

1777

THE FIXATION OF ATMOSPHERIC NITROGEN

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A thesis  
submitted to the faculty of  
the University of Alabama  
in conformity with the requirements  
for the degree of  
Master of Science

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By

Augustus L. Barker.

1911

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## INTRODUCTION.

Nitrogen is one of the most widely diffused of all the elements. In the free condition it constitutes four-fifths of the atmosphere. This free nitrogen is inert and inactive and can not be used for commercial purposes. When the nitrogen is in the form of a compound it is said to be fixed. Nitrogen compounds— nitric acid, nitrates, nitrites, ammonia, &c-- are of vast commercial and industrial importance. They are used for the manufacture of high explosives, fertilizers, and chemicals.

Fixed nitrogen occurs in nature in the form of potassium nitrate or saltpeter, and sodium nitrate or Chili saltpeter. By far the greater part of the world's supply of nitrogen compounds has been derived from the Chilean beds. Although these beds are quite extensive, they are fast being exhausted and the indications are that they will not last much longer than a hundred years. The demand for Chili saltpeter has been increasing faster than the yield and it will be only a few years until we will have to look to other sources for our supply of fixed nitrogen. The exhaustion of the Chilean beds will practically mean the exhaustion of the world's supply of natural nitrogenous fertilizers. The wheat-eating population of the globe is steadily increasing and unless the yield of wheat per acre is increased, famine will be the inevitable result. The only way to increase the yield per acre is to use some kind of nitrogenous fertilizer. With the exhaustion of these beds, there will come the corresponding diminution of the supply for use in the explosives and chemical industries.

Man is called upon to devise a practical method of fixing a part of our boundless supply of atmospheric nitrogen. As Sir William

Crookes has said, the intervention of the chemist and the laboratory will prevent the starvation of the world. The object of fixation is to change the inert, elemental gas into a highly useful compound. The problem at first appears simple enough but it is really very difficult. A great deal of research work has been done on the problem and the failures recorded are numerous. Within the past ten years much systematic work has been done and it now appears that the solution of the problem is in sight.

As there are a number of nitrogen compounds, so there are a number of different methods of fixation. Most attempts have been made along the line of combining the nitrogen with the oxygen of the air in electric arcs. The most successful experiments with electric arcs have been made by Bradley and Lovejoy at Niagara Falls, by the Pauling Brothers in Austria, and by Birkeland and Eyde and the Badische Company in Norway. In the essential principals all these methods are alike. There is not much difference in the yield of grams of fixed nitrogen in the form of nitric acid per kilo-watt hour in the four methods named above. The process of fixation as cyanamide, discovered by Caro and Frank, appears promising. By this method one kilo-watt hour will fix about four times as much nitrogen as by the other methods but there are other difficulties to be overcome. The United States Department of Agriculture has been diligently at work on the problem of fixation by means of nitrifying bacteria. If the efforts along this line are successful, a very simple method of fixation will have been devised.

## FIXATION BY MEANS OF AN ELECTRIC ARC.

### Historical.

About 1781 Cavendish demonstrated that nitrogen could be oxidized at the temperature of the combustion of hydrogen in air. Two years later he showed that it could be oxidized by means of the electric spark. He also showed that the nitric oxide formed in this way reacts with water to form nitric acid. These facts were gathered by Cavendish while he was making his investigations on hydrogen and oxygen.

In 1880 Spottiswoode and Dewar produced and studied electric arcs in air and Dewar<sup>1</sup> showed that both nitrite and cyanogen are formed in the electric arc. Little is known of Dewar's investigations.

Sir William Crookes,<sup>2</sup> in 1892, working with an induction current, showed that both nitrous and nitric acids are formed in the electric arc. In 1895 Perot and Couplier made some investigations on this subject, using a current of high tension. Their work was not very exhaustive.

In 1897 Lord Rayleigh<sup>3</sup> used a current under a tension of 2,000 volts and produced an electric arc in a glass vessel into which a mixture of oxygen and air was passed. His results were very good,-- his yield of nitric acid corresponding to 438 kilograms per kilo-watt year.

The investigations of Muthman and Hofer in 1903 gave no conclusive results. McDougall and Howles<sup>4</sup> demonstrated the rapid dissociation of the peroxide of nitrogen into the protoxide and hence the necessity of removing the product from the influence of the arc as quickly as possible.

<sup>1</sup>Grandeau, La production électrique de l'acide nitrique avec les éléments de l'air, Paris, 1906: 15.

<sup>2</sup>Ibid.

