

imes more than the normal. Further the onion planting revived two of the plants that were about to die.

In an horticultural garden, 5 six months' old papaya plants were jacketed while another set of five was kept as control. After three months, the jacketed trees showed better growth in the size and number of fruits produced. In most of them the fruits were one and half times bigger than in the untreated.

Col. Noel made an experiment of growing wheat in ordinary flower plots as well as in pots made of expanded metal. Both lots were placed on a bed of sand so as to equalise conditions of drainage and evaporation. Wheat grown in pots of expanded metal gave thrice as much yield as in ordinary mud pots. The same experiment was repeated with maize and there too, the cobs produced in the metal pots were twice as big as in the earthenware pots. Again jacketing of trees in Turnab farm had given 30% more yield for the third year in succession.

## MANUFACTURE OF SYNTHETIC NITROGENOUS FERTILIZERS IN INDIA

### Part II. Comparison of different Processes for the Fixation of Atmospheric Nitrogen.

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The three important methods for the fixation of atmospheric nitrogen are, in historical sequence, the arc, cyanamide and the synthetic ammonia processes, though other methods such as the nitride and the cyanide processes have been put forward from time to time. In discussing the relative advantages of these methods we must have certain criteria of judgment, e. g., the capital outlay, running expenses, availability of raw products in the vicinity of the factory and the suitability of the products to the local market.

The arc process requires a much larger outlay and consumes a much greater amount of electricity per unit of nitrogen fixed than the cyanamide and synthetic ammonia methods. Hence it has been adopted only in countries where electric power is abundant and very cheap, e. g., in Norway, Sweden, Canada, etc. Even these countries have now given up the method in favour of the synthetic ammonia process, which is much cheaper.

#### Power Requirements of Nitrogen Fixation Processes.

(Partington and Parker)

Fixation Process.	K. w. hrs. per K. gm. N fixed.	K. w. yrs. (8760 hrs.) per metric ton of N fixed	H. P. yrs. per long Ton of N fixed.
Arc (exclusive of steam raising value of furnace gas)	73.7	8.41	11.45
Cyanamide	16.5 to 19.5	2.03 to 2.37	2.76 to 3.23
Haber (Assuming power supplied electrically)	3.6	0.435	0.592

The Cyanamide process was much in favour in the years preceding the War, but even that method is now giving place to synthetic ammonia processes. The disadvantages of the cyanamide method are the purity of lime and coke required in preparing carbide, the various draw-backs accompanying the use of cyanamide as a fertilizer, which will be dealt with in detail later, and the market partiality for Ammoniacal fertilisers which has necessitated the conversion of cyanamide into ammonia. Ammonia so prepared, is naturally costlier than that obtained by synthetic methods.

The synthetic ammonia processes are the ones generally adopted now, and from the figures given in the following Table, it will be evident that they are now supplying nearly 80% of the nitrogenous fertilizers placed on the market. In addition to lower capital outlay, the synthetic methods yield directly ammonia which can be converted into a number of marketable derivatives (e. g. urea) and can also be easily oxidized to nitric acid without much cost.

**World Production of Nitrogen Compounds in Metric tons of Nitrogen.**

(From the Report of the British Sulphate of Ammonia Federation Ltd.)<sup>\*</sup>

	1932—33	1933—34	1934—35	1935—36
Total World Production	1,677,000	1,792,000	2,070,000	2,378,000
<i>Sulphate of ammonia</i>				
Synthetic	560,000	535,000	533,000	630,000
By-product	258,000	307,000	321,000	365,000
Other forms of synthetic nitrogen e.g. liquid ammonia nitrochalk. Calcitro. urea etc.	462,000	516,000	607,000	720,000
Cyanamide	168,000	195,000	232,000	270,000
Nitrate of lime	118,000	107,000	153,000	156,000
Other forms of by-product nitrogen	40,000	48,000	45,000	45,000
Chilean Nitrate	71,000	84,000	179,000	192,000
Total world consumption	1,747,000	1,878,000	2,071,000	2,400,000
Agricultural consumption	1,586,000	1,673,000	1,812,000	2,068,000

Note:— For the year 1935—36, the synthetic nitrogen products were 75.1%, the by-product nitrogen compounds 17.3% and Chilean nitrate 7.6% of the total world production, based on the nitrogen content.

