FERTILIZERS

1. Introduction

Fertilizers are added to soils to supplement the supply of inorganic nutrients required for plant growth in amounts necessary to eliminate the deficiencies that limit profitable crop and livestock production. The three principal nutrients required for plant growth are nitrogen, phosphorus—as orthophosphate—and potassium.

The chemistry of nitrogen in soils is complex, involving cycling through ammoniacal, nitrate, and organic forms, as discussed in the Entries on Nitrogen Fixation. The total nitrogen content of many soils is of the order of 2 to 4 tons/hectare, but this is almost entirely bound to organic matter and mineral soil material; at any one time only a few kg/hectare are present in available forms as nitrates or exchangeable ammonium. Except in the case of leguminous plants, which have the capacity for the "biological fixation" of atmospheric nitrogen, this amount of available nitrogen is insufficient to meet the needs of high yielding crops, although continually replenished by “mineralization” of the organic forms. The amounts of fertilizer nitrogen that must be added vary greatly in different soils, crops, and climates but generally range up to maximal values of about 250 kg/ hectare.

Soil phosphorus exists in a number of forms, including organic compounds, precipitated minerals, and adsorbed forms, with a very small amount present in the soil solution. Only a small fraction of the total is readily available for uptake by plants. The phosphorus itself is always present as orthophosphate (PO_4) minerals or organically bound orthophosphate. The amount that must be applied to supply enough available phosphate for economic crop growth varies greatly for different soils. In soils with a high capacity for the fixation of phosphate in insoluble forms the amounts that must be added may be 70% greater than the plant requirements. Application rates are usually in the range of up to 70 to 115 kg/ hectare as P_2O_5 or 30 to 50 kg/hectare calculated in terms of elemental P(1).

The primary sources of potassium in soils are the potassium bearing minerals in the parent rock and the clay minerals present in the soil. As these weather, the potassium is released and retained as exchangeable potassium associated with the negatively charged clay minerals and organic matter. This exchangeable potassium is readily available for plant uptake but may not equal the

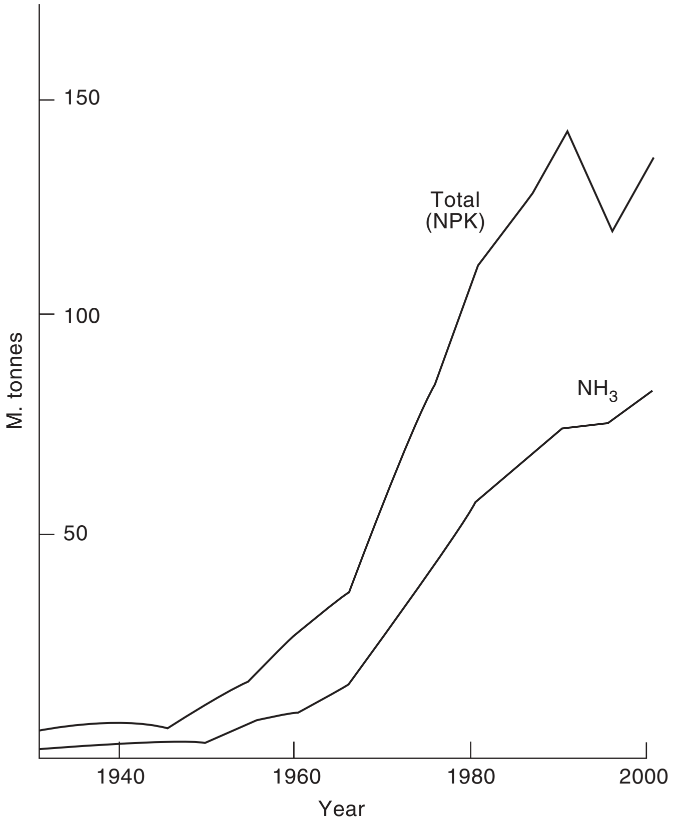

Fig. 1. Annual world fertilizer consumption (Mts/year), 1930–1999 and annual global production of fertilizer ammonia by the Haber-Bosch process (Mts/year) 1930–2000 (3).

Table 1. **Annual World Fertilizer Consumption (Mts/yr), 1930–1999**

Year	N	P_2O_5	K_2O	Total nutrients
1930	1.30	2.77	1.39	5.46
1940	2.34	3.23	2.99	8.56
1949	3.40	5.65	3.87	12.9
1959	9.83	10.37	8.21	28.4
1969	28.6	19.8	15.2	63.6
1979	57.5	31.7	24.1	113.3
1989	79.1	37.6	26.7	143.4
1999	82.8	33.5	22.0	138.3

amount required by the crop over the whole growing season. Except in some tropical soils with high rates of weathering, the rate of release from minerals is often insufficient to support the crop requirement, and supplemental additions from fertilizers are needed. The amounts required are in the range of 50 to 100 kg/hectare in terms of elemental K, or 60 to 120 as K_2O.

