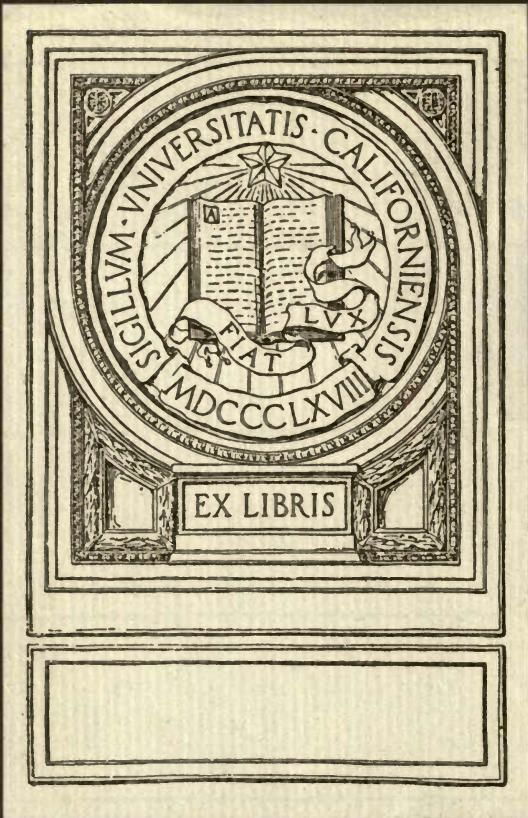


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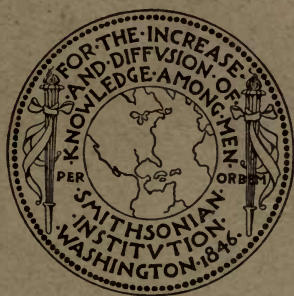
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Univ. of
California

BY

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SMITHSONIAN INSTITUTION

Nitrogen by itself under normal conditions is a gas. Chemically it is a notoriously sluggish inert element in its gaseous molecular state, indisposed toward the activity of entering into mineral-forming combinations with other elements. In the general process of earth evolution its more energetic elemental competitors have effected the various mineral combinations and progressive readjustments involved in the formation of the outer lithosphere, relegating the passive nitrogen element almost exclusively to the atmosphere. Thus it happens to-day that, with four-fifths of the bulk of the atmosphere made up of nitrogen gas, the relative amount entering mineralogically into the make-up of the earth's immediate exterior as a whole is inappreciable. Thus, too, with nitrogen dominating the very air itself in all its intimacy of relationship to life, the world has nevertheless been brought to face a vital problem in the scarcity of nitrogen in substantial form.

Passive and inconsequential though it is in the simple form of nitrogen, combinations with other chemical elements, once formed, are some of them capable of the greatest chemical energy and practical utility. Familiar examples are the particular combination of nitrogen with oxygen, yielding nitric acid, and that with hydrogen, forming ammonia; and it is the bringing about of such combinations on the part of free nitrogen which is implied in the technical expression nitrogen-fixation. Another important form of nitrogen compound, though less familiar in everyday use, is the deadly poisonous one with carbon, known as cyanogen. In addition to nitric oxide, the basis of nitric acid, nitrogen and oxygen also combine in three other ratios, and there are an almost endless number of other chemical compounds in which it appears, from simple ones where it assumes the basic role, such as nitrogen sulphide, to highly complex ones, such as the nitro-phenol derivatives especially noteworthy for their explosive properties. The latter, however, have only specialized uses, and are mostly prepared by the employment of nitrogen already fixed in one or another of the first named forms, so these three—that of

nitrogen with oxygen in the form of nitric acid and the nitrate salts, that with hydrogen in the form of ammonia and ammonia salts, and that with carbon in the form of prussic acid and the cyanide salts—constitute the fundamentally significant group of fixed nitrogen compounds. It is these for which constant search has been conducted in the realms of both organic and inorganic nature with ever-increasing pressure of requirement throughout the history of modern civilization; and more recently it is the inadequacy of the returns from natural sources which has led the search further afield from the realms of the real into those of synthesis, and led to the development of nitrogen-fixation processes.