Below will be found some remarks on the economics and working of the three major processes, viz., (a) arc, (b) Cyanamide and (c) synthetic ammonia. For a historical review and technical working of the processes, reference may be made to text-books on the subject, a list of which is appended hereto. The following remarks presuppose a knowledge of the general working of the processes.

**I. Arc Process for Nitrogen Fixation.** There are different modifications of the Process, such as those of Birkeland and Eyde, Schoenherr, Pauling etc., depending mainly on the shape of the electric arc and on the type of furnace used. The principle adopted is the combination of nitrogen and oxygen of the air at about 3000 C in the electric arc, to form oxides of nitrogen, which are rapidly removed, further oxidized and condensed in

water to form nitric acid. Large installations were started in the beginning of this century at Rjukan and Notodden in Norway, consuming about 320,000 H. P. and fixing about 38,000 tons of nitrogen per year.

The method has got the advantage of simplicity, but the consumption of current is something very lavish. It yields nitric acid directly and, as such, will prove useful in times of war and for the preparation of munitions. In times of peace, calcium nitrate is manufactured and sold as fertilizer. But this salt is deliquescent and has to be further treated to remove this feature. Where considerations of cost of current and interest on outlay do not enter the method can be recommended. It is estimated that through the lightning discharge of thunderstorms, 100,000,000 tons of nitrogen are fixed annually and carried to the earth's surface by precipitation of rain, snow and hail.

Among the advantages of the Arc Process may be listed :—

1. Cheapest cost of nitric acid, if power can be obtained at Rs. 30 per H. P. or less and if the power is efficiently utilised in a large plant running continuously to capacity.
2. Large amount of waste heat available for producing steam for the concentration of nitric acid and for other purposes.
3. Free raw materials.
4. Direct production of nitric acid, without intermediate products.
5. Small amount of labour involved.

Among the disadvantages may be mentioned :—

1. The large power requirements per unit of nitrogen fixed (vide Table on page 1).
2. The low electro-chemical efficiency; only 5% of the total electrical energy is used for actual nitrogen fixation, the rest being dissipated as heat.
3. The extensive and costly character of the absorption plant.
4. Nontransportability of the nitric acid produced; and the deliquescent nature of calcium nitrate.
5. Difficulty of disposing of the nitric acid not needed for munitions.

Most estimates of a nitrogen fixing plant by the Arc Process include the cost of a power Station, since very large power requirements are needed and the Process works continuously day and night. The cost of the Power Station will vary with the situation and the availability of water-power or cheap coal. In India, the capital outlay on hydraulic schemes has varied from Rs. 250 to over Rs. 1000 per H. P.

Excluding the cost of the Power Station, the capital cost of plant including arc furnace installation and concentrators, will be about Rs. 1,200 per ton of nitrogen fixed per year, or about Rs. 270 per ton of nitric acid (100%). The Nitrogen Products Committee (England) estimated in 1917 the cost of production per metric ton of nitric acid (100%) to be £ 2.5 for the production of dilute acid (exclusive of the cost of energy and of interest on capital but including labour, repairs, general charges, amortization of the arc furnace at an equated value of 8%) and £ 2 for concentration of the dilute acid. Assuming electrical power to be available at £ 3 per k. w. yr. and the capital to bear interest at 6%, the total cost will be :—

Per ton of 100%  $HNO_3$ .

For preparing dilute acid	...	£ 2.5
For concentration	...	2.0

Electrical energy, 1.87 k. w. yr. @ £ 3 per k. w. yr.	...	5 61
Interest on capital of £ 20 per ton HNO <sub>3</sub> at 6%	...	1 20
	Total	£ 11.31

The cost of manufacture of concentrated nitric acid by this Process comes to about £ 11.31, as compared with the present wholesale rate in London of £ 16 to 18 per ton.

The cost of production per ton of nitrogen fixed, by the above method, works out to about £ 51, as compared to about £ 30 to 35 per ton of nitrogen fixed by the direct synthetic ammonia process. It is, therefore, evident that if the aim be to fix nitrogen by the cheapest process for use as fertilizer the synthetic ammonia process is cheaper than the arc process by about 30 to 40%. The additional advantages of the manufacture of ammonia rather than of nitric acid for fertilizer purposes have been already referred to.

