oxygen mixture is ignited. The spark of course is necessary only on starting up, after which burning continues unaided and the nitrogen of the air, together with the excess hydrogen, is collected. Each volume of oxygen combines with two volumes of hydrogen to form water, which is removed in the condenser following the burner. The gas mixture from the point of combustion flows down into the mixing chamber and up through the cracked porcelain and shredded copper or copper turnings heated to an elevated temperature by the heat of combustion, and out. The burner operates under 2 pounds pressure which is supplied by positive pressure-blowers. The hydrogen blower should preferably be liquid sealed. Hydrogen and air are admitted to the burner in such volumes that the effluent gas mixture is in the ratio of 3 parts of hydrogen to 1 part of nitrogen. These volumes will be in the ratio of 1 volume of air to 2.75 volumes of hydrogen.

The mixture in the burner is controlled by regulating the volume delivered by the hydrogen and air blowers. Since a definite mixture of hydrogen and air at standard conditions of atmospheric barometer and temperature is required, Venturi meters may be placed before the blowers.

The gas densities of various parts of the system are of interest and importance to the designing engineer. If conditions of operation are such that of 100 volumes of gas leaving the converter, 20 volumes are ammonia and that 15 volumes of ammonia are removed by refrigeration there will then be 80 volumes of the gas mixture ($N_2 + 3\ H_2$) plus 5 volumes of ammonia to be recirculated. Since it requires 2 volumes of ($N_2 + 3\ H_2$) gas to make one volume of ammonia (NH_3) the 15 volumes of ammonia removed must be replaced with 30 volumes of make-up gas. The gas entering the converter will then be 115 volumes, made up of (80 + 30) or 110 volumes of ($N_2 + 3\ H_2$) gas and 5 volumes of NH_3 gas.

$$\text{Density} = \frac{PV}{RT}\ (68°\text{ F and 14.7 pounds) or (20° C and 1 atm.)}$$

Where P = pressure in pounds per sq. ft. = (14.7 × 144) = 2116.8

V = volume in cubic feet

R = 766 for hydrogen

T = temperature, ° Abs. = 460 + 68 = 528.

The densities of the separate gases are as follows:

$$(H_2)\ \text{Hydrogen} = \frac{2116.8 \times 1}{766 \times 528} = 0.00523 \text{ pounds per cu. ft.}$$

$(N_2 + 3\,H_2)$ = 4.25 × 0.00523 = 0.02223 pounds per cu. ft.

(NH_3) = 8.5 × 0.00523 = 0.04446 pounds per cu. ft.

Gas entering converter

$$\begin{array}{lrl} 110 \text{ Vols. } (N_2 + 3\,H_2) = & 95.6 & \text{per cent} \\ 5 \text{ Vols. } (NH_3) = & \underline{4.4} & \text{"} \quad \text{"} \\ & 100.0 & \text{"} \quad \text{"} \end{array}$$

$$\frac{95.6 \times 4.25 + 4.4 \times 8.5}{100} \times 0.00523 = 0.02320 \text{ pounds per cu. ft.}$$

Gas leaving converter

$$\begin{array}{l} 80 \text{ Vols. } (N_2 + 3\,H_2) \\ 20 \text{ Vols. } (NH_3) \end{array} = \frac{80 \times 4.25 + 20 \times 8.5}{100} \times 0.00523 = 0.02667 \text{ pounds per cu. ft.}$$

The deviation of these gases at high pressure from the perfect gas or Boyle's law is also of interest and must be taken into account. Figure VIII[3] shows the compressibility factor for pure hydrogen, pure nitrogen and 75 per cent hydrogen plus 25 per cent nitrogen for pressures from atmospheric to 1,000 atmospheres.

If these gases obeyed the perfect gas laws, the compressibility factor curves would be simply straight, horizontal lines, through the point 1.0 and $\frac{PV}{P_0V_0}$ for 300 atmospheres would equal 1 and $\frac{300}{P_0V_0} = 1$. $P_0V_0 = 300$. However, actually for the $(N_2 + 3H_2)$ mixture $\frac{300}{P_0V_0} = 1.19$ and $P_0V_0 = 254$. One volume of the nitrogen-hydrogen mixture in synthesis proportions at 300 atmospheres pressure will expand to only 254 volumes at atmospheric pressure.

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[3] Bartlett, Jour. Am. Chem. Soc. *49*, 687 (1927).

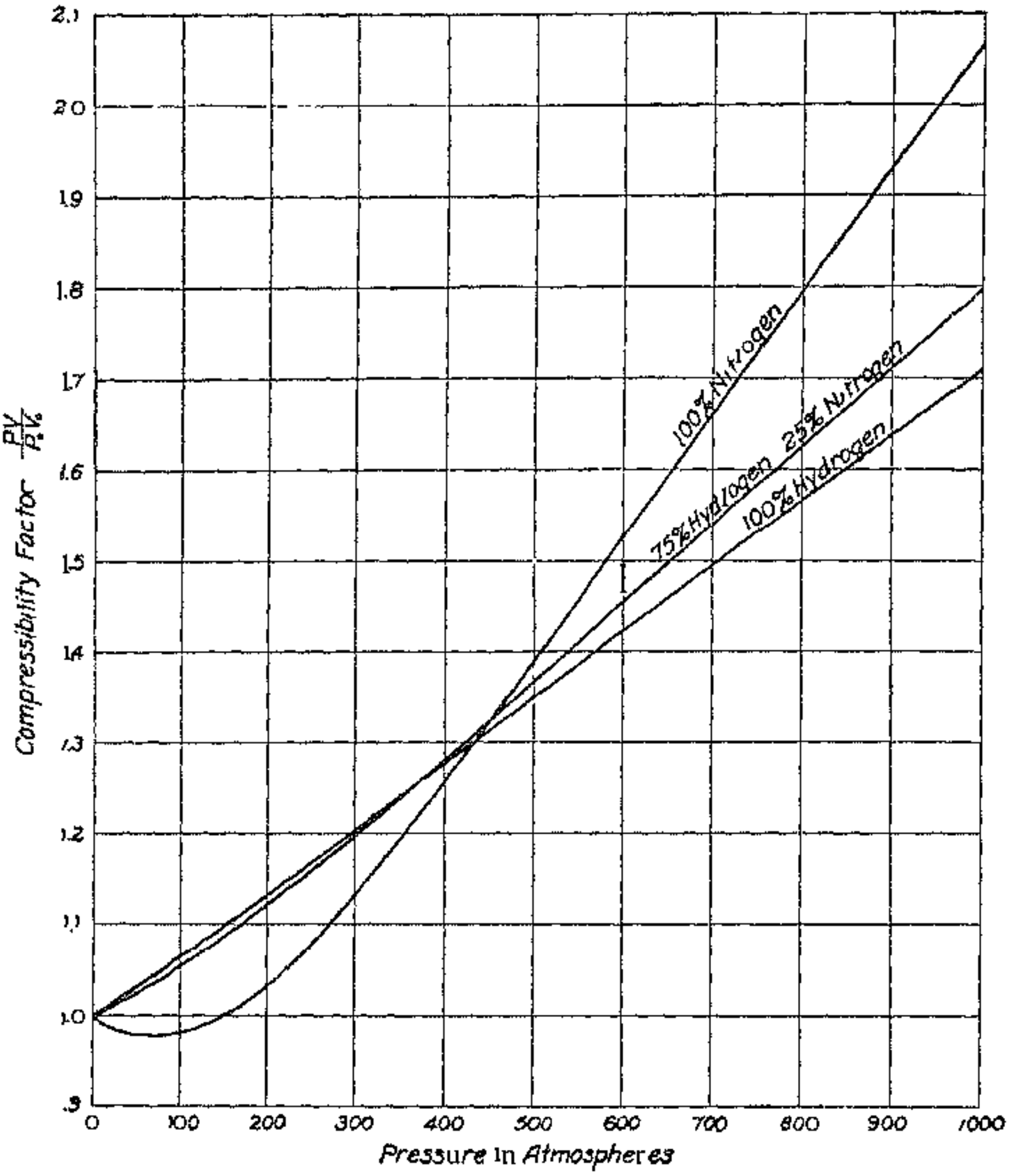


FIG. VII

The following outline of calculations for a 4 stage compressor will give an idea of the effect of these variations from Boyle's law on the proportioning of stage cylinder diameters for a $(N_2 + 3\ H_2)$ mixture discharging at 300 atmospheres.

$$\text{Pressure ratio, } R = \sqrt[4]{\frac{300}{1}} = 4.16$$

P_a = pressure of atmosphere = 14.7 pounds per square inch.

P_1, P_2, P_3, P_4 = pressure at end of 1st stage, 2nd stage, etc.
T_1, T_2, T_3, T_4 = temperature at end of 1st stage, 2nd stage, etc.

$P_1 = R \times P_a = 4.16 \times 14.7 = 61.2$ pounds per sq. in. = 4.16 atm.
$P_2 = R \times P_1 = 4.16 \times 61.2 = 255$ pounds per sq. in. = 17.3 atm.
$P_3 = R \times P_2 = 4.16 \times 255 = 1060$ pounds per sq. in. = 72.0 atm.
$P_4 = R \times P_3 = 4.16 \times 1058.3 = 4410$ pounds per sq. in. = 300 atm.

From Figure VII it is found that the gas volumes are for

4.16 atm. = 4.16
17.3 atm. = 17.3
72.0 atm. = 70.7
300.0 atm. = 254.5

T_1, T_2, T_3, T_4 before intercooler $= 4.16^{0.29} \times 520 = 786°$ Abs.
$= 326°$ F.

It will be assumed that the intercoolers and aftercooler bring the temperature of the gas in each stage down to the temperature of the inlet. Then, if Boyle's law held, the diameter of the cylinders for the different stages would vary as R, and the work of compression would be the same for each stage. Since the gas does not obey Boyle's law and since it is desired to equalize the work of the several stages, it will be necessary to proportion the cylinder according to a new ratio, R′, based on the volumes for the pressures shown above. The effect of this will be to increase the diameter of the last two stages. If such precautions for equalizing the work were not made, the pressure ratio of the first stages would have been increased, thereby lowering the volumetric efficiency and increasing the temperature rise in that stage. The corrected ratios will then be

$$R'_1 = R'_2 = R = 4.16$$

$$R'_3 = \frac{70.7}{17.3} = 4.08$$

$$R'_4 = \frac{254.5}{70.7} = 3.60$$

For a delivery of 215 cubic feet of gas per minute (equivalent to 3 tons of ammonia per 24 hours) at standard conditions, 30 inches barometric pressure and 60° F, a piston speed of 380 feet per minute, single acting, will be considered. A clearance volume of 8 per cent would give a volumetric efficiency of $1 - 0.08\ (4.16 - 1) = 75$ per cent. To provide for leakage at packings, etc., for these higher pressures, a volumetric efficiency of 70 per cent will be assumed. The compressor should be equipped with clearance pockets, which will take care of over-capacity resulting from a possible higher volumetric efficiency. The piston diameters then are:

$$\frac{\text{Piston area (less rod)} \times 380}{144 \times 2} = \frac{216}{0.70}$$

$$\text{Piston area (less rod)} = \frac{215 \times 144 \times 2}{380 \times 0.70} = 233 \text{ sq. in.}$$

Area of 2.375 inch piston rod = 4.43 square inches
Total area of piston = 237.43 square inches

$$\text{Diameter of 1st cylinder} = d_1 = \sqrt{\frac{237.43}{0.25 \times 3.1416}} = 17.4 \text{ inches,}$$

say 17.5 inches.

$$\text{Diameter of 2nd cylinder} = d_2 = \sqrt{\frac{\frac{233}{0.25 \times 3.1416}}{4.16}} = \frac{17.2}{\sqrt{4.16}} =$$

8.43 inches, say 8.5 inches.

Diameter of 3rd cylinder = $d_3 = \frac{8.43}{4.08}$ = 4.17 inches, say 4.25 inches.

Diameter of 4th cylinder = $d_4 = \frac{4.17}{3.60}$ = 2.20 inches, say 2.25 inches.

With an assumed stroke of 17 inches, the revolutions per minute will be:

$$\text{R.p.m.} \times \frac{17}{12} \times 2 = 380 \quad \text{R.p.m.} = 135.$$

A suggestion for the ammonia converter is shown in Figure VIII. The cool gas entering at the bottom of the converter shell travels up through the narrow annular space in immediate contact with the inner surface of the pressure-sustaining shell, to the top of the shell and through a series of holes in the baffle cylinder, as shown in the upper left-hand corner of the drawing. The flow then continues down around the outside of the coiled tubing of the heat interchanging, where it picks up the heat of the hot outgoing gases within the tubes, through the small openings at the bottom of the exchanger, into the heating element well, down around the heating element, and into the catalyst chamber. The gas, after passing up through the catalyst mass, passes out of this chamber through the inside of the tubes of the heat interchanger, where it gives up its heat to the incoming gas, and finally, relatively cool, passes out through the common take-off in the head.