Chemical elements may be totally insignificant as factors in earth structure, and yet contribute very substantially to localized occurrences; in fact, this is commonly the case. Nitrogen, however, has been handicapped with the serious disadvantage of having no stable form of mineral occurrence which is not readily soluble in water. Obviously then an arid climate is essential to the accumulation of nitrate mineral deposits on any great scale. Including with this special requirement the natural indisposition of the element itself toward mineral-forming activity, the combined requirements have proven so nearly prohibitive that so far as is known the desert areas of Chile and Peru alone have been able to meet them to the extent of providing deposits of any great economic importance.

The organisms of life contain nitrogen, and some of this is carried over into such derivatives as peat and coal. As a matter of fact, nitrogen is regularly occurrent in association with carbon, not only in the coal series but also in that of the hydrocarbons. As much as 10 per cent of nitrogen has been reported in this association, but the percentage lies rather uniformly between 1 and 2. Such amounts are, of course, in themselves negligible, and this form of nitrogen occurrence only began to assume importance with the modern development of industrial chemistry's capabilities along the lines of by-product recovery. In a by-product capacity the nitrogen content has already come to be a significant factor in connection with a wide range of chemical industries operating on the products of organic life, both of the present day and of the geologic past. Thus far the list of by-product fixed nitrogen sources in this category includes by-product coking, with its more or less closely related illuminating gas, producer gas, and blast furnace associations, peat treatment, oil shale distillation, sewage disposal, garbage rendering, wine manufacture, and bone carbonizing. Of this list, the coal product group nets the only really important yield at present. Along the other lines

either the supporting industries themselves are as yet undeveloped, as in the case of oil shale operations, or, as in the case of blast furnace operations, the opposite may be true, in the form of a development too mature to afford the flexibility of adaptation to by-product modifications. It is safe to say, however, that the range of possibilities for nitrogen recovery in this general direction has by no means been exhausted, and that other instances will be added to the coal product one, wherein combined nitrogen will appear prominently in contributing to the profit-forming margin by which new or reorganized lines of chemical industry are supported.

With the extension of chemical needs such as are offered by the development of cyaniding in metallurgy, and of refrigeration in the preservation of foodstuffs, and more especially with the extension of the need for artificially provided fertilizers, nitrogen compounds have come to be necessary not only to the welfare, but to the very existence, of a people living under modern conditions of economic development. At the outset the Chilean mineral nitrate deposits bore the brunt of the responsibility in providing for these growing needs; but more recently the gradual development of the by-product feature in chemical industries, more especially in the field of coal products, has introduced a very material competitor with the natural sources, matching their two and a half million tons of annual output in nitrate of soda with around two million tons of sulphate of ammonia. Even the combined sources have, however, proven insufficient to maintain reserves with which to meet the world's ever-increasing demands. In 1898 Sir William Crookes called attention to this inadequacy and pointed to atmospheric nitrogen fixation as the only preventive remedy for an impending economic breakdown. Recent events have emphasized the truth of this prediction, and brought the United States to a consideration of its national responsibilities in this direction.

Various means have been evolved in the chemical laboratory for effecting the fixation of atmospheric nitrogen through enforced combination, such as that with atmospheric oxygen or with hydrogen, both of which resultant combinations are absorbable in water to form nitric acid and ammonia water, respectively. Nitrogen, however, owing to the extreme inertness of its gas molecule, is difficult to stimulate into combination, and as a result most of the processes evolved have been found to offer such little encouragement toward efficient commercial practicability that to include all of them in any purely industrial discussion would serve only to introduce so many profitless elements of complexity. Accordingly, while any one of

the several other processes of more or less claim to merit may in some future time force its way to the front over what seem now to be insurmountable obstacles, there are to-day only three methods which have stood up under commercial test sufficiently to warrant definite consideration in a summary discussion. The three are known as the arc method, the Cyanamide process, and the Haber process of nitrogen fixation. Adding then the coal products source of fixed nitrogen, there are four currently prominent commercial sources of fixed nitrogen available for development to meet varying needs within the country.