<sup>3</sup>Ibid.

<sup>4</sup>Ibid.

## General and Theoretical.

All the commercial processes for the fixation of atmospheric nitrogen by electric discharges are more or less similar. The most important differences are in the construction of the furnaces and in the kind of arc produced.

The air is first blown into the furnace containing the arc. There a part of it is oxidized to nitric oxide. The gases are then passed out of the furnace chambers and through boilers where they give up part of their heat and are cooled down to  $600^{\circ}$  C. The heat is utilized for evaporating and heating purposes. As soon as the temperature gets down to  $600^{\circ}$  C., the nitric oxide begins to unite with the excess of oxygen to form nitrogen peroxide, a brownish-red gas. This oxidation takes place in large "oxidation chambers". Schoenherr<sup>1</sup> says that complete conversion does not take place until the temperature drops below  $140^{\circ}$  C.

The next step is the conversion of the nitrogen peroxide into nitrates, nitrites, or some other marketable form. This is done by passing it through large absorption towers containing pieces of acid proof material over which water, a solution of sodium hydroxide, or milk of lime trickles. The gas is absorbed and nitric acid, sodium nitrate, or calcium nitrate is formed, according to the absorbing liquid used.

Bernthsen<sup>2</sup> says that it is generally accepted that electricity brings about the reaction by means of the high temperature ( $3,000^{\circ}$  to  $3,500^{\circ}$  C.) produced but that it is possible that the electricity also exercises a specific action on the gases. On the assumption

<sup>1</sup>Trans. Amer. electro-chem. soc., 16: 156 (1909).

<sup>2</sup>Trans. Faraday soc., 5: 297 (1910).

that the reaction is a purely thermal one, attempts have been made to form nitric oxide by heating air to high temperatures by other means, but, according to Schoenherr<sup>1</sup>, no appreciable yields have been obtained. The same authority<sup>2</sup> refers to Warburg's claim that effects other than purely thermal ones are brought about by treating air in an arc and to the work of Haber and Koenig, who produced nitric oxide of much greater concentration than could be produced as a result of purely thermodynamical equilibrium. By working under diminished pressure they got nitric oxide of ten per cent concentration. Schoenherr<sup>3</sup> claims that the concentration of the nitric oxide depends upon the proportion of the uniting bodies as well as upon the temperature, and that by using a gas mixture consisting of equal parts of nitrogen and oxygen, the concentration of the nitric oxide is largely increased.

At the high temperature of the arc, the tendency is for the nitric oxide formed to dissociate into its constituents. While the rate of formation of the oxide increases with the temperature, its dissociation also increases. Brode<sup>4</sup> showed that the inner zone of the arc was the hottest and that the formation of nitric oxide takes place there, while the decomposition takes place in the outer zone (Bernthsen). In order to keep the concentration as high as possible, the nitric oxide must be rapidly cooled to 1,500° C. by contact with the outer layers of air. Schoenherr<sup>5</sup> says that all other methods of cooling work too slowly. The use of air as cooling agent is also favorable to the preservation of the nitric oxide formed in that it reduces the concentration of

<sup>1</sup>Trans. Amer. electro-chem. soc., 16: 133 (1909).

<sup>2</sup>Ibid., 16: 135 (1909).

<sup>3</sup>Ibid., 16: 136 (1909).

<sup>4</sup>Trans. Faraday soc., 5: 301 (1910).

<sup>5</sup>Trans. Amer. electro-chem. soc., 16: 135 (1909).

the latter, for the rate of decomposition is reduced by dilution.

#### The Bradley and Lovejoy Process.

In 1902 the first attempts were made to produce nitrates on a large scale. Messrs. Bradley and Lovejoy organized the Atmospheric Products Company at Niagara Falls and proposed to use the water power there to run their dynamos. The apparatus used by these people was very expensive and complicated. The chamber in which the oxidation was brought about was a metallic cylinder about four and one-half feet high and four feet in diameter. The inner wall of the cylinder was lined with vertical rows of fine platinum contact points. These points were connected with the positive pole of a powerful dynamo generating a current under a pressure of 8,000 volts. In the center of this cylinder there revolved a second smaller cylinder. The outer wall of this latter cylinder was lined with contact points connected with the negative pole of the dynamo. When the inner cylinder was put in motion and the current turned on, thousands of tiny arcs were formed. When two oppositely charged points approached each other, a spark was formed and drawn out into an arc and finally extinguished. The inner cylinder revolved at the rate of 500 revolutions per minute and there were formed altogether about 414,000 arcs per minute.