The catalyst space required per ton of ammonia daily production, considering the effluent gases from the converter to contain 20 per cent of ammonia, of which 75 per cent is removed, as previously set forth, and assuming a 20,000 space velocity, is

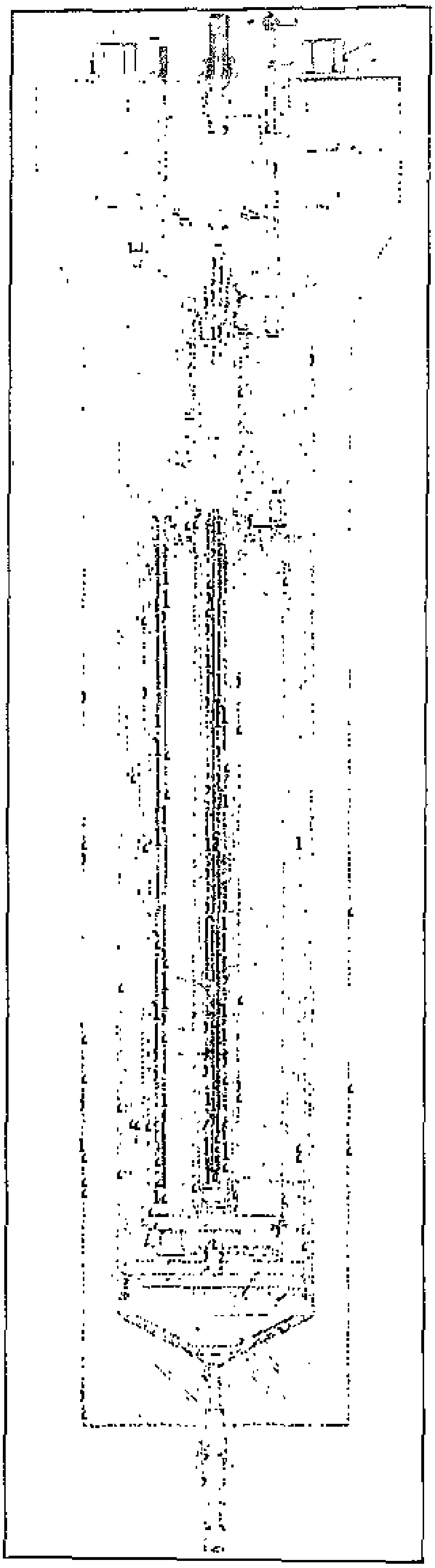


Fig. VIII
Ammonia Converter

$$\frac{\frac{115}{30} \times \frac{90,000}{24}}{20,000} = 0.72 \text{ cubic feet}$$

in which 115 = volumes entering converter, 30 = volumes as ammonia, and $\frac{90,000}{24}$ = volumes of (N_2 + 3 H_2) mixture per hour.

The pressure-sustaining vessel is made up of a steel shell closed by means of a head made gas-tight with a flat copper gasket, and held in place by the ring and bolts as shown. The buttress threads of the ring and shell are interrupted so that in dismantling it is only necessary after loosening the bolts to give the ring a one-twelfth circumferential turn in order to disengage the threads and relieve the head, so that it may be lifted out.

The material for the shell might preferably be of the 2.5 per cent chromium, 0.18 per cent vanadium, 0.30 per cent carbon type of alloy steel especially for such parts as come in contact with the hot reducing ammonia gases. The bolts and bolt ring may be of a 3 per cent nickel steel. As the tensile strength of steels and alloy steels decreases markedly as the temperature is increased from 300° C, it is advisable to keep the converter shell below this temperature. It is for this reason that the cool gas in the case of the converter shown is brought into immediate contact with the inner wall. In cases where it has not been practicable to keep the temperature of the shell down, it has been found necessary to use a nickel-chromium alloy of 80 per cent to 85 per cent nickel and 20 to 15 per cent chromium.

The converter as shown is 16 inches inside diameter by about 6 feet tall. The wall thickness of the shell is 3 inches.

For figuring such thick-walled tubes, the use of a formula $r_2 = r_1 \left(\frac{3T+R}{3T-4R} \right)^{\frac{1}{2}}$ worked up in 1880 by Clavarino as a modification of the formula deduced by Lame in 1833, is still good practice. In this formula r_2 = outside radius, r_1 = inside radius, T = tangential stress, and R = unit internal pressure. For 300 atmospheres operating pressure and an allowable stress of 15,000 pounds per square inch, the wall thickness should be 2.80 inches.

The gasket is a flat, unconfined copper ring, 0.125 inches thick. The theoretical normal load, L required to keep the gasket from blowing and to seal the internal gas pressure from leaking out with friction, F = 0.15 would be the gas pressure against the edge of the gasket divided by twice the friction, 2F, or $L = \frac{P}{0.3}$. It has been found experimentally that a constant C = 2.5 must be introduced for regular " close finish " machining, because of the practical impossibility of machining absolutely perfect the surfaces between which the gasket is squeezed. This formula then becomes $L = \frac{P}{0.3} \times 2.5$. To form a positive gas seal, a small V groove, equivalent to a continuous tool mark, is cut into the surfaces between which the gasket is compressed. The width of the gasket is such that the load applied by means of the bolts is at least 60,000 pounds per square inch causing the copper to flop and the groove is then filled with the flowing copper.

The gasket for the converter is figured as follows:

$$L = \frac{4400 \times 0.125 \times 2.5}{2 \times 0.15} = 4580 \text{ pounds per inch of internal length.}$$

To this must be added the load required to counterbalance the internal gas pressure against the head, as the gasket is made up before pressure is put on the vessel.

$$\frac{16.375^2 \times \pi/4 \times 4400}{16.375 \times \pi} = 18{,}000 \text{ pounds per inch of internal length of gasket.}$$

The total load per inch length of gasket then becomes $4580 + 18{,}000 = 22{,}580$ pounds and the width of gasket is $\frac{22{,}580}{60{,}000} = 0.38$ inch. The width of the gasket will adjust itself to any applied load greater than 60,000 pounds per square inch by flowing, thus increasing its surface area and reaching the equilibrium point of 60,000 pounds per square inch. It is well, for purposes of figuring the bolts and ring, to consider the gasket as being somewhat wider than the actual figured width. If the width is taken as 0.5 inch, the gasket area from the new diameter of $16.375 + 0.5 = 16.875$ inches is $16.875 \times \pi. \times 0.5 = 26.5$ sq. in. At 60,000 pounds per square inch of surface area, the bolts must be able to stand $26.5 \times 60{,}000 = 1{,}590{,}000$ pounds collectively. If fourteen bolts 2.25 inches in diameter with buttress threads are considered, each bolt must take $\frac{1{,}590{,}000}{14} = 114{,}000$ pounds, equivalent to $\frac{114{,}000}{3.24} = 35{,}200$ pounds per square inch compression at root of thread. This stress is transmitted by means of the bolts to the ring and from this into the shell.

The condensers for such a plant might be of the overflow type in which the hot gases pass downward through several pipe coils in parallel, while water or some other cooling medium entering at the bottom of the container surrounding the coils overflows at the top. They might also be of the flood type ammonia expansion in which liquid ammonia which surrounds the coils boils off at the surface, the gaseous ammonia being carried to the utilization plant.

The foregoing are a few of the more important design considerations for a direct synthetic ammonia plant, regardless of the method of operation.

In Germany, where the process was first put to commercial use, operation is carried on according to the original patents of Haber. Hydrogen is produced by the water-gas catalytic method previously described, and often referred to as the Bosch process, after its inventor. The two large German plants, one at Oppau and the other the " Leuna-Werke " at Merseburg, are known as operating the Haber-Bosch process.

At the Leuna-Werke which is located in the province of Saxony, about 100 miles southeast of Berlin, operation is carried out at 200 atmospheres pressure, ammonia is removed by water scrubbing and the uncombined gases are recirculated back to the original catalyst for synthesizing.

When this plant was producing in 1923 at the rate of approximately 220,000 tons of fixed nitrogen annually, there were employed, including the personnel necessary for the coal mining operations, 11,000 laborers, 2,500 operators, and 150 supervising chemists and engineers. Power was produced from brown coal from the company's mines nearby and about 9,000 tons were required per day. At that time coke was used for the production of the hydrogen-nitrogen mixture and about 1,500 tons were required daily. The large quantities of water required, several thousand tons per day, were taken from the Saale River, about a mile distant.

In this plant, 2 volumes of water gas were mixed with 1 volume of producer gas, giving a mixture of approximately 35 per cent hydrogen, 20 per cent nitrogen. 40 per cent carbon monoxide and 5 per cent carbon dioxide, methane, etc. This mixture was then treated as previously mentioned to convert the carbon monoxide with steam to carbon dioxide and hydrogen, after which the composition was approximately 17 per cent nitrogen, 52 per cent hydrogen, 39 per cent carbon dioxide, and 2 per cent carbon monoxide. The bulk carbon dioxide was removed by water scrubbing at 25 atmospheres pressure and the carbon monoxide by scrubbing with cuprous ammonium formate solution at 200 atmospheres. The traces of carbon dioxide remaining were removed by scrubbing with caustic solution.

The catalyst used to effect the synthesis of ammonia is the iron base promoted type. The converters are about 3½ feet in diameter by 40 feet high. The steel casing 5 inches thick is perforated radially with ⅛ inch holes spaced about a foot apart to release gases diffusing through the close fitting steel liner, which serves to protect the pressure vessel from the action of the gases. The effluent gases of the converter contain about 5 per cent of ammonia.

The ammonia is removed by scrubbing the gas mixture with water. The uncombined gases are then returned to the converter by means of a circulating pump for another pass through the catalyst bed.

In the Claude method operation is at 900 atmospheres, and synthesis takes place at about 700° C. There are 5 catalyst tubes or converters, arranged with 2 in parallel, in series with 3 others in series. After each converter there is a condenser for the removal of the ammonia. If it is considered that 50 per cent of the gas mixture is converted into ammonia at each pass and that 200 volumes of gas is used, this 200 volumes will be split, 100 going to each of the two converters in parallel. If 50 per cent of each 100 volumes is converted into ammonia, there will remain after the ammonia removal 100 volumes of the gas mixture to pass through the next converter. Likewise after the removal of the ammonia from this converter number 3, there will be 50 volumes entering converter number 4 and then 25 volumes entering converter number 5. With 50 per cent of these gases being removed as ammonia, 12½ volumes of the original 200 volumes remain to be returned tn the hydrogen purification apparatus.

The compressor for attaining the pressure of 900 atmospheres is of 8 stages arranged 5 on one side and the 3 high pressure stages on the other, of a tandem drive arrangement. Such a compressor for a 5 ton ammonia unit requires a 290 horsepower drive.

The converters are about 6 feet long and 1 foot outside diameter. (Actually 2 meters high by 100 millimeters inside diameter.) They are wound on the outside with nichrome wire for temperature regulation and lagged on the outside. Here again an iron base catalyst is used; it has a life of only 300 hours.

The steel tubing for the conveyance of the gases of a 5 ton unit at this pressure, 900 atmospheres, is of a size such that $\frac{d}{D} = \frac{10}{22}$ where d = inside diameter and D = outside diameter.

The Casale method of operation is based upon thermal control of the ammonia converter. In order to effect this control a certain percentage (supposedly one-third) of the ammonia formed is left in the gases returning to the catalyst, thus retarding the rate of conversion and in turn holding down the generation of heat. Operation is carried on at a pressure within the range of 600 atmospheres to 900 atmospheres and at about 500° C. At 600 atmospheres, 500° C and 12,000 space velocity, the effluent gases of the converter contained 15 per cent of ammonia. The catalyst which is of the iron base promoted type has a life of about 40 days. The converter which for a 7½ metric ton or 8¼ net ton unit is about 20 feet high by 14 inches inside diameter contains about 10 cubic feet of catalyst disposed in an annular ring about 3 inches thick by 18 feet deep. The gas entering the converter through the bottom passes up along and in contact with the inner surface of the shell and at the same time in heat exchange contiguity with the hot outgoing gases. It then passes down over an electrical heater contained in the core of the shell, up through the annular space of catalyst and down in heat exchange contact with the incoming gases, and out.