I. ARC METHOD

If a current of air be passed through an electric arc some of the oxygen and nitrogen of which the atmosphere is composed enter into chemical combination as oxides of nitrogen, which may then be treated chemically for complete oxidation and absorbed in water to form nitric acid. Thus a limitless source of the requisite ingredients is provided right on the spot without the least cost whatever; the chemistry involved is apparently of the very simplest, most direct order, and, moreover, the method is in actual operation on a commercial scale. Superficially, therefore, the project would seem to be just about ideal, and presents one of the most alluring prospects offered in the field of chemical technology. The underlying difficulties in this problem are to be found in the inherent fact that nitrogen is chemically inert and extremely difficult to stimulate into the activity of entering into combination. This fact is forced home by the reflection that throughout the ages of the earth's existence its atmosphere has consisted of the self-same oxygen and nitrogen most intimately mixed, and had there been the least susceptibility on the part of the nitrogen, its complete combination with the oxygen would long ages ago have been effected, and instead of our now being engaged in trying to make them combine, there would be an atmosphere devoid of life-sustaining oxygen, and in place of water our oceans would be of concentrated acid. That same property of chemical inertness on the part of nitrogen which is the salvation of life itself on the earth has proven well-nigh disastrous to the commercial practicability of the arc method of nitrogen fixation, owing to the enormous electric power consumption involved.

In its present state of efficiency the arc method operations require roughly 2.75 to 3.00 H. P. year of electric power per ton of nitric

acid yield.¹ Now the average private cost of power-site development in this country has been over \$120 per horsepower. Counting an operative interest rate of 8 per cent to finance the development proposition, and then including the other necessary items of depreciation, overhead charge, etc., a total of 12 per cent or 13 per cent on each horsepower of development, or about \$15 per horsepower year, is a fair estimate of costs under present-day conditions in this country. Then the 2.75 H. P. requisite for the fixation of the nitrogen in one ton of nitric acid means a cost, roughly, of over \$40 per ton of product in power expense alone.

The item of \$40 per ton of nitric acid, it must be remembered, takes into consideration power costs alone, and, moreover, represents a product for which under ordinary conditions there is no great market, so it would have to be converted to calcium nitrate for use as fertilizer. But calcium nitrate absorbs moisture with avidity, and has not proven itself adaptable to American fertilizer requirements where the cost of labor renders mechanical sowing desirable; and, moreover, its fertilizer equivalent in Chile nitrate of soda is already available at around \$40 per ton, so the arc method cannot be made to stand on its own feet in this country under present conditions to the extent of contributing significantly toward the country's material well-being. Owing to the opportunity for securing lower interest rates, it would be possible for the Government to develop power at a much lower cost, commonly estimated at \$8 per horsepower year. This would cut the power costs to around \$22 per ton of nitric acid, but even then the enormous power requisites and the inadaptability of the product remain as unsurmounted obstacles.

The Government has under consideration at this writing a \$20,000,000 project for atmospheric nitrogen fixation primarily as a military measure, and it may be of interest in passing to interpret the efficiency of such a project in terms of the hydroelectric arc method. If the entire sum were to be put into power-site development, it would furnish somewhere around 150,000 H. P., capable of

¹The atmospheric nitrogen fixation industry is still in its first stages of evolution, and the figures available for the various processes are only such as are divulged from sources still actually involved. Moreover, the whole proposition is one offering no criteria for estimates other than those derived from actual operations. Accordingly, no credit for originality belongs with the publication of this paper, and on the other hand the only responsibility is for an honest attempt at interpretation. Every care has been exercised in checking up figures before their employment and there is every reason, short of actual operative proof, for their acceptance.