Air was passed into the chamber and partly oxidized to nitric oxide. The oxide thus formed was absorbed by water to form nitric acid or by sodium hydroxide to form sodium nitrate.



The principle of the Bradley and Lovejoy process lies in the production of luminous arcs having as great a length and as small a cross-section as possible, in such a way that their surfaces are brought into contact with as large a volume of air as possible<sup>1</sup>.

The Bradley and Lovejoy plant was abandoned in 1904. The high cost of installing and maintaining the complicated machinery, the high cost of power at Niagara, and the lack of sufficient funds, were all conducive to the failure of the project.

#### The Pauling Process.

The Brothers H. and G. Pauling in 1904 installed a plant near Innsbruck in Austria, for the oxidation of atmospheric nitrogen in electric arcs. Since 1908 this process has been employed in a plant at Roche-de-Rame by La Nitrogene, a French company.

In the Pauling process, flaming arcs are used. These arcs are produced between bent electrodes similar to those used in horn-lightning arresters. The electrodes are near together at the lower part but gradually diverge as they pass upward. The arc is lighted at the narrow end and the incoming hot air forces it upward. It is thus pulled out to a considerable length. The flames vary from three and one-half to four feet long. An alternating current is used and at each half period a new arc is produced.

The furnaces used by the Paulings are very simple and compact. They are three feet three inches wide, three feet eight inches long,

<sup>1</sup>Grandeau, La production electrique de l'acide nitrique avec les elements de l'air, Paris, 1906: 17-18.

and ten feet high. With an alternating current of 4,000 volts tension each furnace, which contains two arcs arranged in series, has a capacity of 400 kilo-watts. The furnaces need little care and one man is able to look after six of them. The iron electrodes are hollow and are cooled on the inside with water. These electrodes are set in vertical slots in the refractory brick furnaces. At the lowest point of the two electrodes is a flattened tuyere through which passes the hot compressed air. In order not to hinder the entrance of the air and at the same time to bring the electrodes as near together as possible, thin, knife-blade electrodes are inserted in slots in the electrodes proper. The distance between these knife-blades is regulated by a rack and pinion. The hot air coming in through the tuyere is first spread out. The arc is lighted and then blown out to considerable length. The combination of the nitrogen and oxygen takes place in the flame and nitric oxide is formed. In order to prevent dissociation, this oxide is quickly cooled by means of a current of air from the bottom of the furnaces. The gas leaves the furnaces at a temperature of 700° to 800° C. and contains, according to Lamy<sup>1</sup>, 1.15 to 1.20 per cent of nitric oxide; and, according to another authority<sup>2</sup>, two per cent of nitric oxide.

The gas then passes through a cooling chamber where it gives up some of its heat to be used for various purposes. It then passes through a masonry flue for further cooling, and finally at 35° C. passes into a large oxidizing tower. Thence it passes into the absorption towers, of which there are five in number. The nitric oxide is absorbed by water and a dilute nitric acid is obtained. The concentration of this acid is increased by passing it repeatedly through the towers. The gases remaining are finally passed through a tower containing a solution of sodium hydroxide, and sodium nitrite is formed.

<sup>1</sup>Met. and chem. eng., 9: 103 (1911).

<sup>2</sup>Sci. Amer. sup., 70: 234 (1910).

Thus 96 per cent of the nitric oxide is recovered during normal operation. Russ<sup>1</sup> makes the statement that sixty grams of nitric acid per kilo-watt hour are produced in the Pauling process. "Taken as a whole the Pauling furnace appears simple, compact, to require inexpensive repairs, and the whole process should be practical; in fact, it appears that the Pauling plant particularly has reached a point where it runs regularly and with commercial success!" (Lamy)<sup>2</sup>.

#### Moscicki's Methods.

Moscicki made his first attempts in 1900 at Freiberg. He used a current under a tension of 50,000 volts with a frequency of 6,000 to 10,000 periods through the air-gaps. In 1903 a plant of a hundred horse-power was built at Vevey in Switzerland to make use of this method of Moscicki's. This plant was somewhat similar to that of Bradley and Lovejoy at Niagara Falls. In the plant at Vevey a current under a tension of 50,000 volts with a frequency of 50, was used.

In the center of the iron furnace was an aluminium axle which was one of the electrodes. This axle was equipped with projecting contacts points, while the sides of the furnace were also equipped with similar contact points. The electrodes were so arranged that the points came within ten millimeters of each other. When the axle turned, a spark was produced every time two of the oppositely charged points approached each other. In this way a large number of sparks was produced under a high pressure.