Another European development is that of Engineer Giacomo Fauser. This Fauser method developed in Italy follows very closely the Haber operation, differing principally in some mechanical features. At 250 atmospheres pressure and 550° C to 600° C, 4 per cent of ammonia is obtained as measured in the gases leaving the catalyst. This ammonia is removed by scrubbing with aqua ammonia, which scrubbing medium is also used as the circulating pump lubricant or seal.

There are a number of other developments. All, however, are essentially modifications of the Haber method of operation of the direct synthesis ammonia process. In the United States it is understood that all the companies operating the direct synthetic ammonia process are licensed to operate under the original Haber patents which are controlled by the Chemical Foundation Incorporated.

CHAPTER VI

ECONOMIC CONSIDERATIONS

THE probability of fixed atmospheric nitrogen products being able to compete successfully with Chile nitrate and more recently of Chile nitrate being able to maintain a position of importance in the face of the competition from the newer synthetic ammonia products have been questions of great concern not only to the nitrogen products industries, but to banking institutions as well. Bain and Mulliken, in Trade Information Bulletin No. 170, January 1924, advise, " It may be stated here that the present price of $48 f.o.b. American Seaboard could, by abandonment of taxes (upon which the Chilean Government is dependent), by improved methods, and by the narrowest margin of profits, be reduced to about $35 per ton. This is not given as a probability, but the ultimate base figure which our fixed nitrates must meet before the Chilean industry will cease to function."

There is no doubt but that the fixed atmospheric nitrogen interests have given this serious consideration and are satisfied of being able to offer competing products at an equivalent or even better price than this $35 figure. It is often argued that the new Guggenheim process which has been put into operation recently in Chile will so affect production costs as to restore Chile to its former position of importance in the nitrogen industry. However, it is reported that $30,000,000 was expended on this venture in Chile, for a producing capacity of 600,000 tons of nitrate per year.

This is equivalent to a capital investment of $50 per annual ton, which at 18 per cent capital charges for interest, amortization, taxes and insurance adds $9 per ton to the cost of production. Taxes and insurance at 2 per cent would amount to $1 per ton, which might also be considered the charge for these items in the older officinas. As the investments in these officinas have already been amortized, interest and amortization items need not necessarily be carried. The new method then will be at a disadvantage of $8 per ton of exportable nitrate from the start and must produce at a cost of $8 less per ton before production by this method can compete evenly with the older officinas. Any reduction in cost greater than $8 per ton will be that much to the advantage of the new method. From this it can be seen that not too great an advantage for Chile nitrate is to be expected from new methods of operation even though the old methods seem very crude.

Perhaps the greatest advantage would be the reducing or total abandonment of the export tax of $12.30 per long ton of 96 per cent nitrate. Through this tax the world has supported the Chilean Government during the past 50 years to the extent of $900,000,000. It cannot be assumed, therefore, that in the event this tax was removed, nitrate would benefit to the extent of $12.30 per ton. Chile would have to make up this loss of revenue in some way, perhaps through increased import duties or other taxes which would affect nitrate production as well as other industries, so that abandonment of the export tax would not benefit nitrate to the full amount of the tax, and probably at best only to a small percentage of it.

A comparison of some of the economic features of the atmospheric nitrogen fixation processes, the products of which are replacing Chile nitrate, will be of interest.

Process	*Capital cost per annual ton of nitrogen fixed*	*Immediate fixed nitrogen product*	*Power consumption in kw.hr. per ton of nitrogen fixed*	*Raw materials required per ton of nitrogen*	*First commercial plant started*	*Installed capacity July, 1927, tons of nitrogen*	*Operating capacity July, 1927, tons*
Arc	$600	Nitric acid	61,000	Air Water	1902	44,750	39,000
Cyanamide	$400	Calcium cyanamide	14,000	Limestone 8.14 T Coke — 2.51 T Coal — 0.98 T Electrodes 179 lb.	1905	325,000	175,000
Direct Synthetic Ammonia with Electrolytic Hydrogen	$260	Ammonia	16,000	Steam — 3 Tons Water — 13 M cu. ft. Air	1920	117,000[1]	75,000
Direct Synthetic Ammonia with Water-gas Hydrogen	$240	Ammonia	3,000	Coke — 2 Tons Steam — 11 Tons Water — 28 M cu. ft. Air	1913	539,000[1]	490,000

[1] In addition, there is installed 66,700 tons of nitrogen additional capacity for operation on by-product coke oven gas hydrogen and other by-product hydrogen.

A glance at this chart shows that not only has industrial development in the art of fixing atmospheric nitrogen been in the direction of lower power consumption, but also in the direction of lower plant cost. This it would seem is a natural course of development and indicates that the fixation of atmospheric nitrogen is developing along sound economic principles.

Because of the large power requirements of the arc process, developments of this process have been in the vicinity of large hydro-electric power sources. It is natural then that this process should be giving way to the direct synthetic ammonia process utilizing hydrogen produced by the electrolysis of water. With the electric power requirements for the fixation of one ton of nitrogen by the arc process, four tons can be fixed by the direct synthetic ammonia process, while the plant cost per annual ton of nitrogen is less than half that of the arc process. In addition, the product of the direct synthetic ammonia process is of wider use than that of the arc process, inasmuch as nitric acid, the product of the latter process, can be produced by conversion methods from the ammonia of the former process, while this conversion cannot be reversed. It is because of these considerations that the Norsk-Hydro of Norway is replacing its arc capacity with direct synthetic ammonia capacity. It is expected that the total arc capacity will be abandoned and that such nitric acid as is required will be produced through ammonia oxidation. Nitric acid it is estimated can be produced at a lower cost by such a method than directly by the arc process. This synthetic ammonia development in Norway which is now under way, is apparently sounding the death knell of the arc process.

In a like manner the cyanamide process is beginning to undergo replacement by the direct synthetic ammonia process. In Sweden, the Stockholms Superfosfat Fabrik, the company operating the cyanamide process, is erecting a Fauser synthetic ammonia plant. Another Fauser direct synthetic ammonia installation has been erected and is in operation at the cyanamide plant of the Mitteldeutsch Stickstoff Werke at Piesteritz, Germany. In Japan, the cyanamide process has already been replaced by both Claude and Casale synthetic ammonia plants.

There will undoubtedly be some cyanamide production for some time to come, but the increase in capacity will be according to the direct synthetic ammonia process, resulting in a continually smaller percentage of the fixation according to the cyanamide process. Such shifts in location as the re-erection in Russia of the cyanamide units dismantled in Sweden to make room for synthetic ammonia capacity will tend to create the impression for a time of increase in capacity, but the actual trend is a decrease.

The reason for this shift to synthetic ammonia is a purely economic one. Nitrogen can be fixed in utilizable forms at a lower cost according to the direct synthetic ammonia process than by the other processes.

If capital charges alone are considered, one advantage of the direct synthetic ammonia process over the other processes can be seen immediately. If capital charges are taken at 18 per cent, these charges for the arc process amount to $108 per ton of nitrogen fixed, while for the direct synthetic ammonia process this charge would be $43.20 per ton, or $46.80 per ton according to the source of hydrogen. This is a disadvantage for the arc process of $62 to $65 per ton of nitrogen fixed. In like manner, cyanamide would be at a disadvantage of $26 to $29 per ton of nitrogen fixed.

The effect of synthetic ammonia in the United States is very marked. Before the advent of the direct synthetic ammonia process, liquid anhydrous ammonia was selling in the Eastern states at 32 cents per pound in cylinders. In addition, it was the practice for the dealer to receive a deposit for the cylinder so that his investment was tied up only in those cylinders which were idle at his plant or warehouses. At the present time this ammonia is being purchased by the Government on contract with the Mathieson Alkali Works at 10½ cents per pound in 100 pound cylinders, delivered to point of consumption, and no cylinder deposit is required. In bulk, it has sold for as low as 6 cents per pound.

Probably because it is a relatively new industry, the commercial fixation of atmospheric nitrogen has been sought out as the solution of various problems. Some of these problems, most of which can be answered from the purely economic situation, follow:

(1) "I have 50,000 cubic feet of hydrogen per day going to waste; will it be profitable for me to install a synthetic ammonia plant in order to utilize this otherwise waste material?"

Particularly in the earlier period of commercial development of the direct synthetic ammonia process this question was very frequently presented. There were a number of plants producing oxygen by the electrolysis of water and wasting the resultant hydrogen. These plants were all relatively small, so that while the total of such waste hydrogen would have been sufficient for a fair sized synthetic ammonia plant, the hydrogen available at any one point was sufficient for only from ¼ ton to 1 ton of ammonia per day. The figure of 50,000 cubic feet given is perhaps a fair average and is sufficient for ½ ton of ammonia. A plant for the production of ½ ton of ammonia would entail very nearly as great a capital outlay as would a 1-ton plant. It would require the same operating labor as for instance a 5-ton plant, while the handling and sale of the product would be exceedingly expensive, making the whole proposition thoroughly impracticable. Hydrogen obtained as a by-product of the electrolytic manufacture of caustic soda is being used and to good economic advantage, but not in such small quantities. The Roessler and Hasslacher Chemical Company is operating a 3-ton unit at Niagara Falls on waste hydrogen. The product is consumed in other operations of the company. This company is also erecting a 6-ton addition to its present plant to utilize the by-product hydrogen of the Hooker Electrochemical Company formerly employed by the Niagara Ammonia Company. The Mathieson Alkali Company is operating very successfully a 10 to 12 ton unit at Niagara Falls, on by-product hydrogen. The smallest plant is a 1-ton unit operating on by-product hydrogen at the plant of the Great Western Electrochemical Company, Pittsburg, California. This unit, however, is one of the original more or less experimental units of the Mathieson Alkali Company. It is believed the capacity of this plant will be increased. The Commercial Solvents Corporation erected a plant at Peoria, Illinois, of a capacity of 15 tons of ammonia per day, which plant is now operating for the production of methanol. The hydrogen is secured as a by-product of the fermentation of corn.

While there might be certain locations of unusual conditions which might make such a plant feasible, it can be said definitely that in general the erection of a synthetic ammonia plant merely to utilize 50,000 cubic feet of hydrogen which would otherwise be waste, is commercially impracticable.

(2) "I am operating a liquid air unit for the production of oxygen; will it be profitable for me to utilize the waste nitrogen for the production of ammonia?"

This question has undoubtedly been brought up because of the name, fixed nitrogen, probably indicating nitrogen as the item of cost rather than the fixation. The actual cost of the nitrogen is so small a part of the total cost that it can have no weight in the decision on the erection of a plant unless all other considerations are at least equal. It is then of such small importance in the consideration of the question that generally speaking it would be wholly impracticable to erect a plant for the operation of the direct synthetic ammonia process, in order to utilize otherwise waste nitrogen.

(3) "Can I operate profitably a plant for the fixation of atmospheric nitrogen on 10,000 horsepower which I have available at very little cost for 12 hours per day, or on 20,000 horsepower which I have available continuously for 6 months per year?"

The question of off-peak or seasonal power for use in the fixation of atmospheric nitrogen is very frequently discussed. Both the arc and direct synthetic ammonia processes must be considered here but the answer is the same for each. With operation for 12 hours per day or operation for 6 months continuously out of each year, a two-ton plant would be required to produce an average of one ton per day or the investment per annual ton of ammonia would be just doubled. If the arc process is considered first and power is taken as having a value of $10 per horsepower year, which is certainly high for such use, it can be seen that the saving through the use of free power figured at this rate would be approximately $100 per ton of nitrogen fixed. The plant, however, would cost $1,200 per annual ton of nitrogen fixed, which at 18 per cent would amount to $216, as against $108 for a plant operating continuously. Such a plant, in order to utilize free power which could not have a value for this purpose even continuously of over $10 per horsepower year, would pay $108 for this advantage of a maximum of less than $100. In addition, labor costs would be doubled or nearly so. This proposition then must be considered as being commercially impracticable.

The same answer presents itself from a consideration of the direct synthetic ammonia process. It would not be at all practicable to operate this process 12 hours per day. It might be possible to produce hydrogen 12 hours and convert it with nitrogen into ammonia during 24 hour or continuous operation. This would necessitate large hydrogen storage, however, which would be very nearly if not equally as expensive as the additional plant required for 12 hour operation. The cost of the plant per annual ton of nitrogen fixed as ammonia would be $520, twice that for a plant which would operate continuously; at 18 per cent the capital charges would amount to $93.60 per ton rather than the regular $46.80, while the advantage from the use of free power which might have a full value for this purpose of a maximum of $15 per horsepower year would be $35. Labor charges would be excessive here too.

