

THE SOURCES OF OUR NITROGENOUS FERTILIZERS.

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NITROGEN is one of the most abundant elements on earth and at the same time normally by far the most costly of our fertilizer ingredients. This apparent paradox is explained by the facts that free nitrogen—that is to say, nitrogen uncombined with other elements—is of no use to plants, and that only with difficulty can it be made to combine artificially so as to be useful.

The existing emergency has served to bring sharply home to us our dependence upon fixed, or combined, nitrogen. We find ourselves confronted with the necessity of waging a great war and for that purpose producing vast quantities of powerful explosives. For the making of almost all modern explosives fixed nitrogen is essential. At the present moment tremendous tonnages of combined nitrogen are thus being used for munitions, to be released on the battlefield and pass back into the atmosphere as free nitrogen.

At the same time with this demand comes the necessity of raising more foodstuffs than ever before, that we may have a large export surplus to supply the needs of Europe. Increased acreage of food crops and increased bushels per acre are both essential in meeting this emergency. Increased bushels per acre require applications of fertilizer, and fertilizers are composed of phosphates, potash, and fixed nitrogen.

We have, then, at present an unprecedented demand on the nitrogenous materials of the world, a demand which is increasing daily and which the resources of the world are already being taxed to meet. Sources of supply which in normal times are used almost exclusively for fertilizer purposes are now being drawn on heavily for munitions, while our farmers, in the effort to produce up to the limit of their fields' capabilities, are calling for increased tonnages of

nitrogenous materials. This desire of our farmers to use more fertilizer should receive every possible encouragement. Unfortunately at present the abnormal demands by munition makers on the world's supply make it difficult to furnish the farmer with nitrogenous materials at reasonable prices. This condition is further accentuated by the high freight rates on imported materials.

USE AND EXTENT OF NATURAL DEPOSITS.

The only important natural deposits of nitrogenous material are the extensive beds of nitrate of soda occurring in the arid regions on the west coast of South America, mainly in Chile. This is the source of our Chilean nitrate, Chile salt-peter, nitre, or "soda," as it is called in some parts of the United States. The preservation of the nitrate salt in these beds is due to the fact that the country is practically without rain, since the salt is readily soluble in water and in a humid climate would long ago have been leached out of the rock.

The recovery of the nitrate is simple. The overburden of low-grade and worthless material is removed, and the richer, underlying rock is blasted out and then crushed, the nitrate salt is leached out with water, the resulting brine is evaporated, and the nitrate separated from the sodium chloride and other impurities in the rock and crystallized. Commercial sodium nitrate contains about 15 per cent of nitrogen; it is quickly soluble in water and, consequently, is almost immediately available for plants upon application to the soil. For this reason it is used as a top-dressing for the purpose of giving plants a quick start. It also enters extensively into mixed fertilizers as one of our most important nitrogen carriers. A considerable amount is also used in the production of sulphuric acid, which in turn is used to treat phosphate rock to give superphosphates.

In 1914, the latest year of normal consumption, 564,000 tons of nitrate of soda were imported, of which 162,000 tons were used for fertilizer purposes. In 1916, 1,200,000 tons came into the country and about 250,000 tons entered into agriculture. The greatly increased importations were due to demands by makers of munitions.

Only a small portion of the nitrate fields of Chile have been carefully explored and surveyed, and of known and

surveyed deposits probably not more than a quarter have been mined. It is likely, therefore, that the Chilean deposits will be able to furnish nitrate in large quantities for many years to come.

PRODUCTION OF AMMONIUM SULPHATE.

A second great source of quickly available nitrogen is ammonium sulphate. All coal contains a small percentage of nitrogen. When coal is burned or when it is coked in the beehive oven, this escapes into the air as free nitrogen. When coal is coked in modern retort ovens, this nitrogen is recovered as a by-product combined with hydrogen in the form of ammonia. This by-product ammonia is then treated with sulphuric acid, and ammonium sulphate results. This is a dry, grayish powder, containing about 20 per cent of readily available nitrogen. Ammonium sulphate is one of our most important fertilizer ingredients. It is largely used in the preparation of mixed fertilizers, but in view of its solubility it could probably be advantageously used as a substitute for sodium nitrate as a top-dressing.

If all the coal now coked in this country were coked in by-product retorts we should have a supply of ammonium sulphate amounting to nearly 900,000 tons annually. In fact, we produced in 1916 only about 325,000 tons, since nearly two-thirds of our coke was produced in the wasteful beehive oven. It is gratifying to record, however, that the transition from beehive to by-product ovens has been proceeding rapidly in recent years, and a steadily increasing percentage of our coke is being made in a way which permits of the recovery of the valuable minor constituents in the coal. At present large quantities of by-product ammonia, as in the case of sodium nitrate, are going into the manufacture of explosives and the price has advanced very sharply.