yielding in the neighborhood of 50,000 tons of nitric acid, or about one-fourth the estimated military emergency requirement alone; and at that, the entire cost of the plant installation and operation, running into the millions of dollars, would have to be additional. To satisfy Government estimates of around 200,000 ton war-time requirements would entail a power generation of around 600,000 H. P., or some 50,000 H. P. more than the total Niagara power development. Such a project would cost around \$80,000,000 to eventuate, and in its operation during peace times as an agricultural proposition in competition with other sources would necessitate an annual subsidy running into the millions of dollars, without offering a single advantage excepting as a preparedness measure. Norway, with three or four dollar power, has been able to develop the arc method on a self-supporting basis, but with a power consumption of around 3 H. P. per ton the difference between \$3 and \$15, or even the possible \$8 of Government cost, is precisely that between success and failure.¹

II. CYANAMIDE PROCESS

The so-called Cyanamide process of nitrogen fixation is dependent upon the fact that calcium carbide may be induced with comparative ease to absorb nitrogen, thus forming a combination of calcium, carbon and nitrogen, known commercially as cyanamide. Thus, unlike the direct arc product, cyanamide involves raw materials in the form of limestone and coal, or, rather, their derivatives, lime and coke. The lime and coke are fused together to form carbide, which is then inserted in finely ground condition in an electric furnace where a temperature of 1,000° C. is maintained, while a stream of nitrogen gas already separated out from the oxygen of the air is fed in and absorbed by the powdered carbide. The product is a mixture of cyanamide, excess carbide, and lime, which, after being hydrated to get rid of the free carbide and caustic lime, is ready for the market as nitrogen-bearing fertilizer. By treating this cyanamide with superheated steam its nitrogen may be released to enter into combination with the hydrogen of the steam, forming ammonia, which, if desirable, may in turn be burned with air to form nitric acid.

¹ It is to be borne in mind throughout this paper that any and all estimates and deductions refer purely to developments of nationally significant scale, and have not the least bearing upon the feasibility of localized private enterprises with the special opportunities which may be afforded. The one attempt to apply an arc process in this country, the purely experimental one at Nitrolee, South Carolina, may, however, be quoted in substantiation.

Thus the Cyanamide process affords three main products in direct sequence from the raw ingredients employed, namely, cyanamide, ammonia, and nitric acid, with nitric acid the end point instead of the first product to be derived, as is the case with the employment of the arc method. Carrying the process clear through to the nitric acid stage, the power consumption is approximately $\frac{1}{2}$ H. P. year per ton of nitric acid, or about one-sixth to one-fifth that requisite for the arc method; the raw materials employed are roughly a half ton each of lime and coke; the labor items involved in the two processes are to all practical purposes equal; and the normal peace time first product from the Cyanamide process, calcium cyanamide, has proven thoroughly applicable to agricultural use. Comparison of the two processes with reference to their relative values toward meeting the country's needs offer, first of all, a saving of four-fifths to five-sixths the power consumption in favor of the Cyanamide process. To appreciate the significance of this item it is only necessary to reflect that, whereas the country's estimated 200,000 tons requirement calls for a power supply of over a half million horsepower year in the one case as against one of only 100,000 H. P. year in the other, the difference is not merely one of economics, but of availabilities as well. Again, the normal product from the arc method is one whose chief demand is founded upon abnormal war times, while the normal first product from the other is an agricultural one, fitting into normal conditions. Again, the regular product from the arc method is not convertible to meet peace-time requirements adequately, while the product from the other is readily convertible to the emergency nitric acid form. Standing alone in prominent opposition is the fact that raw ingredients enter into the manufacture of the cyanamide product; but even this one opposing element will hardly loom so conspicuously when the carbon electrode consumption involved indirectly in arc method procedure is considered. Ignoring indirect elements, however, the raw materials employed entering into cyanamides involve a resource expenditure about the equivalent of a fifth that of arc method power under average American conditions. The difference between the two in significance amounts to that of three-fifths to two-thirds of the total power involved in arc method manufacture, plus the value of a product normally in demand as against that of one for which there is very little normal demand.¹

¹ Since power cost is the dominant item of expense in the arc method while it represents only about a third of the fundamental expense connected with the cyanamide method, it is obvious that as power costs are reduced the purely