These considerations indicate rather clearly that under ordinary conditions at any rate the processes for the fixation of atmospheric nitrogen are more or less continuous processes and not well adapted to the use of off-peak or seasonal power.

(4) "I have a Delco unit on my farm which generates 8,000 kilowatt hours of electrical energy per day in excess of my requirements; can I use this for the production of atmospheric nitrogen fertilizers for use on my farm?"

The answer to the question of using such small power as might be available from a farm Delco light unit can be found in the previous considerations. It is most certainly not economically practicable. The electrical energy cited in this case as being available is about enough for the production of ½ ton of ammonia per day, which could be transformed into 2 tons of sulphate of ammonia per day for instance. However, the actual cost of this material, if all costs were considered, would be nearly twice that of the equivalent material on the market delivered at the same site. The investment for the necessary plant would be approximately $100,000. The only justification for such production, it would seem, would be to provide an occupation of interest where cost considerations were of no consequence.

(5) "Is it economical to utilize the hydrogen of the natural gas wells for the fixation of atmospheric nitrogen?"

This question is one which has had and indeed is now having considerable time and study devoted to it. The principal wells now being considered are those of the Thermatomic Carbon Company at Sterlington, near Monroe, Louisiana. This company is cracking the natural gas for the removal of carbon as carbon black, thereby releasing to the atmosphere millions of cubic feet of gas of an approximate composition of 92 – 94 per cent hydrogen and 8 – 6 per cent methane with slight other impurities. This it would appear is a source of hydrogen for the production of synthetic ammonia, which is of great value. However, there are several drawbacks which have undoubtedly prevented industrial interests from using this gas. In the first place, the removal of the methane is an unsolved problem industrially, and secondly, there is no certainty of supply. Any or all of the wells of this field might shut off almost over night. It might be argued that a water-gas plant could then be erected while the advantages of the natural hydrogen would have been enjoyed as long as the supply lasted. The difficulty there is that a water gas plant would naturally be erected at a site near low priced coal and coke, which site or sites may not be in close proximity to the gas well. Such is the case at Monroe.

This question is far from settled, however, and this hydrogen may yet be utilized. A report later denied was published to the effect that the I. G. Dyestuffs Corporation of Germany had secured an option to a lease or purchase of the properties at Monroe. It is known that several groups of technicians of these German interests, of which the Badische Anilin und Soda Fabrik was foremost, made a very detailed study of the situation and it is believed that some of the members of the commission reported favorably on the project.

(6) " Is it economically feasible for the city gas companies to utilize their off-peak gas producing equipment for the production of hydrogen for the fixation of atmospheric nitrogen as ammonia? "

A pamphlet of the American Gas Association shows that there are large city gas production units which are idle about 11 months of the year in order to take care of the peak load of the year, the period from Thanksgiving to Christmas. Consideration has been given by this association to the feasibility of utilizing this off-peak equipment for the production of hydrogen for, among other materials, the production of synthetic ammonia.

A study of the situation, however, discloses that the equipment available at a city gas works for use in the synthesis of ammonia represents only 10 per cent of the total cost of a new plant built from the ground up. A plant utilizing this off-peak equipment could then by operating 90 per cent of the time just break even with a complete new plant operating 100 per cent of the time. The advantage would be that the investment in this gas equipment would be taken care of during the time it would otherwise be idle. However, there are a number of conditions such as unsuitable plant location, perhaps, and certain operational difficulties from such dual use of equipment which would undoubtedly offset this advantage and render the use of such equipment impracticable. Here again there might be certain local conditions in a few instances which would render this attractive but generally speaking it can be considered as not commercially feasible.

CHAPTER VII

AMMONIA CONVERSION PRODUCTS

THE preceding chapters indicate that from the present viewpoint at least the nitrogen source of the future will be the direct synthetic ammonia process for the fixation of atmospheric nitrogen. Chile nitrate, the arc process and the cyanamide process are all gradually but nevertheless effectively being displaced as sources of supply by the synthetic ammonia process.

Sir Max Muspratt, a director of Imperial Chemical Industries, Ltd., recently made the statement in London that the "fixation of atmospheric nitrogen through the intermediate stage of ammonia seems to have established itself as definitely superior to other methods of fixation." He advised further that the production of cyanamide is "certainly waning," and that the natural nitrate of soda from Chile has the greatest difficulty in competing with fixed nitrogen of synthetic origin.

In view of this condition, then, it is of the greatest importance to those interested in the fixation of atmospheric nitrogen to consider the conversion products of ammonia, the immediate fixed nitrogen product of the direct synthetic ammonia process. Although ammonia is used as such in refrigeration and the chemical industry, its greatest use at this time is undoubtedly as the nitrogen carrier for various fertilizer salts. As was mentioned earlier, these salts may be formed by the neutralization of various acids with ammonia.

In Figure VIII are shown diagrammatically the flow charts for the materials ammonium sulphate, urea, nitric acid, ammonium nitrate and ammonium phosphate. These are the materials of perhaps most immediate concern and from which various combinations can be prepared.

Although sulphate of ammonia is very widely produced at this time and it is felt in some quarters that the market is supersaturated, it is believed that because the sulphate is so well known to the fertilizer trade, it will be given serious consideration as a consumer of further increases in synthetic ammonia production.

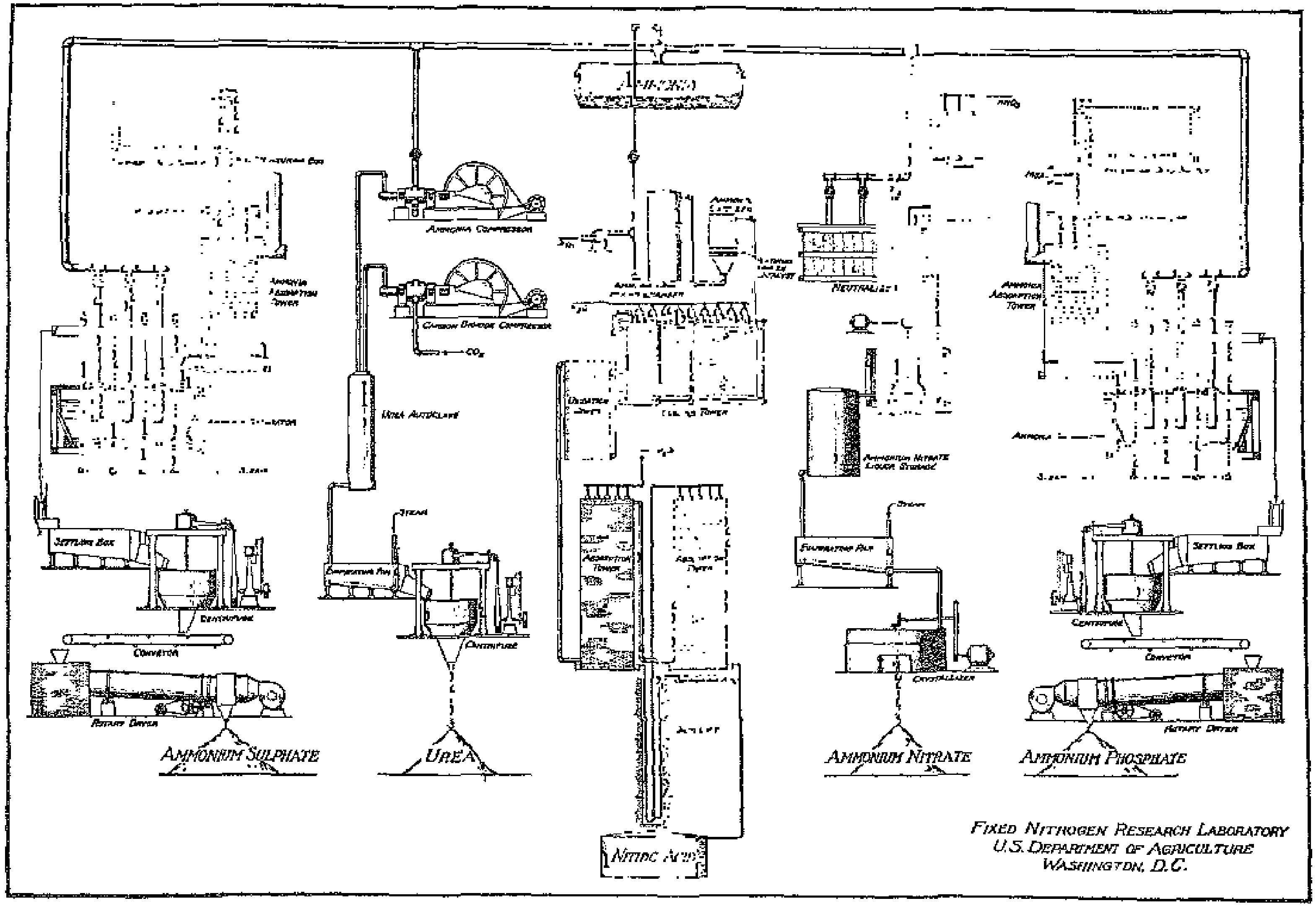
Utilizing sulphuric acid, ammonium sulphate may be produced by either the cold or hot method.

In the first method, usually employed at the by-product coke ovens, the gas containing 1 to 2 per cent of ammonia as it comes from the ovens is partly cooled and passed through the tar extractor to the ammonium sulphate saturator containing dilute sulphuric acid. The resulting salt is ejected from the saturator to the drain tables or settling boxes, while the gas minus its ammonia passes out through an acid trap.

The saturator in this case is maintained at about 60° C (140° F). The excess water introduced with the sulphuric acid and as wash water is carried off with the large volume of gas passing through the saturator.

In the hot method, which will be discussed here, the ammonia is introduced as practically 100 per cent ammonia gas and the saturator maintained at 105° C (221° F). The excess water in this case passes off as steam.

The flow for this operation is shown in the diagram. From an acid supply the 60° Be. sulphuric acid flows by gravity through a measuring box to the tower distributor,



FLOW DIAGRAM FOR AMMONIA CONVERSION PRODUCTS over the checkered packing of the absorption tower, and into the saturator.

Ammonia gas brought in through a main enters the saturator through the ammonia distributor, from which it bubbles up through the liquor which absorbs it. Any ammonia not absorbed passes out into the tower, where it is picked up by the descending acid spray and returned to the saturator.

By means of the steam ejectors, the resulting crystal-laden liquor is ejected to the trough serving the settling boxes. In these boxes the crystals are permitted to build up while the liquor drains off to the return trough and is returned to the saturator. When sufficient crystals have collected in the settling box, they are raked to the centrifugal drier, where they are wrung free of the larger part of the liquor. Final drying takes place in the rotary drier, from which the sulphate may be removed to storage.

Because the size of the crystals decreases as the acidity of the saturator is increased, it is very important to maintain this acidity at a low concentration. In plants using by-product coke-oven gas, the acidity is maintained at about 2.5 per cent. This is possible because this gas, as previously mentioned, is relatively low in ammonia. It would not be practicable when utilizing 100 per cent ammonia gas, however, to drop this acidity below 4 per cent, the range being usually 4 to 7 per cent sulphuric acid. For the present purpose, the acidity of the saturator will be considered as being 7 per cent.

The reaction with heats of formation per mol from the elements, for the substance in the state indicated is:

$$\begin{array}{ccccc} 2\ NH_3\ (\text{gas}) & + & H_2SO_4\ (7\%) & = & (NH_4)_2SO_4\ (\text{aq.}) \\ 23{,}780\ \text{cal.} & & 209{,}680\ \text{cal.} & & 281{,}000\ \text{cal.} \end{array}$$

The heat evolved, therefore, is 47,540 calories per mol of sulphate. In addition there is evolved a heat of dilution of acid, 77.67 per cent (60° Be.) sulphuric acid to 7 per cent of 8,669 calories per mol. The total heat evolved, then, is $47{,}540 + 8{,}669 = 56{,}209$ calories per mol of sulphate.

Let it be considered that all this heat is utilized in converting water at 20° C to steam at 100° C. Each gram of water vaporized will consume $80 + 538.7$ (latent heat of vaporization) or 618.7 calories. 56,209 calories per mol of sulphate are equivalent to $\frac{56{,}209}{132}$ or 426 calories per gram. Then $\frac{426 \times 454}{618.7 \times 454} \times \frac{2000}{8.4} = 164$ gallons of water may be evaporated per ton of sulphate produced.