The adoption of the arc process for atmospheric nitrogen fixation is, therefore, not to be recommended.

**II. The Cyanamide Process.** This was the method largely used before the War and the procedure was to prepare calcium carbide from coke and lime in the electric furnace and to use the carbide so prepared for the fixation of atmospheric nitrogen. The product obtained was calcium cyanamide, which was used directly as fertilizer. When, however, the demand arose during the War for a larger supply of ammonia and nitric acid, the cyanamide was decomposed with steam under pressure to yield ammonia, which was later oxidized catalytically to nitric acid.

Large plants were started in the War and post-War period in Germany, Canada and America, but many have since closed down or have changed to the manufacture of synthetic ammonia. The Cyanamide process is very good for the manufacture of cyanamide, as such, for fertilizer purposes, but the use of this fertilizer has remained almost stationary at about 200,000 to 250,000 tons of nitrogen per year (vide Table on page 383) as compared with the increase of synthetic ammonia products from 250,000 tons of nitrogen in 1925 to about 1,300,000 tons of nitrogen in 1935.

The disadvantages of cyanamide as fertilizer are:— (1) its loose and dusty nature, which creates difficulty in spreading it on land; (2) its corrosive action on the exposed parts of the body while using it; (3) the presence of free lime, which prevents its being used along with superphosphate; and (4) the toxic effect produced in the soil under certain conditions, due to the presence of free calcium carbide and also due to the formation in the soil of dicyandiamide and tricyantriamide.

The demand now is for ammoniacal and nitrate fertilizers and most of the output of cyanamide in the present factories is further converted into ammonia and nitric acid, which naturally increases the cost of production of these materials, as compared with the synthetic ammonia process.

The raw materials required for cyanamide production are:— (1). High grade lime-stone, free from phosphate and containing 97 to 98%  $\text{CaCO}_3$ . According to Bingham<sup>4</sup>, the impurities should be less than:—  $\text{MgO}$ —0.5%  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ —0.5%,  $\text{SiO}_2$ —1 to 1.2%; only traces of sulphur and phosphorus. But it is interesting to note that limestone of the following composition was successfully used in America for the process<sup>6</sup>:—  $\text{CaCO}_3$ —96.41%,  $\text{MgCO}_3$ —2.3.7%,  $\text{SiO}_2$ —0.77%, Fe and Al oxides 0.55%.

(2). A coal or coke as low in ash and phosphorus as possible, akin to Anthracite coal of South Wales. The coke should contain less than 7½% of ash and 0.04% of  $\text{P}_2\text{O}_5$ .

Dr. L. L. Fermor<sup>6</sup> contributed an interesting article on the "Manufacture of Calcium Carbide, Calcium Cyanamide and Cyanides in India" to the Indian Munitions Board Hand book (1919) and gave estimates for a plant of 6000 tons annual capacity of carbide; but in a foot-note he adds that he later finds that the capacity of the Factory must be at least double, if it is to be a commercial proposition. In fact, cyanamide factories must be run on a fairly large scale with a very cheap source of electricity and satisfactory availability of the required raw materials near at hand, if they are to compete with their more advantageously placed competitors viz. the synthetic ammonia plants. The cyanamide plants which continue to work at the present day are situated at centres of cheap power, e. g. in Norway, Canada Switzerland, etc.

The capital cost of a cyanamide plant, exclusive of the power plant, will average about Rs. 500 per annual ton of nitrogen fixed. If it be intended to convert the cyanamide subsequently into ammonia and nitric acid, the capital cost may go up to Rs. 1000 per annual ton of nitrogen fixed.

Official tests carried out by the U. S. A. Government on the working of their cyanamide plants<sup>7</sup> (U. S. A Nitrate Plant No. 2) in 1918, showed the following to be the requirements per ton of nitrogen fixed in the form of calcium cyanamide (21.34% N; weight of crude cyanamide 4.685 tons):— (1) Nitrogen gas, 97,7000 cu. ft; (2) Lime, 4.865 tons; (3) coke, 2.117 tons; (4) coal, 1.4 tons; and (5) electrical energy, 12,213 k. w. hrs. or about 1.4 k. w. yrs.

