RECENT PROGRESS IN NITROGEN FIXATION.

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Ever since about 1830 Chile has furnished the world with most of its fixed nitrogen in the form of sodium nitrate. By fixed nitrogen we mean nitrogen in some available form such as ammonia or nitric acid or sodium nitrate. A sure supply of fixed nitrogen is a fundamental necessity in peace times or war. In peace times we must have fixed nitrogen to produce fertilizers, nitric acid and other necessary chemicals. In war a supply is absolutely necessary in order to supply armies with the constant stream of high explosives demanded in modern warfare. During the Great War, Germany was cut off from the Chilean nitrogen. Yet, because German chemists had developed a commercially successful process for converting the never failing supplies of nitrogen in the air into available "fixed nitrogen," Germany was able to carry on her war activities and maintain the fertility of the soil. Today Germany leads the world in this line and produces 90 per cent of its own requirements. Dr. Frederick Cottrell of the Fixed Nitrogen Laboratories at Washington, estimates that the current year will show a total world production of 44 per cent from this source. Just prior to the war only 10 per cent was produced by nitrogen fixation methods. Recent developments in our own research laboratories indicate that in a few years' time we shall be able to compete with Chilean nitrate and produce a large share of our fertilizer nitrogen by fixation.

Present Commercial Status.—At the present time, practically all commercial plants producing fixed nitrogen, use one of three methods, (1) the Arc, (2) Cyanamid or (3) Ammonia Synthesis. Below is a statement of the power requirements of each and the percentage of world production from each process.

Process	Kw. Hrs. per Metric Ton Fixed Nitrogen	Total Fixed Nitrogen Produced—Per Cent
Arc	68,000	7.3
Cyanamid	15,000	28.2
Direct Ammonia Synthesis—		
Electrolytic Hydrogen	20,000	2.0
Water Gas Hydrogen	4,000	62.5

The Arc process is chemically the most simple of the three but as will be seen from the above statement, consumes an enormous amount of electrical power. It is little used outside of Norway where electrical power is cheaply produced by water power. Two huge plants utilize about 380,000 horsepower in making nitric acid by this method. By this method air is rapidly passed through a furnace at the center of which is an enlarged electric arc. In passing through this arc the nitrogen is converted to nitric oxide, then quickly cooled and further

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oxidized to nitric per-oxide and absorbed in water to form dilute nitric acid. Much of this acid is converted to calcium nitrate, a very satisfactory fertilizer material and sold as "lime salt petre," or "land salt petre."

The Cyanamid process is used now in some 33 plants in nine different countries. A quarter of the world's production is obtained by this method. It was widely used in war times, because it was well understood and used only a quarter of the power required by the arc. However, the process seems rather on the wane as the newer ammonia synthesis method is supplanting it in many localities.

In this process limestone is first converted into calcium carbide in an electrical arc furnace and tapped into pots to cool. The finely pulverized carbide is next charged into relatively small electrically heated fixation ovens. Here very pure nitrogen, obtained by fractionating liquid air, is passed into the carbide. The carbide rapidly absorbs the nitrogen, forming calcium cyanamid, the primary product of this process. A considerable amount of cyanamid is used in mixed fertilizers. During the war much of the cyanamid was converted to ammonia by autoclaving with steam at 300 pounds pressure. Ammonia can readily be oxidized by the Ostwald catalytic method to nitric acid and then combined with ammonia to form ammonium nitrate for high explosives.

In this country we have one small arc plant near Seattle which produces three tons per day of sodium nitrite. The American Cyanamid Company operates a carbide plant on the Canadian side near Niagara Falls. Crude cyanamid and crude sodium cyanide are produced there. Near New York this company also operates a plant which converts cyanamid into ammonia and absorbs much of the ammonia in phosphoric acid from Florida phosphate rock. The product is called Ammos-Phos and is mostly exported. It is a high grade fertilizer material.

In order to assure the steady supply of nitrates for explosives, a cyanamid plant was built at Muscle Shoals. The plant cost the government $70,000,000, and was rated at an annual production of 40,000 tons of ammonia. Part was to be converted into nitric acid by the Ostwald method of oxidation and part into ammonium nitrate for the production of Amatol, the high explosive used in shell bursting charges. The plant never really produced during the period of the war but was given a very thorough test during 1919 with satisfactory results. The plant has been in stand-by condition ever since. The ultimate disposal of this plant awaits the report of the president's special commission.

The Direct Ammonia Synthesis Method is the newest of the three processes. Germany alone of the warring nations understood how to operate it, thanks to the immense labors of Dr. Haber and associates which culminated in a plant at Oppau, to produce 110,000 tons of ammonia per year, finished in 1913. This plant operated all through the war. Another plant at Mercesberg of 220,000 tons capacity was 75 per cent operating at the close of the war. This process requires very pure nitrogen and very pure hydrogen, and unites these gases in molecular proportion to form ammonia in the presence of a carefully selected catalyst under conditions of high pressure and temperature. In the German process 200 atmospheres pressure and a temperature of 500 degrees C. is used. The gas mixture is obtained, in Germany, by mixing water gas and producer gas. Carbon monoxide is next converted by means of steam under pressure and the inevitable catalyst into carbon dioxide and hydrogen. The carbon dioxide is scrubbed out with water under high pressure and the other harmful impurities absorbed in cuprous ammonium formate solutions. This, in brief, is the Haber-Bosch process as used during the war and it is understood, still used in much the same form today in Germany.