Calcium and sulfur are also essential plant nutrients present in fertilizer materials but are not regularly included in listings of composition and are not used to calculate application rates. Calcium is present in superphosphate fertilizers as calcium phosphate or calcium sulfate; it may also be added to soils in limestone, which is not considered as a fertilizer but a soil additive used to correct soil acidity. Where ordinary superphosphates are used, the sulfur needs of crops are usually more than adequately met by the sulfate which these contain. In areas where sulfur deficiencies do occur, these may be overcome by supplemental additions of gypsum, which is generally regarded as a soil amendment rather than a fertilizer material.

The growth in the world consumption of fertilizers, illustrated in Figure 1, has shown a steady increase since 1930 with a marked acceleration after about 1960 due to the increasing consumption of nitrogen, which reached about 60% of the total nutrient consumption in 1999. The data presented in Table 1 show that there has been no corresponding increase in the consumption of either phosphorus or potassium since 1970. The geographic distribution of production has also changed, with Asian production increasing from about 16% of the 1970 total to close to 50% of a larger market in 1999; this area includes both India and China, which were the most rapidly growing markets at the end of the century. In contrast, North American production stagnated at about 21 ± 1.3 MT/year after 1980, and European production remained at a level of about 21 ± 0.8 MT/year since 1990, after being at a steady level of about 31 ± 1.8 MT/year between 1980 and 1990. This general pattern of world production is expected to continue into the immediate future (1).

2. Nitrogen Fertilizers

2.1. Production.

Ammonia Synthesis. The Haber-Bosch process for the "fixation" of atmospheric nitrogen, developed in Germany between 1908 and 1910, is now the primary process in the production of over 99% of nitrogen fertilizer materials. In this process, a mixture of pure hydrogen and nitrogen with a 3:1 atomic H/N ratio ("synthesis gas") is passed over an iron oxide catalyst at 530 °C at a pressure of 35 MPa (= app. 350 atms), which facilitates the reaction $N_2 + 3H_2 \rightarrow 2NH_3$. Conversion of the synthesis gas is not complete in a single pass, but production of large amounts of ammonia are achieved by its removal from the gas stream and recycling of the unreacted synthesis gas.

The process is dependent on supplies of pure hydrogen and nitrogen, and the production of these is an integral part of the overall process. In the original process, hydrogen was made using the "water gas" reaction in which water vapor is passed over glowing coke to give the reaction $C + H_2O \rightarrow CO_2 + H_2$. The introduction of more water in the product gas in the presence of an iron oxide/chromium oxide catalyst resulted in conversion of carbon monoxide to the dioxide with an increased amount of hydrogen: $CO + H_2O \rightarrow CO_2 + H_2$. The CO_2 was removed in a scrubber and excess CO in a second scrubber containing cuprous ammonium formate. Pure nitrogen was obtained from the Linde process for the liquefaction of air, which has remained as the source of pure nitrogen up to the present time.

Since its inception in 1910, the process has been further developed and improved in many plants throughout the world. One of the more important of these improvements has been the improvement in energy efficiency. The total energy requirement of the process includes the fuel and electrical energy used plus the heat equivalent of the chemical energy in the feedstocks. The initial coke-based Haber-Bosch process of 1910 required more than 100 GJ/ton of NH_3, but this requirement has now been reduced to less than 30 GJ/ton (2). One of the most important improvements in the 1950s was the introduction of hydrocarbon alkanes in place of coke as the basic feedstock for the water gas reaction, which may then be written $C_nH_{(2n+2)} + nH_2O \rightarrow nCO + (2n + 2)H_2$. Although mixtures of light hydrocarbons may be used, methane—often available in natural gas—is the most economical because it has the highest H/C ratio of 4, when the value of n in the above equation is, of course, 1.0.

The growth in the amount of nitrogen fixed by the Haber-Bosch process since 1930 is shown in Figure 1 and Table 2.

Other Processes. Other processes, now of minor importance, include electric arc production, the calcium cyanamide process, and ammonia recovery from coke ovens.