The data given by Caro and Besemfelder<sup>5</sup>, based on German experience, go to show that one ton of nitrogen fixed by the process requires 2.75 tons of coke, 1.25 tons of coal, 0.22 tons of electrode carbons and about 1.9 k. w. yrs. of electrical energy. Ernst<sup>6</sup> (U. S. A.) estimates the requirements of raw materials per ton of nitrogen fixed to be limestone 8.14 tons, Coke 2.5 tons coal 0.98 ton, electrodes 179 lbs.

With regard to the possibilities of manufacturing calcium cyanamide in India, there are few places in this country which combine the advantages of a cheap source of electric power near at hand with the availability of cheap coal. The big hydro-electric installations in India are situated in the Bombay and Madras Presidencies and in Mysore, while the main coal fields are situated in Bihar and in Bengal.

Two alternatives are therefore possible one to situate the cyanamide factory near a coal field and obtain electrical energy from coal itself, or situate it near a big hydro-electric station and import coal from outside for the manufacture of carbide. The presence of limestone of the required purity in the vicinity will also determine the location of the Factory.

If a Factory is projected in the Madras Presidency near a centre of cheap hydro-electric energy, e. g. Mettur, the following may be taken to be a rough estimate of the production costs per ton of nitrogen fixed in the form of calcium cyanamide (20 to 21% N).

5 tons of lime @ Rs. 10 per ton	...	...	Rs. 50
2½ .. of coke @ Rs. 25 per ton	..	...	62.5
1½ .. of coal @ Rs. 20 per ton	...	...	25
1/10 .. of electrode @ Rs. 250 per ton	...	...	25
Nitrogen gas. 10,000 cu. ft.	...	...	10
Electric power, 2 k. w. yr. @ Rs. 40 per k. w. yr.	...	...	80
Labour and Staff	...	...	30
Miscellaneous charges	...	...	20
Repairs @ 5% on capital value	...	...	25
Depreciation @ 10% on capital value	...	...	50
Total production expenses per ton nitrogen fixed			<u>Rs. 377.5</u>

The above price of Rs. 377.5 per ton of nitrogen fixed, may be compared with the whole-sale market price in London of calcium cyanamide at £ 7/15 per ton, which works out to about Rs. 550 per ton of fixed nitrogen.

Hence the manufacture of calcium cyanamide in India, at certain favourably situated centres, is a practical proposition. But the market for this product being very limited and the tendency among the present cyanamide factories being to convert the cyanamide into ammonia and nitrates, in order to satisfy the current market requirements, the question must be carefully considered whether at the present time, when cheaper methods of fixing nitrogen are available, we should undertake the manufacture of calcium cyanamide.

One possible advantage of undertaking the manufacture of this compound is that we have the necessary raw materials within the country itself and need not depend on imported sulphur, as we may have to do, if we should undertake the manufacture of ammonium sulphate. But it will be pointed out later that even in the synthetic ammonia process, it is possible to prepare ammoniacal fertilizers other than sulphate, which would satisfy the market demands and still be independent of imported sulphur. This has actually been done with success by countries such as Germany and England, which have no local sources of sulphur of importance.

III. **Synthetic Ammonia Processes.** These depend on the direct synthesis of ammonia from purified nitrogen and hydrogen gases with the help of a catalyst such as finely divided platinum, "promoted" iron, iron cyanides etc. The process was first worked out on a commercial scale in Germany (Haber-Bosch Process adopted at Oppau in 1913 and later at

Leuna-Meresburg), but has since been modified by various investigators in regard to important details, such as : (a) the method of obtaining hydrogen and nitrogen ; (b) temperature of reaction ; (c) pressure ; (d) nature of catalyst, etc. These modifications are generally known after their originators e.g. the process of Casale, Claude, Fauser, Mont Cenis etc.

The merits of the synthetic ammonia processes, in general, are their smaller outlay of capital, running expenses, lower power consumption and cheaper production of ammonium compounds. The capital outlay will average about Rs. 600 to 750 per annual ton of nitrogen fixed. The power consumption is about 2,500 k. w. hrs. per ton of nitrogen fixed, if hydrogen is obtained from water-gas and about 16,000 k. w. hrs. if the hydrogen be obtained electrolytically.

The relative efficiencies of the different processes that have been developed for the production of synthetic ammonia vary, however, widely and need special consideration. In the next part we will attempt a comparative study of some of the more important methods, keeping in view their suitability to conditions in this country.

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