<sup>1</sup>Electroch. and met. ind., 7: 432 (1909).

<sup>2</sup>Met. and chem. eng., 9: 103 (1911).

Air entered the furnace at the bottom, the nitrogen and oxygen united to form nitric oxide, and the hot gases passed out of the top of the furnace. After further oxidation, the gases were passed through the absorption towers. In order to prevent the absorption of the nitric oxide to form nitrous acid, the absorbing solution was kept above 60° C.

This scheme of Moscicki's was a failure. The complicated machinery was too costly to allow an economic production of nitric acid and Moscicki abandoned this plan and turned to another.

In his second method Moscicki took advantage of the magnetic deflection of an arc and in this respect the method was similar to that now in use by Birkeland and Eyde. He used two concentric ring electrodes and the current passed from one to the other in a radial direction. By means of a magnet the arc was kept constantly moving. He used two copper electrodes, a copper rod and an outer copper cylinder, with an air-space of fifteen millimeters between them. The copper rod was cooled on the inside with water. With this arrangement an alternating current of 3,000 volts tension and 50 periods was used. The yield of one such furnace corresponded to 525 kilograms of nitric acid per kilowatt-year, which, according to Moscicki<sup>1</sup> is the minimum. Though this method of Moscicki's is still in the experimental stage, the results so far are very satisfactory and they are to be continued on a larger scale.

<sup>1</sup>Electroch. and met. ind., 5: 493 (1907).

## The Birkeland and Eyde Process.

Within the past eight years some very successful work has been done by Birkeland and Eyde in Norway. These men found that the most effective way was to use large quantities of energy in the arc, and they have practically revolutionized the synthetic nitrate industry. Between the two electrodes, which are close together, there is established an easily movable and flexible current which is maintained in a highly magnetic field.<sup>1</sup> (Eyde).

The first work was done ~~at~~ in 1903 at Frognerkillens, where a trial factory using twenty five horse-power was established. In 1905 they were using 2,500 horse-power at Notodden, and in 1907, 30,000 horse-power at the Svaelfos-Notodden factory.<sup>2</sup> (Grandeau). The current supplied by the Svaelfos is in the form of a three phase, fifty cycle current under a tension of 10,000 volts.

Two pointed, hollow, copper electrodes, fifteen millimeters in diameter, are placed equatorially between the poles of a powerful electro-magnet so that the terminals are in the middle of the field. The points of the electrodes are eight millimeters apart. The current passes between the two electrodes and a short arc is formed in a strong and extensive magnetic field.<sup>3</sup> (Birkeland). A current which crosses a magnetic field is constrained to put itself in motion. Consequently the arc moves in a direction perpendicular to the lines of force, at first with tremendous velocity; and the extremities of the arc retire from the terminals. With the lengthening the tension is heightened until it is sufficient to create a new arc at the points of the electrodes. Then

<sup>1</sup>Jour. Royal soc. of arts, 57: 568 (1909).

<sup>2</sup>Grandeau, La production électrique de l'acide nitrique avec les éléments de l'air, Paris, 1906: 15.

<sup>3</sup>Trans. Faraday soc., 2: 104 (1906).

the outer longer arc is extinguished. The effect of the magnet is to deviate the arc and spread it out in the shape of a disc about six feet in diameter.

The flame-disc is produced in a central chamber three or four inches wide and six feet long. This central chamber itself is enclosed in a furnace about seven feet high. The furnace is constructed of cast iron and steel and is in the shape of a large lens. The flame chamber is made of fire-clay brick and the air enters through the sides of the chamber.

The air enters the chamber, passes through the arc, and is heated to a temperature of  $3,000^{\circ}$  to  $3,500^{\circ}$  C. Some of the nitrogen in the air is oxidized to nitric oxide. If the gases are rapidly cooled, the nitric oxide is imprisoned. This cooling is brought about by contact with the outer layers of air which are much cooler. The escaping gases, cooled down to  $800^{\circ}$  or  $1,000^{\circ}$  C., are led into the boiler house where they are further cooled, the heat being used for concentrating the products, heating the buildings, etc.

The gases then pass to the cooling house where they go through coolers containing aluminium tubes over which cold water runs. The gases next pass into the oxidation tanks which are vertical iron cylinders lined with stone. After the oxidation to nitrogen peroxide takes place, the gases pass to the absorption towers. These towers are filled with pieces of quartz over which water trickles. The gas is absorbed by the water in the towers to form nitric acid of varying strength. The remaining weak gases pass over a sodium hydroxide solution which absorbs the last traces of nitric and nitrous gases. This product contains sodium nitrate, sodium nitrite, water, and sodium bi-carbonate. The nitrite is easily recovered and is used in the chemical industry.