In this country Nitrate Plant No. 1 was built during the war at Sheffield near Muscle Shoals at a cost of about $13,000,000, with a capacity of about one-fifth that of Plant No. 2 at Muscle Shoals. This plant was built under the supervision of the General Chemical Company. The process installed was a modification of the Haber process, the catalyst and general procedure for which had been worked out by the General Chemical Company. Because of lack of confidence in the process, Plant No. 2 was projected and built. The fears for the success of Plant No. 1 apparently were only too well founded. The plant never operated in a satisfactory manner. After the war the General Chemical Company, starting with the experience gained from this plant built a plant at Syracuse, N. Y., which is now successfully operating and producing about 26 tons of anhydrous ammonia per day. The price of anhydrous ammonia for refrigeration has virtually been cut in half during the last year, largely because ammonia from fixation plants has entered the market. One result of this new factor in the ammonia market will be the production of more ammonium sulphate for the fertilizer trade at by-product coke plants.

At Niagara a plant using the Italian modification of the Haber process is to be built. This method uses electrolytic hydrogen which requires very little purification to be satisfactory for synthesis. A pressure of 600 to 750 atmospheres is used.

The papers have had a good deal to say lately about the new Dupont Plant near Charleston, West Virginia. This plant is to produce 25 tons per day of anhydrous ammonia, all of which will be consumed by Dupont. The process uses the Claude modification of the Haber process. It requires a very high pressure, about 1000 atmospheres. It is understood that at this high pressure the ammonia yield is better and that less sensitive catalysts can be used. The hydrogen for the process is to be produced by converting West Virginia soft coal into water gas. The nitrogen is produced by the following simple but very effective procedure. By mixing the proper proportions of air and water gas together in a special burner, the oxygen is all burned out of the air and the gases remaining are in the right proportion to make ammonia when passed through the converter. The final purification is accomplished by passing the mixed gases through a purification tube under the same pressure used in the ammonia converter. Here in the presence of a catalyst, the residual carbon monoxide is converted to methane, a gas which does not poison the catalyst in the actual ammonia converter. The product is anhydrous ammonia. In this method of ammonia synthesis several converters, in series, are used instead of one as in the Haber method.

Results of Recent Research. Great progress has been made in modifications and improvements on the existing fixation processes during the last two or three years. In Italy the Casale modification of ammonia synthesis has been successfully worked out. It is to be given a tryout at a small plant at Niagara Falls. As already stated it uses electrolytic hydrogen. Hence it is best applied where cheap electric power is available. It is felt that large power plants with off peak power available may use this process in small units to advantage.

In France, Claude seems now to have perfected his high pressure method of synthesis. This is to be used by Dupont at the West Virginia plant. In a large plant it is almost necessary to produce the hydrogen from water gas because the cost of hydrogen is such a large item in the total cost of production.

In this country a large share of all we know about recent progress in fixation methods comes from the Fixed Nitrogen Research Laboratories at Washington, D. C. The laboratory is in its sixth year and is now under the direction of Dr. Frederick Cottrell. It has a staff of about 75 men and a budget of about $250,000. The laboratories have done an immense amount of research in many widely divergent fields, that touch this great problem in some way. The recent results in ammonia synthesis are probably of greatest interest at the present time. A process using 300 atmospheres is used.

The hydrogen is obtained by electrolysis. The nitrogen is obtained from the air, the excess oxygen being burned out in much the same way as at the Dupont plant. The mixed nitrogen and hydrogen gases are passed through a pressure purification tube in the presence of a catalyst similar to the one used in the actual converter, but less sensitive. Here some ammonia is formed, sufficient to balance the cost of the purification step. The ammonia is condensed out as anhydrous ammonia and with it practically all gases which would poison the catalyst. The pure gases are next passed through the regular catalytic converter and the resultant ammonia condensed. Unconverted gases are returned to the process. The purification step results in a long life for the catalyst and high yield of ammonia. One of the most successful catalysts found is said to consist of the following mixture: iron oxide, 96 per cent; potassium aluminate, 4 per cent.

Research has proved that the iron catalysts are best and that "promoters" greatly improve the yield. The potassium aluminate is the promoter in the mixture quoted above. Study has also clearly proved that two properly chosen promoter substances act far better in the catalyst mixture than any single substance.

Based on small semi-commercial production the laboratories have now worked out a typical layout for a three-ton ammonia plant, using the above process. This modification is to be called the American Process of Ammonia Synthesis. It is expected that a good many small plants for producing ammonia for refrigeration, etc., will be modeled after this layout.

Both the Arc process and Cyanamid processes have been studied, but it is generally felt that these processes will produce only a small percentage of the total fixation nitrogen in the future. It is hoped that urea and some other ferilizer materials to be used in concentrated fertilizers, can be produced from cyanamid or direct from calcium carbide. Recent research seems to indicate that this can be accomplished economically on a commercial scale.

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