USE OF ORGANIC AMMONIATES.

In point of tonnage one of our largest single sources of nitrogen for fertilizer purposes is cottonseed meal. This is the dried residue of the cotton seed after the oil has been extracted. It contains between 5 and 8 per cent of available nitrogen as well as small percentages of phosphoric acid and

potash. It is used very extensively throughout the South as a fertilizer material and 325,000 tons were used in 1914 by fertilizer manufacturers. In addition, a large tonnage was undoubtedly applied by the farmers direct.

In recent years the practice of feeding organic ammoniates, like cottonseed meal and tankage, has increased, and this reduces the amount available for fertilizer. The use of these organic substances as a feed for cattle should be encouraged, however, as in this way they are made to serve a double purpose, since a very large proportion of the fertilizing elements reappear in the manure. The value of cottonseed meal as a feeding stuff has long been recognized by European cattle raisers, and normally large quantities of this material are exported to countries like Denmark and Holland, where intensive dairying is practiced.

Any decided increase in the use by our farmers of organic nitrogen carriers will force us to look elsewhere for nitrogen for fertilizer purposes, and this fact lends additional importance to the investigations now being carried on looking to the fixation of atmospheric nitrogen.

Two important nitrogenous fertilizer materials, dried blood and tankage, are derived from slaughterhouse waste. Dried blood is precisely what its name implies. It carries from 10 to 13 per cent of readily available nitrogen, and has long been recognized as a valuable fertilizer ingredient. Tankage is the dried residue after the grease has been extracted from slaughterhouse wastes. Such materials as can not be used in the meat, leather, soap, glue, or bone industries find their way ultimately to tanks, where they are thoroughly cooked with steam. The grease is removed and the residue pressed, dried, and marketed as tankage, which contains from 6 to 12 per cent of nitrogen in readily available form.

Another important organic ammoniate is fish scrap. The capture and utilization of menhaden for fish oil and fish scrap has become an established industry on the Atlantic coast. The fish are taken in immense quantities in nets carried by steam trawlers and are treated in much the same way as slaughterhouse wastes, being cooked, freed from oil, and the residue pressed and dried. Fish scrap contains, in addition to about 8 per cent of nitrogen, about 5 per cent of

phosphoric acid. On the Pacific coast considerable fish scrap is manufactured as a by-product by using the wastes from fish-canning factories. In 1914 approximately 63,000 tons of fish scrap entered into fertilizer manufacture.

Such materials as fur, wool, hair, leather, hoofs, and horns all contain percentages of nitrogen, and in the industries using these materials large quantities of waste accumulate. The nitrogen in these materials is not readily available, so that they are not used in the raw state for fertilizer purposes. They are, however, treated by mixing with acid phosphate, the action of the acid rendering the nitrogen available. This mixture is known to the trade as base goods, and furnishes a considerable quantity of the nitrogen in mixed fertilizers. Bone, ground or steamed, though primarily a phosphate carrier, also contains varying percentages of nitrogen.

FIXATION OF ATMOSPHERIC NITROGEN.

Chemists have long recognized in the atmosphere about us a huge reservoir which must ultimately supply our increasing needs in the way of fixed nitrogen. A tremendous amount of research has been done on the problem of fixing this atmospheric nitrogen in useful form. Nature accomplishes the result by means of bacteria, particularly those forms which cause the nodules on the roots of leguminous plants. The Romans knew the value of legumes in a rotation and put the knowledge in practice without knowing why. We understand why soil conditions are improved by legumes, but are still confronted with the unanswered question of how bacteria fix the nitrogen.

The artificial fixation by chemical or electrochemical means is difficult and costly. Several methods are in actual operation and others are in the experimental stage of development. That the problem will be solved and cheap fixed nitrogen be made available for our farmers is as nearly certain as anything in the future can be called certain.

The three general processes now in operation are the arc, the cyanamid, and the synthetic ammonia processes.

The principle of the arc furnace is based upon the well-known fact that if the nitrogen and oxygen in the air are subjected to the action of an electric arc portions of the two

gases combine to form nitric oxide. Thus traces of nitric oxide can be detected in the air after a severe lightning flash.

Using this fact as a basis, electric furnaces of various types have been constructed for producing either a broad or a long electric arc and passing air through it.