The acid formed in the towers is repeatedly pumped up automatically and run through until it reaches a concentration of 30 per cent, when it is drawn off. This 30 per cent acid is poured over limestone, and calcium nitrate is produced. The solution is then evaporated in a vacuum to save heat. The product hardens into a brittle crystalline mass which is crushed up. It is put up and sold in barrels weighing one hundred kilograms net. This calcium nitrate can be manufactured by the Birkeland and Eyde process 30 per cent cheaper than Chili saltpeter can be mined. It contains 13.5 per cent of nitrogen and experiments show that it makes a better fertilizer than sodium nitrate.

#### The Badische Process.

In 1905, Dr. Otto Schoenherr, working for the Badische Anilin- und Soda-Fabrik, devised a process of oxidizing atmospheric nitrogen by an entirely new method. The process of Dr. Schoenherr makes use of an arc of great current density which burns quite steadily and is maintained in a stable condition. Formerly great stress was laid upon the necessity of preventing the air from remaining for a long time in the sphere of action of the arc, and it was consequently blown through the arc at right angles to it. Schoenherr, on the other hand, passed the air to be treated quietly along the arc in a spiral direction. In this way highly concentrated gases were obtained and there was little danger of disturbing the stability of the arc.<sup>1</sup> (Schoenherr).

The Badische company erected an experimental factory at

<sup>1</sup>Trans. Amer. electro-chem. soc., 16: 141 (1909).

Kristianssand in south Norway and it started operations in the autumn of 1907. The energy is derived from the Saeterstal, sixteen miles away, and it is transmitted in the form of a three phase current under a tension of 25,000 volts. In the factory, the tension of the current is reduced to 7,200 volts.

The apparatus is very simple. The arc is produced in a long iron tube. In one end of this tube there is arranged an insulated electrode. The walls of the other end of the iron tube serve for the other electrode. In lighting the arc, the distance between the insulated electrode and the wall of the tube at one place is made so small that, on open circuit, a spark will jump across. In the furnaces this is done by means of the ignition lever. A massive iron bar is moved from the wall of the tube, which for the time being acts as the second electrode, to the insulated electrode. When the two approach each other the spark jumps across and the arc is lighted. The bar is then moved back to its proper place, out of the way. The air coming through the tube in a rotary motion keeps the long arc burning in the axis of the tube, and the end of the arc strikes the wall at a considerable distance from the insulated electrode.

The rotary motion of the air is obtained by blowing the air into the tube in a tangential direction. The air enters through various openings in the sides of the tubes. These openings can be so regulated that the air is made to go in a spiral direction

The insulated electrodes are hollow copper tubes, cooled on the inside by water. The wear and tear on them is very slight and they can be easily replaced when necessary. The upper part of the tube is also cooled by water which flows around it somewhat like the water in a Liebig condenser. By so regulating the supply of current and of air, the arc can be made to end at a certain definite point on the upper



electrode.

The air is heated before entering the furnace. As it is led along the arc, it remains for some time in contact with it. The air coming in contact with the arc is heated to a high temperature and is partially oxidized to nitric oxide. The gases are then cooled down rapidly by contact with the cold surrounding air and decomposition is avoided. They are further cooled by the water surrounding the upper part of the tube. The escaping gases, at a temperature of  $1,200^{\circ}$  C., have a concentration of two per cent of nitric oxide. The hot gases then pass to a boiler where they give up more of their heat. As soon as the temperature drops to  $600^{\circ}$  C., the nitric oxide begins to unite with the excess of oxygen present to form nitrogen peroxide. This takes place in the oxidation chambers. The conversion of the oxides into nitric acid, nitrates, and nitrites is strikingly similar to that in the Birkeland and Eyde system.

Schoenherr<sup>1</sup> claims that the efficiency of the arc flame is 92 to 96 per cent. He says that because of the fact that the air is acted on for a comparatively long time in the arc flame, there can be obtained essentially higher yields than according to the process of Birkeland and Eyde. About three per cent of the energy fed into the arc flame is utilized in the production of nitric oxide.

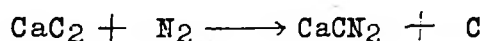
In this process, as in all the processes using an electric arc, cheap power is the principal factor. The raw materials used are very cheap and abundant. Many problems are yet to be solved but with capable men working on them, their solution will be forthcoming.