One ton of sulphate of ammonia is the equivalent of 515 pounds of ammonia and 1,912 pounds of 60° Be. sulphuric acid. Allowing for loss of acid, it can be considered that one ton of sulphate requires one ton (2,000 pounds) of 60° Be. sulphuric acid. A ton of this acid contains approximately 447 pounds or 53 gallons of water. The difference between the 164 gallons of water which may be evaporated and the 53 gallons brought in with the acid, or 111 gallons, is the quantity to be admitted to the system as wash water.

Although this wash water should be hot as used, perhaps 80° to 90° C, and so enter the saturator at something over 20° C, yet the recirculated water loses some of its heat in circulating from the saturator through the troughs, settling boxes, and centrifuge back to the saturator and enters the saturator at something below 100° C. These two divergences from the assumed conditions can be considered as approximately balancing each other, leaving the result unchanged.

If it is considered that a centrifuge when loaded contains the equivalent of 250 pounds of dry sulphate, then each wringing of a batch of sulphate may be washed with approximately 14 gallons of water. As the centrifuge operator, however, need not be skilled, but rather mechanically trained to this operation, and as the sulphate is not weighed into the centrifuge nor the wash water measured, this figure of 14 gallons serves merely as a guide. Actually, a careful check of conditions within the saturator must be maintained. It is very easy to admit too much water, requiring additional acid to keep up the acidity, and thus build up the quantity of liquor beyond the capacity of the saturator.

The quantity of sulphate as centrifuged would build up a cake 6 to 8 inches thick round the inner periphery of the basket. During loading the centrifuge should be rotated so as to build up a cake of uniform thickness. At the same time, however, rotation should be slow enough to prevent excessive lose of sulphate through the holes in the basket and also to prevent splashing beyond the confines of the centrifuge of the hot liquor. A maximum speed of 150 r.p.m. has been found satisfactory while loading after which for drying purposes this speed should be increased to 350 r.p.m. and maintained at that speed for approximately 5 minutes.

With an acidity of the saturator of 7 per cent, the resulting sulphate crystals are very small. More rapid rotation of the basket than 350 r.p.m. packs the cake so tight as to render it difficult to remove. Because of a rotation of only 350 r.p.m., however, the sulphate discharged from the centrifuge contains about 3 per cent of moisture, necessitating further drying, as by the rotary drier shown in the diagram, to less than the allowable limit of 0.5 per cent.

In both Germany and England, at the synthetic ammonia plants of the Badische Anilin and Soda Fabrik and the Synthetic Ammonia and Nitrates, Ltd., respectively, sulphate of ammonia is produced from synthetic ammonia through the use of gypsum (calcium sulphate), rather than sulphuric acid. While there are large deposits of gypsum in Germany, there are no important sources of sulphuric acid.

In this method of production, gypsum is ground to a very fine powder and treated while in suspension in water with ammonia and carbon dioxide in a closed vessel for 6 to 9 hours. The reaction is expressed by the equation

$$CaSO_4 + H_2O + 2\ NH_3 + CO_2 = CaCO_3 + (NH_4)_2SO_4$$

Both calcium carbonate and ammonium sulphate are formed. The precipitate of calcium carbonate is filtered off and the solution of ammonium sulphate evaporated to obtain the solid salt. In the Merseburg plant in Germany, 2,300 tons of gypsum were being consumed daily in this operation in 1923, for the production of 2,000 tons daily of sulphate of ammonia. The gypsum is obtained from the company's own mines in the Harz Mountains, about 60 miles southeast of the plant.

The disposal of the calcium carbonate sludge is somewhat of a question. It is for the most part run out onto the ground, forming large puddles or lakes. Some small quantity of it has been disposed of as a chalk or lime for soil conditioning and an attempt is now being made by the English company to reduce the hygroscopicity of ammonium nitrate by mixing the two in such a proportion, nearly ton for ton, that the resulting material will contain 15.6 per cent nitrogen, as does Chile nitrate. It is understood that the Badishche company experimented with this some years ago and found it to be rather unsuccessful.

The gypsum method of sulphate of ammonia production is rather well adapted to that form of the synthetic ammonia process which utilizes hydrogen from water gas, as the necessary carbon dioxide is a waste gas in the production of hydrogen from water gas.

It is the availability of carbon dioxide in such ammonia production that makes the synthesis of urea attractive. The general flow for this formation is shown in the diagram.

In practice, ammonia and carbon dioxide either separately or a mixture are compressed to about 100 atmospheres and admitted to an autoclave. The mixture of these gases forms ammonium carbamate, a very corrosive material, which is the reason for admitting the gases under pressure separately to the autoclave for mixing. The autoclave, which may be lead lined, is maintained at about 150° C for two hours, after which a mixture of ammonium carbonate, ammonium carbamate, urea and water is discharged. This autoclave operation may be more or less continuous with the compressed ammonia and carbon dioxide entering at the bottom and the resulting materials discharged at the top. This mixture is then treated in a still at about 80° C, where the ammonium carbonate and carbamate are broken down to gaseous ammonia and carbon dioxide. These gases are then separated in a column and returned separately for recompression and treatment. The solution of urea is discharged and the water evaporated from it, leaving the solid.

Urea is the most highly concentrated of the nitrogen solids, containing about 46 per cent nitrogen. Because of this high concentration, it is very well suited for small garden plot fertilization, and is generally applied in solution, a teaspoonful in a gallon of water. It has not, however, proven very attractive to the fertilizer trade, although attempts were made through cost concessions to introduce it.

There are two general forms of nitrogen in the fertilizer trade, ammonia nitrogen and nitrate nitrogen. Although it was once considered necessary to supply the bulk of the nitrogen in the nitrate form, this idea has gradually changed with the increased supply of ammonia nitrogen, until it is conceded that the proper balance may be maintained with at least 60 per cent of the nitrogen in the ammonia form. The remaining 40 per cent, however, must be a nitrate nitrogen, which, if the nitrogen is fixed as ammonia, must be a conversion product of the ammonia.

The flow for the oxidation of ammonia to form nitric acid is shown in the diagram. The process consists in passing a mixture of air and 10 per cent of ammonia through a catalyst at a temperature of about 800° C, resulting in the formation of nitric oxide and water essentially as shown by the equation

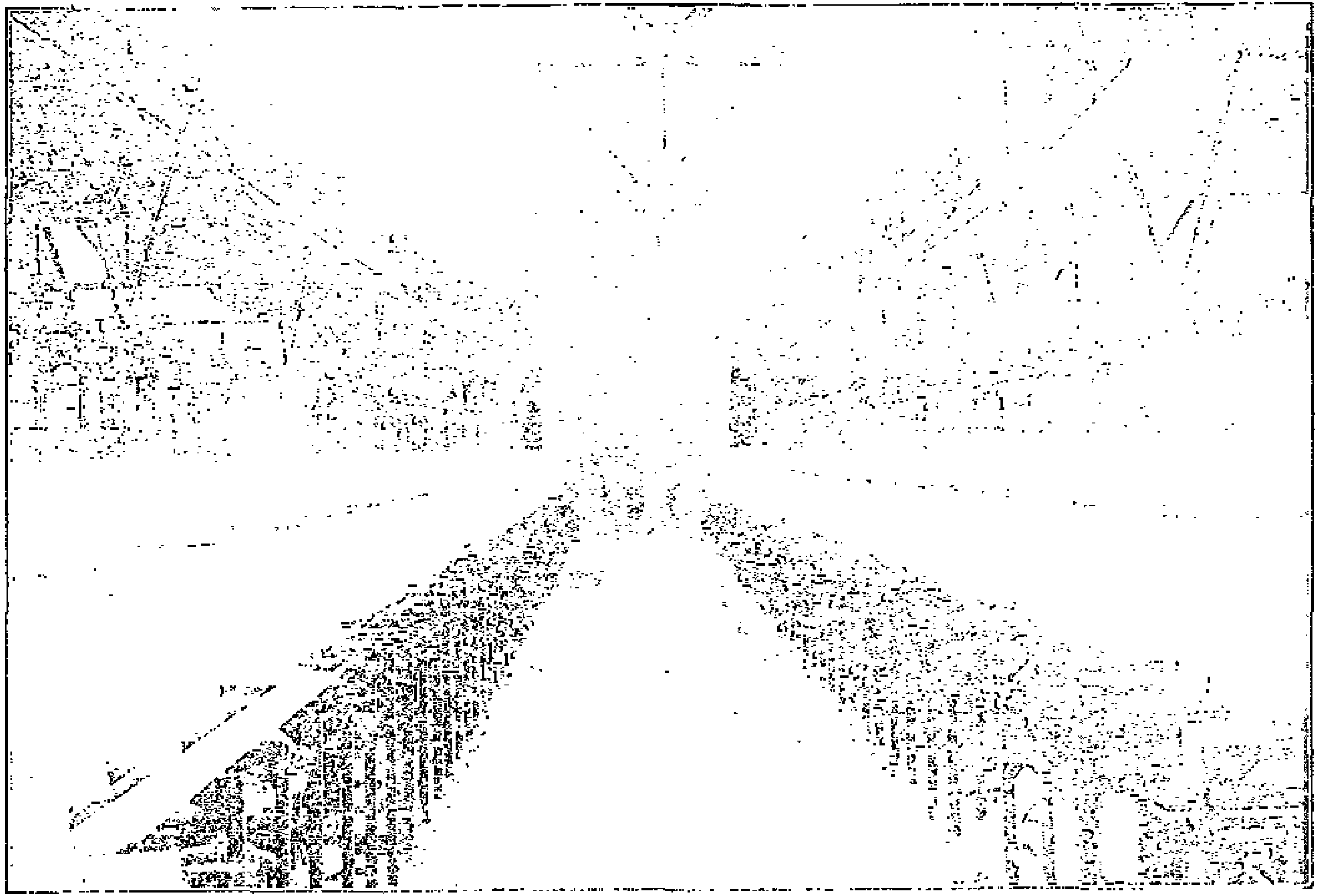
$$4\ NH_3 + 5\ O_2 = 4\ NO + 6\ H_2O.$$

As in the arc process, the nitric oxide thus formed is oxidized and absorbed in water, producing nitric acid of 50 per cent HNO_3 strength, according to the reactions

$$2\ NO + O_2 = 2\ NO_2$$

$$3\ NO_2 + H_2O = 2\ HNO_3 + NO$$

The catalyst in general use to effect the oxidation of ammonia is platinum drawn to fine wire and woven into a fine-mesh gauze. Theoretically there is very little loss of platinum, so that the gauze is simply a capital charge in the cost of the nitric acid. Actually, however, there is a mechanical loss of platinum which must be considered in the cost of the nitric acid. The platinum should be free from iron and all



Ammonia Oxidizers of the Flat Platinum Gauze Type other impurities except that a small amount of iridium, perhaps less than 1 per cent, is not harmful. The gauze is often woven with an iridium wire selvage edge to add strength. The gauze used in the oxidizers at the U. S. Nitrate Plants was of 80 mesh, woven of 0.003 inch wire.

There are two types of oxidizers, that requiring a flat rectangular gauze, and that requiring a circular gauze. The flat gauze is heated electrically to the reaction temperature, 700° C to 1000° C, while the circular type needs no heating or even preheating of the gases. The heat of oxidation maintains the gauze at proper temperature. The electrically heated catalyzer, however, has good temperature control, which enables it to work successfully on impure ammonia gas. The flat type is held along all four edges, while the circular type is held along only two selvage edges, which are then inactive. In the United States, flat gauzes 13 inches by 27 inches with an exposed area of 12 inches by 24 inches and circular gauzes of 13 inches by 114 inches, rolled in a cylinder of 4 thicknesses of gauze, each with an exposed area 11.5 inches by 9 inches in diameter, or a surface area of 11.5 inches by 28.3 inches, have been used. At the higher temperatures, the platinum has much greater capacity for oxidizing ammonia than at lower temperatures and is much less affected by catalytic poisons.

Base metal catalysts have been used but not with the success achieved with platinum. Further work is now being done at various places on base metal catalysts and excellent progress is being made in this direction. Attempts are also being made to carry out the reaction with oxygen rather than air in order to facilitate absorption of the nitrogen oxides formed or to enable the product to be obtained in the form of liquid nitrogen tetroxide. This liquid has been studied with a view to its utilization in the direct nitration of organic compounds, and in the production of nitrogenous fertilizers by absorption in various carriers.

The development of high chromium steel alloys for use in tower and tubing construction for the absorption system has made possible economies in the operation of ammonia oxidation. Instead of the former massive brick towers, smaller circular towers of this 17 per cent chromium steel are now used.