III. HABER PROCESS

Bearing in mind that ammonia is a chemical combination of nitrogen and hydrogen in the ratio of one atom of the former to three of the latter, synthetic ammonia would result if a properly proportioned mixture of the two gases in purified condition can be prevailed upon to react chemically. With the two essential ingredients readily available, the one from air, the other from water, the only problem is that of inducing chemical reaction. By what is known as the Haber process a means of effecting the necessary stimulus has been provided, and the Haber process of fixation is on a commercial basis in Germany, where, from the last available figures, it was netting at the rate of about 200,000 tons of ammonium sulphate per year. The agency for combination employed in the Haber process is compression of the mixed gases in the presence of a catalyzing agent. This results in a partial combination of the two gases to form ammonia, which may be absorbed out and the uncombined portion of the original gaseous charge returned for renewed treatment. The process does not make the high demands on electrical power required by the other processes of atmospheric nitrogen fixation in use, but involves technical difficulties in the way of manipulation which have prevented the proportionate extension of its use, even in Germany under present exigencies. No opportunity for an analysis of comparative costs is available, but the fact that the use of the process has not been extended proportionately even in Germany, where cheap skilled labor and military exigency have combined to give it every advantage over conditions in this country, may well be taken as evidence that the process has not yet been perfected to a point where it is able to qualify for final consideration.

IV. BY-PRODUCT AMMONIA

Mention has already been made of combined nitrogen as a by-product from chemical industries based upon the products of organic life both of the present day and of the geologic past; and coal-product operations were cited as the most advanced forerunner in this direction. With the wastefulness of method characteristic of

financial aspects of the two methods converge. These converging lines cross at the point indicated by \$5.00 power. It would seem, however, out of the question that under present-day conditions power on sufficiently huge scale to carry a significant arc process plant is capable of development in this country, and, accordingly, the fact of convergence toward a \$5.00 H. P. year point, while interesting, can hardly enter as a determining factor.

American industrial practice, by-product development, even with reference to coal, has been unreasonably slow, and out of a possible 700,000 tons the actual combined nitrogen recovery in the form of ammonium sulphate is only about 225,000 tons. Of late, however, the rate of increase has been stimulated to such an extent that with the completion of the by-product ovens now building the annual capacity for output will be around 400,000 tons, and it is fair to assume that if the tendency is unchecked by external influences the full coking yield of ammonia will be available to the country's use within the next few years.

The actual development of combined nitrogen returns from other by-product directions has been negligible, and they assume significance only in their possible bearing upon the future establishment and growth of industries important to the country's welfare. From this viewpoint their potential significance is scarcely less real than it is with reference to by-product coking. This country is bound to be the greatest coke manufacturing one in the world, and the desirability of developing the enormous by-product possibilities thus opened up, entirely apart even from the half million to million tons of ammonium sulphate now directly under consideration, is scarcely to be overestimated. The country cannot afford to take any step which will further hinder progress along these general lines.

The normal first product from the arc method of atmospheric nitrogen fixation is nitric acid; that from the Cyanamide process is calcium cyanamide; that from the Haber process is sulphate of ammonia; and that of by-product derivation is also ammonia, either in the form of ammonia liquor or ammonium sulphate. For munitions use the acid form is required, while agricultural and other more usual requirements employ either ammonium sulphate or some other neutralized form of combined nitrogen. The original character of first product is not necessarily of any great moment, however, in view of the fact that, once fixed, the form of combination is susceptible of change. Thus, the original nitric acid of the arc method may be neutralized to a nitrate salt, usually that of calcium because of the cheapness of the calcium source in limestone; cyanamide may be forced to yield up its nitrogen in the form of ammonia, which in turn may be oxidized to nitric acid; and the same is true of the Haber process sulphate. By-product ammonia, however, offers at present an obstacle to such flexibility of application, in the form of impurities which stand in the way of effecting the delicately balanced reactions involved in the oxidation of ammonia to nitric acid.