<sup>1</sup>Trans. Amer. electro-chem. soc., 16: 152 (1909).

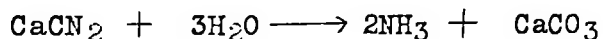
## FIXATION AS CYANAMIDE.

Bunsen and Playfair obtained cyanides by passing nitrogen over a mixture of carbon and alkali at a high temperature. Frank and Caro suspected that the formation of carbides preceded that of cyanides. On investigation they found that this was correct.<sup>1</sup> (F. Savorgnan Di Brazza).

They also found that when nitrogen is passed over calcium carbide heated to 1,000° C., the following reaction takes place:



This calcium cyanamide,  $\text{CaCN}_2$ , when heated with high pressure steam or let stand for some time in a warm place, passes over into ammonia and calcium carbonate, according to the following reaction:



Since 1894 Frank and Caro have been developing what they considered the most efficient of all the processes<sup>o</sup> for the fixation of atmospheric nitrogen. In 1900 they entered into co-operation with the Siemens-Halske Company, the leading electrical interests in Germany, and since that time they have been perfecting the process. They operated a commercial plant in Italy, where they obtained cheap water-power, for two years before the process was known outside of their own councils.

In 1903 all the processes and patents for the manufacture of calcium cyanamide in all parts of the world were assigned to the Societa Generale per la Cianamide of Rome. This Societa has since licensed companies to manufacture cyanamide in many parts of the world.

<sup>1</sup>Sci. Amer., 97: 256 (1907).

During recent years calcium cyanamide plants have been built in Germany, Italy, France, Norway, Switzerland, Japan, and the United States . Plants are now in operation in all these countries and others are in course of construction in Bavaria and Dalmatia. The industry has made great advances within the last year.

The first item to be looked out for in the manufacture of this substance is cheap water-power. The raw materials, coke, lime and nitrogen are all abundant. Carbon in the form of coke and lime are placed in an electric furnace where, at a temperature of over  $2,000^{\circ}$  C., they combine to form calcium carbide. This carbide is then crushed and milled in an atmosphere of nitrogen and then placed in retorts into which nitrogen is led. The retorts and contents are then heated to  $800^{\circ}$  to  $1,000^{\circ}$  C., when the carbide and nitrogen react to form calcium cyanamide and carbon. This heating may be done in an electric furnace or over coal. The conversion is complete after two hours.

The product from the retorts consists mainly of calcium cyanamide and carbon. There is some lime present. This is converted into calcium hydroxide by hydration. There is but a slight trace of unused calcium carbide in the product. The final product contains approximately the equivalent of nineteen per cent of ammonia.

Most of the factories obtain their nitrogen by the Linde process. Air is first liquified and then subjected to fractional distillation. On account of the widely different boiling points of liquid nitrogen and liquid oxygen, the two can be separated in this way.

The American Cyanamid Company at Niagara Falls has full American rights to manufacture and distribute calcium cyanamide in this country. This company has been operating on a commercial scale since January 1, 1910, and the capacity is now 15,000 tons per year. This

company does not use the liquid air process for the manufacture of its nitrogen but uses a modification of the well known copper process. Air is passed over heated copper. The copper is oxidized by the oxygen in the air and the nitrogen is obtained free from oxygen.

The demand for calcium cyanamide has been so great that the factories have not been able to supply it. The crop making power of cyanamide has been demonstrated by extensive experiments. It may be used directly as a fertilizer or it may be used in the manufacture of mixed fertilizers. As such it is far superior to calcium or sodium nitrate. Calcium cyanamide is also of great value in the arts. It can be used in the manufacture of various chemicals, such as ammonia, ammonium sulphate, potassium cyanide, nitric acid, and certain organic compounds. In this respect it also surpasses the nitrates.

Calcium cyanamide is manufactured more cheaply than calcium nitrate. The cost of fixing , per kilogram of nitrogen, is about twenty cents as compared with thirty two and a half cents for calcium nitrate.

## FIXATION BY MEANS OF BACTERIA.

From the earliest times it has been known that certain plants belonging to the Leguminosae have a deciding enriching effect upon the soil in which they grow, in much the same way as if it had been treated with some nitrogenous fertilizer. It was at first thought that these plants could assimilate the nitrogen in much the same way as they can carbon dioxide, but it has since been learned that the nitrogen must be in the form of a compound before it can be taken in as food by the plants.