The hot gases coming from the oxidizers are cooled in the gas cooler constructed of chromium steel and then pass to the oxidation and absorption towers. The number and size of the towers varies with local conditions and the capacity of the plant. These towers are usually operated under atmospheric pressure and are packed with spiral tower packing rings. The gas passing through these towers in series passes countercurrent to the supplied water, which is added at the end of the system, so that the strongest acid meets the most concentrated gases and the weakest gases are scrubbed with nearly pure water.

The 50 per cent acid obtained may be concentrated through the use of strong sulphuric acid. A tower similar to the absorption tower is supplied with strong sulphuric acid and the weak nitric acid which trickles down over the tower packing and is treated with steam introduced at the base of the tower passing counter current to the flow of the acid mixture. The distilled concentrated nitric acid is drawn off near the top of the tower and condensed in the condenser tubes, while the sulphuric acid is drawn off at the bottom, concentrated and used over again.

Parsons[1] gives a cost comparison of nitric acid from

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[1] Ind. Eng. Chem. *19*, 789 (1927).

ammonia oxidation and from Chile nitrate, as follows:

I. *From Ammonia*:	Per Ton HNO_3 (100 per cent)
As NO gas	\$3.00 + cost of 564 lb. NH_3
As 50 per cent HNO_3	10.60 + cost of 581 lb. NH_3
As 95 per cent HNO_3	23.60 + cost of 606 lb. NH_3
II. *From Chilean Nitrate:*	
As 95 per cent HNO_3	\$32.00 + cost of 2840 lb. N_aNO_3

If the cost of ammonia is considered as being as high as 6 cents per pound and Chile nitrate taken at the present quotation of \$2.25 per 100 pounds, the cost of 95 per cent nitric acid as worked out from this table is \$59.96 per ton through ammonia oxidation and \$63.90 through Chile nitrate.

In the production of ammonium nitrate through the neutralization process as shown in the diagram, ammonia gas is passed into nitric acid and the solution evaporated until practically all of the water has been eliminated. The reaction involved is essentially as expressed by the equation

$$HNO_3 + NH_3 = NH_4NO_3.$$

Ammonia gas and nitric acid are continuously fed into the inclosed neutralizing tank, the feed being so regular that a practically neutral solution is obtained. This solution overflows into a tank where it is adjusted to neutrality. The temperature in the neutralizer rises to about 100° C, due to the heat of neutralization. The steam thus generated, together with unabsorbed ammonia, passes out through the top of the neutralizer into a cooler in which the moisture is condensed and drains back into the neutralizer. The unabsorbed ammonia is recovered in an absorbing tower in which it is scrubbed out with acid. The solution adjusted to neutrality is evaporated until it contains less than 3 per cent of water, and is then crystallized in jacketed grainers by continuous stirring for several hours while its temperature is properly controlled by admitting steam or cold water to the jacket. The grained product is discharged from the grainer after it reaches a temperature of about 70° C.

Although ammonium nitrate gives excellent results as a fertilizer, it unfortunately is extremely hygroscopic, which renders it very difficult to handle. Because it is a concentrated material containing 35 per cent of nitrogen and is such a good fertilizer material, much work has been done on the development of a treatment to counteract its hygroscopic nature. Inasmuch as means such as graining and mixing with other salts have been developed for reducing this hygroscopicity, and since it is a nitrate form of nitrogen, it is believed it will be given serious consideration for use in this country.

Ammonium phosphate, because it is a concentrated material containing two plant foods, is sure to become an important fertilizer salt in this country. It is already occupying attention in Europe and is being produced in Germany. The American Cyanamid Company has been producing it in this country under the trade name of "Ammo-Phos," one grade of which is a mixture of ammonium sulphate and phosphate obtained by neutralizing a mixture of phosphoric and sulphuric acids with ammonia. It is produced in two grades, one of 14 per cent ammonia and 47 per cent P_2O_5, and the other 20 per cent ammonia and 20 per cent P_2O_5. The regular mono-ammonium phosphate contains 14.7 per cent ammonia and 61.7 per cent P_2O_5.

"Ammo-Phos" because of its high cost, being produced with ammonia from cyanamide, has not been able to find a market in this country but has been exported chiefly to the Orient. The longer the freight haul, the greater is the possibility of sale as one ton of the 14-47 grade is the equivalent of approximately 3½ tons of the necessary ammonium sulphate and acid phosphate to supply the same plant food. The freight on 2½ tons of material may then be used to offset any manufacturing cost differential.

The flow for the manufacture of ammonium phosphate as shown in the diagram is the same as for the sulphate. In fact, the identical plant could be used, providing concentrated phosphoric acid were available. If weak acid such as results from the wet method of treating phosphate rock with sulphuric acid is employed there is no use for the centrifuges. The liquor as it comes from the saturator is led into tanks where it is adjusted to neutrality. This liquor although very thin is then led into the rotary drier from which the contained water is evaporated, resulting in the salt, phosphate of ammonia. Triple effect evaporators have been tried in the system immediately before the driers, but in evaporating it is difficult to maintain the solution neutral and the acid material quickly eats out the interior of the evaporator. In the rotary drier a protecting cake of phosphate is built up on the walls.

The advantage of ammonium phosphate over the sulphate salt for instance is in the fact that the acid ammonia carrier is in itself a plant food.

The foregoing are the principal immediate conversion products of ammonia. There are, however, a large number of combinations of nitrogen materials now being worked up for fertilizer use. The physical properties of most of the fixed nitrogen products which contain nitrogen as the only fertilizer ingredient are far from satisfactory in that they readily absorb moisture from the air, and cake or possess other properties which greatly interfere with their use as fertilizer. Considerable attention is being given to methods for improving the mechanical condition of these materials. This might be done by granulation, by coating with insoluble materials, or by the formation of two constituent fertilizer salts such as the ammonium phosphate just mentioned and potassium nitrate. These substances are among the least hygroscopic of soluble materials and mixtures with each other or with potassium phosphate will give a complete concentrated fertilizer.

In addition to the salts ammonium sulphate, ammonium phosphate, "Ammo-Phos," and urea previously mentioned, there are other fertilizer materials containing fixed atmospheric nitrogen now on the market. The principal ones of these are:

Leuna-salpeter, a double salt of ammonium nitrate and ammonium sulphate containing nitrogen equivalent to 31.5 per cent ammonia. About one-fourth of the nitrogen is nitrate and the remainder is ammonia nitrogen. It is mixed approximately 1,245 pounds of sulphate and 755 pounds of the nitrate per 2,000 pound ton. This material is produced by the Badische company at the Leuna-Werke in Germany from which the name is derived.

Nitrate of lime or calcium nitrate is a compound of lime and nitric acid so treated, for instance by atomizing with air, as to give a material suitable for broadcasting. It contains 15.5 per cent nitrogen and 28 per cent lime.

Potassium-ammonium nitrate is a mixture of potassium and ammonium nitrate containing 15.5 per cent nitrogen, half as ammonia and half as nitrate nitrogen, and 27 per cent potash. This is a very fine fertilizer material of good physical properties.

Diammonium phosphate, exploited in Germany, is another ammonium phosphate containing twice the ammonia of the monoammonium phosphate and is produced by treating monoammonium phosphate liquor with additional ammonia. This material contains 23 per cent of ammonia and 47 per cent of phosphoric acid.

Leunaphos is also a product of the Leuna plant. It is a compound of diammonium phosphate (diammonphos) and ammonium sulphate containing 24 per cent of ammonia and 15 per cent P_2O_5 (phosphoric acid).

Leunaphoska, another material of this plant, is a mixture of leunaphos and potash salt which contains 13 per cent nitrogen, equivalent to 15.7 per cent ammonia, 10 per cent of phosphoric acid and 13 per cent of potash.

Many other materials comprising mixtures of ammonia, phosphoric acid and potash are being worked on but all of the above are being commercially exploited.

CHAPTER VIII

STATISTICS

THE world's demand for inorganic nitrogen is increasing at the rate of about 100,000 tons of fixed nitrogen per year and according to the reports of several individuals thoroughly conversant with the situation, of whom Sir Max Muspratt, previously mentioned, is one, there is no expectation of any lower rate of increase in sight.

The world figures for the three years ending June 30, 1925, 1926 and 1927 are given below.

Tons of Nitrogen for year ending

	June 30 1925	June 30 1926	June 30 1927
Chile nitrate	421,000	355,000	298,000
By-product ammonia	302,000	330,000	341,000
Fixed atmospheric nitrogen	495,000	641,000	807,000
Total	1,218,000	1,326,000	1,446,000

From these figures it can be seen that fixed atmospheric nitrogen not only supplied the increased demand of 100,000 tons of nitrogen per year, but it has also made up the difference due to the falling off of Chile nitrate. This decrease in Chile nitrate amounted to over 50,000 tons of nitrogen per year for the past three years so that the increase in fixed atmospheric nitrogen has been approximately

150,000 tons of nitrogen per year. Even with this large yearly expansion, it is believed that the saturation point in consumption of nitrogen is not yet in sight and that there is room for all producers now engaged in the industry. Col. Pollitt, of Nitram, Ltd., of England, has pointed out in a recent speech in Edinburgh, that for at least 500,000 years a human being very little different from his present form has inhabited the earth. In all that time up to A.D. 1800, the world's population had increased from its beginning to a figure estimated at 800 millions. In the next 100 years from A.D. 1800 to A.D. 1900, it rose to 1,730 millions, or more than doubled, and this rate of increase or one very nearly as great, is continuing today. This increase obviously cannot be continued indefinitely under any circumstances, and it cannot go on at all unless the productivity of the soil keeps pace with it.

For the year ending June 30, 1927, Chile supplied 20 per cent of the world's inorganic nitrogen consumption, the by-product coke ovens supplied 24 per cent, while atmospheric nitrogen fixation processes supplied 56 per cent. This is in contrast to the situation 30 years ago, the time of the warning sounded by Sir William Crookes, when the world was very nearly 100 per cent dependent upon Chile.

Of the 807,000 tons of nitrogen represented by the 56 per cent from the atmosphere, only 39,000 tons or less than 5 per cent was fixed by the arc process, 175,000 tons or less than 22 per cent was fixed according to the cyanamide process, while 593,000 or over 73 per cent was fixed according to the direct synthetic ammonia process. A comparison of these figures with those for the previous year leaves no doubt of the trend of development. Of the 641,000 tons produced during the year ending June 30, 1926, the arc process accounted for 41,000 tons or 6½ per cent, the cyanamide process produced 185,000 tons or 29 per cent, while 413,000 tons or 64 per cent was produced by the direct synthetic ammonia process. Not only did the increase of 178,000 tons in the year in direct synthetic ammonia process capacity account for the total increase in fixed atmospheric nitrogen production, but it also accounted for the decrease in production by the arc and cyanamide processes. Thus, the breach is growing larger from both ends, the decrease in production of the two earlier processes and the increase in production of the newest process, the direct synthetic ammonia process.

Fixed atmospheric nitrogen and more especially the direct synthetic ammonia process is fast approaching the position once enjoyed by Chile nitrate, but it can never from present indications actually achieve that position. Ammonia it is believed will always be produced as a by-product of the operation of the coke ovens. The production of by-product ammonia will increase, but it is believed its increase will be very slow.

All statistics point clearly to the fact that the important source of fixed atmospheric nitrogen of the future, as it is of the present, will be the direct synthetic ammonia process. The maximum annual capacity of all the plants now operating is 720,660 tons of nitrogen per year, while there is under actual construction additional capacity of 225,345 tons of nitrogen, or nearly 1,000,000 tons capacity operating and under construction.

Germany, of all the countries of the world, is by far the largest producer and during the year 1926–1927 her production exceeded consumption of Chile nitrate even for 1917, the year of greatest consumption. Of 593,000 tons of nitrogen fixed in the world for the past year, the plants of Germany fixed 440,000 tons, divided into 125,000 tons fixed at the Oppau plant and 315,000 tons at the Leuna-Werke at Merseburg. In addition to this, the cyanamide interests of Germany are erecting a direct synthetic ammonia plant of the Fauser method at their cyanamide plant in Piesteritz, which it is expected will be brought into operation shortly.

The closest competition with Germany at this time, if indeed she can be considered as having competition, is from England. That country, through the Synthetic Ammonia and Nitrates, Ltd., a subsidiary of the Brunner-Mond and Imperial Chemicals, Ltd., now operating a direct synthetic ammonia plant at a capacity of 22,000 tons of nitrogen per year for fertilizer materials and actively erecting an addition of 53,000 tons of nitrogen per year, is planning on further increasing capacity by addition of a 75,000 ton unit, bringing the total capacity of the plant to 150,000 tons of nitrogen per year. It is expected that the 53,000 ton addition will be in operation by the first of the year 1928. Hydrogen, here as in the case of the German plants, is secured from water gas.