In view of the feasibility of effecting chemical readjustments, the problem before the country is not one purely or even primarily of military exigency, but rather of agricultural betterment with military reservations. The country is capable of absorbing an indefinitely greater amount of nitrogen compounds agriculturally, and of doing so to ever-increasing advantage to all concerned, provided only there is no sudden glutting of the market demand for it and that the cost is maintained sufficiently low to put a premium on intensive land cultivation. The real problem, then, is that of developing sources of combined nitrogen such that their costs will not, as they do to-day, counterbalance the farmer's returns, making intensive effort profitless, and at the same time of avoiding any such precipitancy of action with reference to new sources as will tend to demoralize the market. If it fails to do the former, now that the matter has come up definitely for action, it will be failing to meet national responsibility of the greatest importance; if it fails to do the latter, consequences as disastrous to the country's welfare as any nitrogen shortage will result in the further hindrance of by-product development.

The nitrogen situation is one involving the whole structure of the country's economic development. Off hand, exception may be taken to this assertion on the grounds that the fundamental issue is one of military importance and may well be kept within those confines. Let any one who is disposed toward such an opinion evolve a solution whose efficacy is based purely upon a military need; then let him proceed to work out a balance sheet covering the operation of the resultant project over a period even of only five years. The scope of the issue broadens to include an agricultural aspect. Since nitrogen compounds may be prepared which are convertible between agricultural and military needs, and since an adequate nitrogenous fertilizer supply constitutes an invaluable economic asset, it may appear next that the situation resolves itself fixedly into the mere problem of determining the means calculated to provide the largest output of convertible nitrogenous compounds at the least cost. But industries no less important than a nitrogen-fixation one to the country's economic balance are involved in this field, and any governmental action in the nitrogen situation which would be disastrous in its effect on private initiative in the related industries would be inadvisable. Thus the scope of the issue widens not only beyond the strict confines of military need, but beyond those of agriculture as well, and action, to be of well-founded, permanently constructive value, must take cognizance of the whole situation.

SUMMARY

To summarize a situation of such magnitude adequately in a few pages is not only difficult, but becomes increasingly so the more it unfolds with study. Accordingly, in the foregoing pages the aim has been rather to point out in a general way the nature of the problem confronting the country than to attempt any analysis of its various factors, much less to offer any complete solution. In substance, the following expressions with reference to conditions and the inferences seemingly afforded are offered:

Nitrogenous compounds are essential not only to self-defense but to the country's capacity for self-support, and to be effective the source must be such that the product may be adaptable to meet either requirement.

The arc method has not thus far demonstrated capacity to meet the agricultural requirement at all, or even the defense requirement efficiently.

Definite knowledge concerning the Haber process is lacking, but its record of achievement is against it, and it would seem, moreover, unsuited to American conditions, at least in the present state of its development.

The Cyanamide process is capable of a development which will meet the requirements for a cheapened nitrogenous fertilizer source whose form of nitrogen content is readily convertible to nitric acid. The process is already a prominent factor in the economic well-being of most countries of older civilization, and is capable of similar extension in the United States.

By-product coking operations afford a source of nitrogenous compounds netting the country an annual production at the rate of over 200,000 tons of ammonium sulphate now, and due to raise this total to about 400,000 tons with the completion of the ovens now building. A total of about 700,000 tons would be possible if all coking were of by-product nature, and this total should be attained within the next few years. No practicable means for its oxidation to nitric acid have yet been found in this country.

By-product ammonia constitutes the country's one actual asset in the form of nitrogenous compounds. It has a rapidly growing yield of very great importance in itself, but of even greater importance as a factor contributing largely to the commercial possibilities of a number of industrial lines, especially that of coal products. The country cannot afford to run any risk of checking development along these lines.

The evolution of a practicable process for the oxidation of by-product ammonia to render present resources available, with the development of an atmospheric nitrogen fixation output by the Cyanamide process carefully timed to meet growing demands following a reduction in the retail price of nitrogenous fertilizer, would appear to be the desirable governmental procedure as being the one least liable to disastrous consequences.

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