Thaer<sup>1</sup> in 1809, without any experimental facts whatever, advanced a theory that leguminous plants took up nutriment from the air and deposited it in the soil through the roots and stubble. John<sup>2</sup> later demonstrated that after a leguminous crop, there is a definite increase in nitrogen as well as in humus. In 1854 Boussingault<sup>3</sup> promulgated his classic experiments demonstrating that plants could not assimilate free nitrogen gas. His work was substantiated by Gilbert, Lawes and Pugh, working jointly.

It was noticed that the legumes flourished in a soil devoid of nitrogen and some difficulty was met with. In 1886 Helriege<sup>4</sup> announced that the source of the nitrogen for the plants was the atmosphere and in 1888 he and Willfarth<sup>5</sup> demonstrated that nodules or swell-

<sup>1</sup>Rationelle Landwirthsch., 1 Aufl., Bd. 1, 1809.

<sup>2</sup>Kuhn's Ber. a. d. Lab. d. ~~Lab.~~ Landwirthsch. Inst. Halle, 1895: 111.

<sup>3</sup>Mem. de Chim. Agric. et de Physiol., Paris, 1854.

<sup>4</sup>Tagebl. der 59 Versamml. Deutsch. Naturforscher u. Aerzte in Berlin, 1886.

<sup>5</sup>Verlagsheft zu der Zeitschr. des Vereins fur Rubenzucker-industrie des Deutschen Reichs, Berlin, 1888.

ings are developed on plants grown in soil free from nitrogen. Before that time numerous explanations had been offered to account for these nodules. Soon the work of Helriegel and Willfarth was verified by other workers and came to be generally accepted by botanists and scientific men.

In 1891 Schloesing and Laurent showed that there are certain organisms which have the power of directly fixing nitrogen from the atmosphere. Others showed that these bacteria were each capable of fixing a definite amount of nitrogen. Many opinions as to the cause and result of the nodules on legume roots had been advanced by various authorities.

Atwater and Woods<sup>1</sup> made the first practical demonstrations in regard to the beneficial effect of the nodules. They planted legumes in quartz sand which had been burned to free it from nitrogen. Pot number one was inoculated with nitrogen-fixing bacteria and watered with a nutrient solution devoid of nitrogen; pot number two was not inoculated but was watered with the same nutrient solution; pot number three was uninoculated but was supplied with nitrogen in the form of potassium nitrate. The following results were obtained: plants in pot number one averaged 6.16 grams in weight; plants in pot number two, .33 grams in weight; plants in pot number three, 2.65 grams in weight. Thus it is seen that the inoculated plants greatly exceeded in weight those not inoculated with the bacteria. Moore<sup>2</sup> says that one of the first and most satisfactory demonstrations of the beneficial effects of nodule-forming bacteria upon leguminous plants was made by Prof. J.F. Duggar<sup>3</sup> at the Alabama Experiment Station in 1896-97.

<sup>1</sup>Conn. Storrs Ag. Exp. Sta. Rept., 1889: 211 and 1890:312.

<sup>2</sup>Bureau of Plant Industry, Bulletin 71, 1905: 17.

<sup>3</sup>Ala. Exp. Sta. Bul. 76, 1897.

There are two classes of bacteria that have the power of fixing nitrogen in the soil: (1) those not associated with any particular crop, and (2) the root-nodule forms associated with legumes. The first group gets its food from the carbohydrates in the decaying matter in the soil. The second group gets its food from the carbohydrates supplied by the host plant. In certain soils where the conditions of temperature, air and food supply are favorable, the independent soil forms do well but in general they do not do as well as the root-nodule forms.

A number of investigations have been made as to the exact nature of the organisms. It has been found that there are many varieties but that they all belong to the same species. Woods<sup>1</sup> states that the immediate efficiency of the bacteria depends upon the natural or artificial inoculation of that legume with the strain of bacteria best adapted to it. The nitrogen fixing power of the bacteria depends partly upon the conditions under which they have been growing. The cultivation of selected strains for a few generations greatly increases their fixing power and their value for inoculating purposes.

In order to introduce the bacteria into areas where they have not existed before, inoculation is resorted to. This may be done by transferring soil already inoculated or by the use of pure cultures. The soil-transfer method has not proved entirely satisfactory. It is very cumbersome and expensive, and there is also great danger of bringing in injurious and disease-producing bacteria, fungi and troublesome weeds. Pure culture inoculation therefore replaced the soil-transfer method.