Three types of such furnaces are now being commercially operated. The Birkeland-Eyde furnace draws out the arc by the action of magnets into a broad sheet of flame through which the air is passed. The Schoenherr type employs a long arc produced by the blast of the passing air driven at high pressure up a steel cylinder. The Pauling furnace produces a fan-shaped flame by the action of the air under pressure between two diverging electrodes. A fourth type, the Kilbourn-Scott, employs three electrodes, and the air, entering under pressure below the arc, produces a cone-shaped flame. This last type is reported to be in operation on an experimental scale in England.

Unfortunately the reaction of the nitrogen and oxygen in the electric arc is a reversible one, and unless the temperature of the gases is immediately dropped from about 3,000° C., the temperature of the arc, to about 1,200° C. the nitric oxide again reverts to free nitrogen and oxygen. This sudden drop in temperature is difficult to accomplish, and under the best operating conditions no arc process recovers more than 2½ per cent of the entering air in the form of nitric oxide. For this reason large amounts of electric current are necessary per unit of nitrogen fixed, and arc processes can be operated commercially only where current can be generated in large amounts and very cheaply.

Owing to the topography of the country these conditions can be met in Norway, where both the Birkeland-Eyde and the Schoenherr processes are in operation on a large scale, the power being furnished by hydroelectric installations. The nitric-oxide gas is drawn into large towers, where it reacts further with oxygen and forms other oxides of nitrogen, after which it is blown through absorption towers, where it encounters water or dilute acid, and in this way weak nitric acid is formed. This is neutralized with lime and calcium nitrate formed. As marketed it contains about 9 per cent of nitrogen, and prior to the present war small amounts were exported to this country from Norway.

The Pauling process has been installed in several places in Europe where power is available at a cheap rate. A small installation for using this process was erected some years ago in South Carolina, but nitrate of lime from this plant has never entered the market in any quantity.

It is doubtful whether the arc processes in their present stage of development can be used successfully in this country, owing to the high cost of power. To develop the power in most of our streams is a very expensive undertaking, and even where conditions permit of the production of power at low cost, as at Niagara Falls, other industries as a rule stand ready to buy it at a price that makes its use for the arc process of nitrogen fixation impracticable.

The cyanamid process for fixing nitrogen involves the production of calcium carbide by melting a mixture of lime and coke in an electric furnace. The carbide is ground and again heated and pure nitrogen is forced through the mass. At about 1,000° C. a reaction takes place and calcium cyanamid is formed, containing about 20 per cent of fixed nitrogen. Upon treatment with superheated steam, cyanamid gives up its nitrogen in the form of ammonia, which may then be oxidized to nitric acid or treated with sulphuric acid to produce ammonium sulphate.

The cyanamid process requires large amounts of cheap power, and so far has never been used commercially in this country. A plant on the Canadian side of Niagara Falls, operating under a long-term contract which insures it a limited amount of power at a cheap rate, has produced cyanamid commercially for some years, most of which has found a market in the United States.

The Haber process of nitrogen fixation involves the production of ammonia directly from its elements, hydrogen and nitrogen. If the two gases be compressed to 1,500 pounds to the square inch, heated to 600° C., and passed over spongy iron, a certain percentage of the mixture is combined as ammonia. This process and the cyanamid process have had very wide development in Europe, and especially in Germany, since 1914, owing to the demand for fixed nitrogen for explosives. Though the mechanical difficulties involved in the Haber process are great, the power cost is

small, and it seems to offer possibilities for development in this country more attractive than either the arc or the cyanamid process. The Bureau of Soils has installed a synthetic ammonia plant at its Arlington laboratory, and is at present experimenting with the process, with the object of reducing the mechanical problems to the simplest form and determining the best conditions of pressure and temperature, and the most efficient catalyzers.

In addition to the above there are several processes which are not as yet operating commercially but which seem likely to be of importance in nitrogen fixation in the near future.

The Bucher process, which fixes nitrogen as cyanide, involves heating a mixture of carbonate of soda, coke, and iron in an atmosphere of nitrogen. Laboratory experiment has demonstrated the chemical feasibility of the process, but up to the present no satisfactory furnace for continuous large-scale operation has been devised.

Recently attention has been called to a new process, involving the use of carbide, which appears to have advantages over the cyanamid method. This is the Reid process, in which the carbide is produced by coking a mixture of ground coal and lime and reducing this lime-coke to carbide in a type of electric furnace which permits of the use of "off peak" power. By this is meant power available at most electric plants during that portion of each 24 hours when part of the power which the plant is capable of producing is not being taken by its regular consumers. Such power can always be had at very cheap rates. The Reid process nitrifies the carbide at a lower temperature than the cyanamid method, and by the use of a catalyzer reduces the time required for the nitrification process. Finally the nitrified product differs from cyanamid in that it gives off its nitrogen as ammonia under the action of waste or wet steam. It seems probable that by the economies effected this process may be able to operate successfully under American conditions.