In the United States the combined total capacity of the seven operating direct synthetic ammonia plants is 28,500 tons of nitrogen per year, equivalent to 99 tons of ammonia per day, while the capacity operating is only 23,000 tons of nitrogen per year, equivalent to 80 tons of ammonia per day. All of this production has gone into the refrigeration and chemical industry, but it has practically completely supplied that demand, having replaced ammonia from the gas works and coke ovens.

The plants operating in this country, with their capacities are:

Name	*Location*	*Rated Daily Capacity Tons Ammonia*	*Daily Operating Rate Tons Ammonia*	*Yearly Nitrogen Equivalent in Tons*
Atmospheric Nitrogen Corp.	Syracuse, N. Y.	40	40	11,550
Lazote, Inc. (Dupont subsidiary)	Charleston, W. Va.	25	15	4,350
Mathieson Alkali Works	Niagara Falls, N. Y.	10	10	2,900
Niagara Ammonia Co. (Dupont subsidiary)	Niagara Falls, N. Y.	17	8	2,300
Roessler-Hasslacher Chem. Co.	Niagara Falls, N. Y.	3	3	865
Pacific Nitrogen Corp. (Dupont subsidiary)	Seattle, Wash.	3	3	865
Great Western Electro-chemical Co	Pittsburg, Calif.	1	1	290
Commercial Solvents Corp.	Peoria, Ill.	15	0	0
Totals		114	80	23,120

Of this capacity of 114 tons of ammonia daily, 65 tons or 57 per cent is for operation on water-gas hydrogen, 37 tons or 32 per cent is for operation on hydrogen, a by-product of other chemical industries, while only 12 tons or less than 11 per cent is for operation on electrolytic hydrogen. Of the operating rate of 80 tons per day, only 3.7 per cent is on hydrogen from the electrolysis of water, while 70 per cent is on water-gas hydrogen and over 26 per cent on by-product hydrogen.

The difference of 34 tons between the rated daily capacity of 114 tons and the daily operating capacity of 80 tons is caused by Lazote diverting 10 tons ammonia capacity to the production of methanol; by the fact that 9 tons capacity of the Niagara Ammonia Company is idle due to the fact that it is not economically practicable in the United States to use electrical energy as a substitute for coal in the fixation of atmospheric nitrogen (the 8 ton capacity operating utilizes hydrogen a by-product of the Hooker Electrochemical Company chlorine plant); and by the Commercial Solvents Corporation converting its 15 ton ammonia unit to the production of 4,000 gallons of methanol per day.

The Atmospheric Nitrogen Corporation, now operating the largest direct synthetic ammonia plant in the United States, is preparing for the erection of a large plant for this process for the production of fertilizer materials at Hopewell, Virginia. Indeed it is reported that construction has already started on the Hopewell site and that much of the equipment has been ordered and the fabrication of some completed. This plant will mark the entrance of the direct synthetic ammonia process for fertilizer production in this country and it is expected that expansion will be rapid.

The plant of Lazote, Inc., operating at Charleston, W. Va., is somewhat novel, in that the purification step of removing carbon monoxide from the water gas is accomplished by converting it with hydrogen into methanol. Thus the two synthesis processes are linked together and the purification step which used to be a costly one is turned to a profitable one. It is reported that large expansion of this plant in the near future is planned. In fact, it has been said that the plant will eventually, within the next few years, be enlarged to a capacity of 300 tons of ammonia per day. It is believed that this company is carrying on extensive research looking to the development of new uses for ammonia.

The plant of the Mathieson Alkali Company is operating on hydrogen which is a by-product from their caustic manufacture. It is not believed that there will be much if any expansion in this project, but because of the favorable situation as regards hydrogen costs this company will always be able to produce.

The Niagara Ammonia Company, operating the Casale process and lately acquired by the Dupont interests, was erected for operation of about half capacity on hydrogen obtained by the electrolysis of water and half on hydrogen as a by-product of caustic manufacture of the Hooker Electrochemical Company's plant next door. With the cut in price of ammonia, however, the electrolytic plant had to be shut down, as hydrogen produced through the electrolysis of water, even with the rather favorable power rate prevailing on the older contracts at Niagara Falls, was too costly. The remaining part of the plant using by-product hydrogen has maintained operation.

The Roessler and Hasslacher Chemical Company, operating a 3 ton per day ammonia plant on hydrogen, a by-product of its own operations, is enlarging its plant. The ammonia produced at this plant is used in its own operations.

The Pacific Nitrogen Corporation plant at Seattle, Washington, is the only plant in the country now operating on hydrogen from the electrolysis of water. Although the power rate of $30 per kilowatt year is not particularly attractive for this operation, production is continued economically because of other sectional conditions.

The Great Western Electrochemical Company is operating a one-ton unit which had formerly operated as somewhat of an experimental unit at the plant of the Mathieson Alkali Company at Niagara Falls, N. Y. The hydrogen is a by-product of caustic manufacture. It is reported that this plant is to be enlarged by the addition of two more one-ton units.

The Commercial Solvents Corporation, operating corn fermentation plants at Terre Haute, Indiana, and Peoria, Illinois, for the production of butyl alcohol (butanol) has been wasting to the atmosphere from this operation about 2,500,000 cubic feet of hydrogen daily. In the interest of utilizing this valuable gas, a plant of a rated capacity of 15 tons of ammonia per day was erected at Peoria, Illinois. After operating this plant for the production of ammonia for a few weeks, the few necessary changes were made to operate it for the production of methanol according to a process which permits of the use of hydrogen with carbon dioxide, another waste gas of the fermentation process, rather than with the carbon monoxide ordinarily employed. In view of the fact that it can be readily changed over for the production of ammonia again, this plant can be considered as potential capacity. Whether the product of the plant will be methanol or ammonia at any time will undoubtedly depend on the market conditions.

The development of the industry in France is largely according to methods which will permit of the utilization of coke oven gas. Although the capacity is made up of rather a large number of plants, their combined capacity upon the completion of present construction will be about 125,000 tons of nitrogen per year, equivalent to 153,000 tons of ammonia. There is one relatively large plant included in this group, that of the French Government, at Toulouse, which is to have a capacity of 57,000 tons of nitrogen per year. Water gas is to be the source of hydrogen. Of the remaining 68,000 tons capacity, 63,000 tons are to operate on hydrogen from by-product coke oven gas. It will be noted that in the countries of greatest actual and contemplated development, Germany, England, France and the United

States, coal is depended upon as the means of hydrogen supply.

Although not a large consumer, Italy has been increasing steadily in nitrogen consumption at a rate of from 15 to 25 per cent each year for the last 5 years. Domestic production has kept pace with this increased consumption, so that through these years, although imports increased, the domestic production for each year amounted to about half the consumption.

This increase in domestic production has been through the direct synthetic ammonia process. As Italy has practically no coal, but has many excellent water-power resources, hydrogen for these new operations is all being derived from the electrolysis of water.

Japan like Italy does not possess extensive coal deposits, but has large water-power resources, which lend themselves to low cost development. In freeing herself of dependency on importation of sulphate of ammonia, Japan is utilizing these power resources for the production of electrolytic hydrogen for the fixation of atmospheric nitrogen according to the direct synthetic ammonia process. In making this development, the cyanamide plants are closing down to make room for this process of lower production costs.

In Norway, the Norsk Hydro Company is replacing its arc process capacity by direct synthetic ammonia capacity, utilizing electrolytic hydrogen. By so doing, this company can utilize the same power now being consumed in the fixation of 35,000 tons of nitrogen annually to fix 140,000 tons. The first unit of this replacement is being installed by an American company, the Nitrogen Engineering Corporation of New York.

Sweden is replacing its cyanamide capacity with direct synthetic ammonia capacity and this latter process is also operating in three plants in Spain and in Belgium to a capacity of 55,000 tons of nitrogen per year, while plants are projected or actually building in Poland, Czechoslovakia, Russia, Yugoslavia, Brazil and Australia.

It can be seen that world development is following the direct synthetic ammonia process and that this process is rapidly replacing the two older and more costly processes, the arc and cyanamide. It will shortly come about that to speak of the capacity or of the production by the direct synthetic ammonia process will be tantamount to speaking of fixed atmospheric nitrogen capacity or production.

APPENDIX A

The cost of Chile nitrate, as given by Hobsbawn in the magazine, Chile, Vol. 1, No. 5, p. 205, as one of the better officinas, is as follows:

			Per long ton of 96% nitrate
(A) Manufacture of nitrate			$11.61
(1) Mining raw material		$3.57	
(a) Wages	$3.00		
(b) Explosives	0.42		
(c) Stores	0.15		
(2) Transport of raw material		2.41	
By carts			
(a) Wages	0.76		
(b) Fodder	0.85		
(c) Stores	0.24		
By rail			
(a) Wages	0.28		
(b) Fuel stores	0.28		
(3) Elaboration of raw material			
Crushing, elevating & conveying		5.63	
(a) Wages	0.192		
(b) Power	0.075		
(c) Stores	0.050		
Leaching			
(a) Wages	1.130		
(b) Power	1.140		
(c) Repairs	0.280		
(d) Fuel	2.230		
(e) Stores	0.298		
(f) Water	0.107		
(g) General management	1.125		

		Per long ton of 96% nitrate
(B) Baggage and lading		1.86
(C) Railway freight to port		2.70
(D) Export duties		12.30
(E) Shipping charges		1.06
(F) Commission		0.44
(G) Capital charges (investment, $40 per annual ton of nitrate-producing capacity)		7.60
Amortization at 5 per cent	2.00	
Interest, taxes, insurance, etc. 9%	3.60	
Repairs, additions, renewals, etc., 5%	2.00	
TOTAL, f.a.s. Chile		$37.57

If the ocean freight charge is $7.50 per ton, the cost f.a.s. port of consuming country is $45. It is often necessary to rebag the material at the port of entry. This cost must, of course, be added to the f.a.s. port of entry cost.

Location	*Annual Capacity*	*1927 Rate of Production*
GERMANY:		
Piesteritz	35,000	30,000
Trostberg	35,000	35,000
Waldshut	12,000	8,000
FRANCE:		
Bellegarde	5,000	3,250
Lannemezan	15,000	10,500
Marignac	6,000	2,500
Brignoud	6,000	3,000
Modane	4,000	1,000

APPENDIX B

The locations of the world's plants for the fixation of atmospheric nitrogen by the various processes are as follows:

NITROGEN FIXATION BY ARC PROCESS

Location	*Annual Capacity*	*1927 Rate of Production*
	Net Tons	Net Tons
Rjukan, Norway	31,000	
Notodden, Norway	8,000	38,000
Rhina, Germany	4,500	0
La Roche de Rame, France	250	250
Patsch, Austria	1,000	1,000
Total	44,750	39,250

NITROGEN FIXATION BY CYANAMIDE PROCESS

NITROGEN FIXATION BY CYANAMIDE PROCESS—*Continued*

Location	*Annual Capacity*	*1927 Rate of Production*
ITALY:		
Terni	10,000	5,500
Domodossola	3,500	1,000
Ascoli Piceno	2,500	1,000
San Marcel	1,000	500
SWITZERLAND:		
Martigny	2,500	2,500
JAPAN:		
Osaka Hokkaido Fuchan Mandschurei	20,000	5,000
UNITED STATES:		
Muscle Shoals, Ala.	40,000	0
CANADA:		
Niagara Falls	25,000	25,000
JUGOSLAVIA:		
Sebenico	7,000	7,000
Almissa	7,000	
POLAND:		
Chorzow	30,000	17,000
CZECHOSLOVAKIA:		
Karlsbad	6,000	4,000
NORWAY:		
Odda	15,000	4,500
ROUMANIA:		
Ungar-Altenburg	5,000	3,000
SWEDEN:		
Ljunga	3,000	2,500
Alby	3,000	2,500
Total	315,500	174,250

	Electrolytic Hydrogen		
Seattle, Wash., U.S.A.	Pacific Nitrogen Corp.	865	
Soulom, France	Ste. des Engrais Azotes et Composes	15,120	
Terni, Italy	Società Italiana Ricerche Industriali Siri	1,545	
Nera Montoro, Italy	Terni Società per l'Indústria & l'Electricita	9,765	
Dalmazia, Italy	Società Italiana Forse Idrauliche della Dalmazia		15,000
Novara, Italy	Società Piemontesse Ammonia (Montecatini)	5,750	
Merano, Italy	Montecatini	37,800	
Mas (Belluno), Italy	Montecatini	1,000	
Sabinandigo, Spain	Energia Industrias Aragonesas, S.A.	4,725	
Nobioka, Japan	Nippon Chisso Hiryo Kabushiki Kaisha	19,500	
Minamata, Japan	Nippon Chisso Hiryo Kabushiki Kaisha	18,900	12,600
Viege, Switzerland	Usines Electriques de la Lonza	2,200	5,000
Ljunga, Sweden	Stockholm Superfosfat Akt.		2,500
	Total	117,170	35,100