Nobbe first conceived the idea of inoculation by means of

<sup>1</sup>Yearbook of the U.S. Dept. of Agriculture, 1906: 133.

pure cultures. The right organisms are first isolated and then developed in a specific medium. This culture of bacteria was first called 'nitragin'. Some of the results with it were successful while others were not. In transportation the cultures were subjected to varying conditions. The efficiency therefore could not be maintained, and the method was abandoned.

The United States Department of Agriculture, various German factories, and Prof. Bottomley in England, have all been striving to turn out cultures of the highest efficiency. Within recent years a number of improvements in the methods relating to pure cultures have been made by the Department of Agriculture, through the Bureau of Plant Industry. Many difficulties have been overcome. The directions for the use of the cultures have been simplified and put on a more systematic basis. The directions in brief are as follows: A small quantity of sugar and the tablet supplied are dissolved in one gallon of pure water, previously boiled and cooled. The liquid culture is then poured into the solution and the mixture allowed to stand in a warm place (70°) for twenty four hours. The seeds are then moistened with this solution and as soon as they have dried, they are ready for planting in the usual way. If preferred, the solution may be mixed with dry earth. This is then distributed over the land and immediately harrowed in to prevent the sunlight from killing the bacteria.

The work of Prof. Bottomley of King's College, London, is very important. He produced a powder preparation of bacteria which maintained its vitality for a period of two years. This was called 'nitro-bacterine'. The method of inoculation with this culture was similar to the one outlined above. These cultures have been used with great success in England and Ireland. Prof. Bottomley claims to have developed new physiological varieties of the ordinary bacillus of leg-



uminous plants, which are capable of symbiosis with non-leguminous plants. He removed bacteria from a legume root and placed it in an infusion of tomato roots, where it became adapted. Nodules were formed on the tomato root and the crop was greatly improved. He did similarly with other plants, and in every case nodules were formed and the yield was increased<sup>1</sup>. (Renouf).

Kellerman<sup>2</sup> says that it is impossible at present to determine whether the fixation by bacteria in symbiosis with non-leguminous plants is a scientific curiosity or a fact of practical value. Though bacterial nodules occur on a number of species, these nodules are markedly different in some respects from the nodules of legumes.

Years of research work along this line may be necessary but if the work of Bottomley is confirmed, the problem of nitrogen fixation will have been solved.

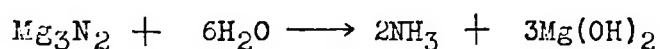
<sup>1</sup>Amer. chem. jour. 39: 791 (1908).

<sup>2</sup>Yearbook of the U.S. Dept. of Agriculture, 1909: 225-6.

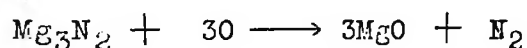
## OTHER METHODS OF FIXATION.

### The Nitride Method.

The first experiments along this line were carried out with magnesium. This element when highly heated combines with nitrogen to form a nitride,  $Mg_3N_2$ , which reacts easily with water. The following is the reaction:



It also burns easily:



Whitehouse<sup>1</sup> says that for the successful use of a nitride for commercial purposes, one of three methods of treatment must be possible:

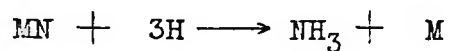
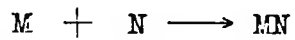
1. The nitride must be directly reducible with hydrogen, giving ammonia and a lower nitride or a hydride of the metal.
2. A nitride when treated with steam always gives ammonia and the oxide of the metal; but if this process is used, the oxide must be one that is reducible with hydrogen or carbon.
3. If the nitride can be made to react with hydrogen sulphide or hydrochloric acid, this reaction can be used, provided the sulphide or chloride is reducible.

A large number of experiments were made with magnesium nitride, but it could not be made directly reducible with hydrogen between  $400^\circ$  and  $1,000^\circ$  C.

The same difficulty was encountered with titanium nitride. Among other elements used were boron, cerium, molybdenum, columbium, and tantalum, but the experiments were not very successful from a com-

<sup>1</sup>Electroch. and met. ind., 5: 361 (1907).

mercial point of view. They cycle could not be completed according to the theoretical reactions:



Theoretically then the metal M. can be used over and over again. It merely acts as a carrier for the nitrogen. Whitehouse<sup>1</sup> says that the trouble is that with the rare elements we may be able to produce either the first or the second reaction but not both together. Those nitrides which can be directly reduced by means of hydrogen can not be formed from the elements, and vice versa.

<sup>1</sup>Electroch. and met. ind., 5: 363 (1907).

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