NITROGEN FIXATION BY DIRECT SYNTHETIC AMMONIA PROCESS

Net Tons Nitrogen per Year

Location	*Company*	*1927 Operating Capacity*	*1927 Capacity under Construction*
	Water-gas Hydrogen		
Syracuse, N.Y., U.S.A.	Atmospheric Nitrogen Corp.	7,750	
Hopewell, Va., U.S.A.	Atmospheric Nitrogen Corp.		35,000
Charleston, W.Va., U.S.A.	Lazote, Inc.	6,350	
Oppau, Germany	Badische Anilin und Soda Fabrik.	125,000	
Merseburg, Germany	Badische Anilin und Soda Fabrik.	375,000	
Billingham, England	Synthetic Ammonia & Nitrates, Ltd.	20,500	52,000
Montereau, France	Société Chimique de la Grande Paruisse	1,500	
Toulouse, France	French Government		57,000
Willebrock, Belgium	Société Evence Coppé		10,000
Hiroshima, Japan	Suzuki & Company	3,000	
Ninjinougorod, Russia	Severny Chimicecky Trust		7,560
	Total	539,100	161,560

Nitrogen Fixation by Direct Synthetic Ammonia Process

(Continued)

Location	*Company*	*1927 Operating Capacity*	*1927 Capacity under Construction*
	Coke-oven Hydrogen		
Bethune, France	Compagnie des Mines de Bethune	6,000	12,000
St. Étienne, France	Houilleres de St. Étienne	540	3,260
Decazeville, France	Societe de Commentry Fourchanbault et Decazeville	3,000	
Henin Lietard, France	Ste. des Mines de Dourges	4,725	
Pont a Vendin, France	Ste. des Mines de Lens	7,000	
Henin Lietard, France	Cie des Mines de Vicoigne Noeux & Drocourt	4,725	
Anzin, France	Cie des Produits Chimiques Anzin Kuhlmann	7,000	
Calling, France	Ste. Houillère de Sarre et Moselle		4,725
Firminy, France	Cie des Produits Chimiques de Roche La Moliere	4,725	
Vado, Italy	Societā Azogeno		3,000
Ougree, Belgium	Societe Belge de l'Azote	4,500	
Ostend, Belgium	S.A. des Fours a Coke Semet Solvay and Piette	7,500	
Felguera, Spain	Societe Iberica del Nitrogen	3,150	
Knurow, Poland	Societe Fermiere des Mines Fiscales de l'Etat Polonais		3,000
Ignatz, Czechoslovakia	Societe Czechoslovakia d'Azote		4,500
Marles, France	Societe des Mines de Marles		7,500
Selzaete, Belgium	Etabilissements Kuhlmann		7,500
Waziers, France	Soc. l'Ammoniazue Synthetique		4,350
	Total	52,865	49,835
	By-product Hydrogen		
Syracuse, N. Y.	Atmospheric Nitrogen Corp.	3,800	
Niagara Falls, N. Y.	Niagara Ammonia Co.	2,000	
Niagara Falls, N. Y.	Mathieson Alkali Works	2,880	
Niagara Falls, N. Y.	Roessler-Hasslacher Chem. Co.	865	865
Pittsburg, Calif.	Gr. Western Electrochemical	300	
Piesteritz, Germany	Mitteldeutsch Stickstoff Werke		2,500
Widnes, England	United Alkali Co., Ltd.		3,150
St. Auben, France	Cie d'Alais Froges et Camarque	730	3,150
Bussi, Italy	Societā Azogeno	1,500	
Flix, Spain	Sociétē Iberica del Nitrogeno	700	
		12,775	9,665
	Grand Total	721,910	256,160

APPEN

Some nitrogen statistics of domestic production, exports, im
Great Britain, France, Italy and Japan for various years from

(Expressed in net

	1910	1913	1916	1919
				Germany
Domestic Production:				
By-product ammonia	86,059	124,664	144,200	53,200
Fixed atmospheric nitrogen	4,108	11,550	166,980	142,768
Total production.........	90,167	136,214	311,180	195,968
Exports:				
Chilean nitrate	4,112	4,299	0	0
By-product ammonia	16,570	17,222	0	0
Fixed atmospheric nitrogen	0	6,366	0	0
Total exports............	20,682	27,887	0	0
Imports:				
Chilean nitrate	128,990	133,179	0	13,602
By-product ammonia	6,901	7,860	0	34
Fixed atmospheric nitrogen	0	11,191	0	0
Total imports............	135,891	152,230	0	13,636
Total consumption.......	205,376	260,557	311,180	209,604
				United States
Domestic Production:				
By-product ammonia	22,901	39,330	59,383	86,960
Fixed atmospheric nitrogen	0	0	0	276
Total production.........	22,901	39,330	59,383	87,236
Exports:				
Chilean nitrate	0	0	9,337	2,384
By-product ammonia	119	0	104	12,100
Fixed atmospheric nitrogen	0	0	0	0
Total exports............	119	0	9,441	14,484
Imports:				
Chilean nitrate	92,457	109,351	212,867	71,200
By-product ammonia	19,022	13,481	2,991	542
Fixed atmospheric nitrogen	560	5,403	5,847	12,497
Total imports............	112,039	128,235	221,705	84,239
Total consumption.......	134,821	167,565	271,647	156,991
				Great Britain
Domestic Production:				
By-product ammonia	85,490	99,814	100,064	89,470
Fixed atmospheric nitrogen	0	0	0	0
Total production.........	85,490	99,814	100,064	89,470
Exports:				
Chilean nitrate	1,244	1,859	127	38,494
By-product ammonia	65,412	74,510	59,808	24,950
Fixed atmospheric nitrogen	0	0	0	0
Total exports............	66,656	76,369	59,935	63,444

102,401	73,501	97,747	139,550	126,357	123,600
270	200	740	5,910	11,110	13,050
102,671	73,701	98,487	145,460	137,467	136,650
3,456	5,765	2,265	9,146	1,325	1,587
20,300	23,563	33,831	34,569	27,240	28,445
0	630	514	1,240	1,620	2,180
23,756	29,958	36,610	44,955	30,185	32,212
230,480	66,249	94,581	155,468	171,900	193,920
459	1,075	1,123	813	1,381	2,294
29,590	2,338	6,070	11,814	12,515	27,550
260,529	69,662	101,774	168,095	185,796	223,764
339,444	113,405	163,651	268,600	293,078	325,566
94,280	59,760	81,600	99,700	93,880	97,500
0	0	0	0	8,000	13,300
94,280	59,760	81,600	99,700	101,880	110,800
8,283	134	2,176	593	954	830
31,100	26,580	42,380	56,820	56,450	59,402
0	0	0	0	7,500	12,500
39,383	26,714	44,556	57,413	64,904	72,732

DIX C

ports, and apparent consumption for Germany, United States, 1910 to 1925, are given below.

tons of nitrogen)

1920	1921	1922	1923	1924	1925
62,000	88,000	90,750	60,500	56,650	73,150
147,520	206,800	256,300	273,900	300,500	374,678
209,520	294,800	347,050	334,400	357,150	447,828
705	36	90	50	1,366	2,647
897	629	589	6,980	3,630	19,064
5,164	2,437	3,761	22,240	21,658	61,800
6,766	3,102	4,440	29,270	26,654	83,511
5,381	41	5,403	1,937	1,985	4,208
32	23	409	73	191	72
374	234	1,420	102	16	456
5,787	298	7,232	2,112	2,192	4,736
208,541	291,996	349,842	307,242	332,688	369,053

Italy

Domestic Production:				
By-product ammonia	1,625	3,049	3,406	1,482
Fixed atmospheric nitrogen	638	2,966	4,981	3,324
Total production.........	2,263	6,015	8,387	4,806
Exports:				
Chilean nitrate	17	11	0	0
By-product ammonia	0	0	0	0
Fixed atmospheric nitrogen	0	0	0	0
Total exports............	17	11	0	0
Imports:				
Chilean nitrate	10,525	11,596	14,732	2,208
By-product ammonia	4,710	4,919	641	1,072
Fixed atmospheric nitrogen	0	0	0	0
Total imports............	15,235	16,515	15,373	3,280
Total consumption.......	17,481	22,519	23,760	8,086

Japan

Domestic Production:				
By-product ammonia	253	1,816	8,675	16,995
Fixed atmospheric nitrogen	0	1,386	4,752	0
Total production.........	253	3,202	13,427	16,995
Exports — None				
Imports:				
Chilean nitrate	2,422	4,597	7,916	11,275
By-product ammonia	15,764	25,315	1,626	22,939
Fixed atmospheric nitrogen	0	0	0	0
Total imports............	18,186	29,912	9,542	34,214
Total consumption.......	18,439	33,114	22,969	51,209

(Expressed in net

	1910	1913	1916	1919
				Great Britain
Imports:				
Chilean nitrate	22,107	24,628	71,515	4,279
By-product ammonia	0	0	0	0
Fixed atmospheric nitrogen	2,610	5,958	22,115	7,536
Total imports	24,717	30,586	93,630	11,815
Total consumption	43,551	54,031	133,759	37,841
				France
Domestic Production:				
By-product ammonia	13,220	16,917	5,677	10,197
Fixed atmospheric nitrogen	198	1,485	19,800	5,799
Total production	13,418	18,402	25,477	15,996
Exports:				
Chilean nitrate	807	904	2,028	72
By-product ammonia	190	261	335	67
Fixed atmospheric nitrogen	110	138	909	2
Total exports	1,107	1,303	3,272	141
Imports:				
Chilean nitrate	59,367	55,404	93,001	6,861
By-product ammonia	5,937	5,198	4,823	4,998
Fixed atmospheric nitrogen	85	1,652	1,318	1,264
Total imports	65,389	62,254	99,142	33,123
Total consumption	77,700	79,353	121,347	48,978

1,818	1,263	1,760	1,850	2,130	2,600
5,326	4,233	7,400	9,350	13,200	19,800
7,144	5,496	9,160	11,200	15,330	22,400
9	94	0	0	21	12
0	0	0	0	0	0
0	0	0	0	0	110
9	94	0	0	21	122
7,440	3,257	6,747	8,895	9,780	11,030
1,599	1,119	2,493	2,521	3,030	4,750
0	0	324	2,064	6,448	8,240
9,039	4,376	9,564	13,480	19,258	24,020
16,174	9,778	18,724	24,680	34,588	46,298
18,100	18,373	19,100	19,000	19,560	20,003
11,780	3,545	20,140	21,970	21,450	20,760
29,880	21,918	39,240	40,970	41,010	40,763
21,032	3,123	9,075	11,500	6,925	6,550
16,337	17,952	21,025	33,010	33,130	19,912
0	0	486	2,084	5,890	29,948
37,369	21,075	30,586	46,591	45,945	56,410
67,249	42,448	69,826	90,564	86,955	99,363

tons of nitrogen)

1920	1921	1922	1923	1924	1925
25,713	9,732	7,985	12,663	14,340	14,179
0	0		0	0	0
8,100	1,900	3,600	4,200	5,300	4,720
33,813	11,632	11,585	16,863	19,640	18,899
88,710	44,678	48,629	59,150	56,616	56,967
11,330	11,783	14,690	20,001	22,530	23,200
3,007	3,090	6,710	10,630	13,050	23,960
14,337	14,873	21,400	30,631	35,580	47,160
401	1,194	658	1,707	1,883	536
199	890	2,736	1,499	1,513	1,843
224	38	1,065	354	220	785
824	2,122	4,459	3,560	3,616	3,164
45,430	53,889	27,792	46,063	48,400	56,000
6,912	15,363	17,080	16,682	17,400	19,015
2,313	1,460	1,560	4,983	13,322	14,900
54,655	70,712	46,432	67,728	79,122	89,915
68,168	84,463	63,373	94,679	111,086	143,911

APPENDIX D

BIBLIOGRAPHY

This bibliography has been compiled with the hope that the readers whose interests have been aroused by the perusal of the previous pages may find herein help in seeking reliable articles giving more technical and more detailed discussions of the various phases of the subject. It is selective rather than exhaustive, and when it was necessary to choose between two comparatively worthy works upon the same subject, in many instances the general accessibility and the references within the particular article have been influential in deciding which one should be included in this list.

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