Electric arc processes depend upon the formation of relatively small amounts of nitrogen oxides by the reaction $N_2 + O_2 \cdot 2\ NO$ when air is passed

Table 2. **Annual Global Production of Nitrogen Fertilizers by the Haber-Bosch Process, (kt N/yr)**[a]

Year	Production	Year	Production
1929	930	1970	30,230
1940	2,150	1980	59,290
1950	3,700	1990	76,320
1960	11,290	2000	85,130

[a] Ref. 3.

through high voltage discharges at temperatures above 3,000 °C. Because the reaction is reversible, rapid cooling is necessary to reduce the back reaction with condensation of the oxides to nitric acid, which is then reacted with lime to produce calcium nitrate. The reactions are:

$$2\ NO + O \Longrightarrow N_2O_3$$

$$N_2O_3 + H_2O + O_2 \Longrightarrow 2\ HNO_3$$

$$2\ HNO_3 + CaO \Longrightarrow Ca(NO_3)_2 + H_2O$$

The high energy requirements of this process have limited its usefulness, except where cheap hydroelectric power has been available. Despite some development in Norway during the first part of the twentieth century, the process is no longer a significant source of fixed nitrogen.

Calcium cyanamide is made by heating calcium carbide (CaC_2) in a pure nitrogen atmosphere at 1,000 to 1,100 °C. The calcium carbide itself is made in a preliminary process requiring the fusion of lime and coke in an electric furnace. The reactions are: $CaO + 3C \rightarrow CaC_2 + CO$ and $CaC_2 + N_2 \rightarrow CaCN_2 + C$. The calcium cyanamide itself may be used as a nitrogen fertilizer or used as a source of ammonia when treated with superheated steam: $CaCN_2 + H_2O \rightarrow CaCO_3 + 2NH_3$. The multiple steps in this process complicate production schemes, and this, together with the high energy requirements, limit the commercial usefulness of the process.

During the heating of coal to remove coal tar and coal-gas in coke production, about 15% of the nitrogen present in the coal is released as ammonia, which can be captured by passage of the gas through a solution of ammonium sulfate in dilute sulfuric acid. The yields are relatively low, equaling about 3 kg NH_3/tonne of coal. The ammonia recovery is secondary to the primary production of coke, and the cost of the necessary recovery plant makes this economically uncompetitive with Haber-Bosch product as a source of ammonia.

Nitric Acid Production. Nitric acid, HNO_3, which is required for the manufacture of ammonium and calcium nitrates, both used as nitrogen fertilizers or components of mixed fertilizers, is commercially produced by the oxidation of gaseous ammonia to nitrogen oxides with catalytic assistance according to the reactions:

$$4\ NH_3 + 5\ O_2 \Longrightarrow 4\ NO + 6\ H_2O$$

$$2\ NO + O_2 \Longrightarrow 2\ NO_2$$

$$4\ NO_2 + H_2 \Longrightarrow HNO_3 + NO$$

Although these reactions were previously known, the industrial development of the process was undertaken in Germany in the early years of World War I for the manufacture of ammonium nitrate for use in munitions and explosives.

2.2. Nitrogen Fertilizer Materials.

The nitrogen compounds present in fertilizers are listed in Table 3.

Ammonia. Anhydrous ammonia itself, or as a concentrated solution in water (aqua ammonia), is used extensively as a nitrogen source in the US, representing about 30% of the national requirement of agricultural nitrogen use. In

Table 3. **Nitrogen Compounds in Fertilizers, Formulas, and % Nitrogen Content**

Compound	Formula	Nitrogen Content, %
anhydrous ammonia	NH_3	82
aqua ammonia	NH_4OH	Varied
ammonium nitrate	NH_4NO_3	35.0
ammonium sulfate	$(NH_4)_2SO_4$	21.2
ammonium phosphates	$(NH_4)H_2PO_4$	16.1
	$(NH4)_2HPO_4$	21.2
calcium nitrate	$Ca(NO_3)_2$	17.0
urea	$(NH_2)_2CO$	46.6

many areas in Texas, Louisiana, and the Middle West "Corn Belt" states, direct delivery by pipeline to distribution centers offers favorable economics, reducing freight costs and avoiding the need for on-farm storage facilities. Both fertilizers are applied by injection to a depth of several centimeters into the soil.

Ammonium Nitrate. Ammonium nitrate is one of the two leading nitrogen fertilizer materials on a world basis: 10% in 1997. The high N content is advantageous for the reduction of freight and application costs per unit weight of nitrogen. The presence of 50% of the nitrogen in the highly available nitrate form makes it suitable for use in regions growing crops with a short vegetation period but has the disadvantage that, because the NO_3^- ion is not adsorbed by soil, it may contribute to relatively large nitrogen losses by the leaching of increased soil nitrate into streams and groundwater. Although the application of any nitrogenous fertilizer results in some degree of soil acidification, the nitrate form is notably less acidifying than ammonium sulfate and has a lower tendency for the loss of nitrogen to the atmosphere as gaseous ammonia. The hygroscopic character of the crystalline material, coupled with its explosive nature, contributes to difficult storage and handling properties and the need for the production of purified and stabilized forms.

Ammonium Sulfate. Ammonium sulfate was the first nitrogenous fertilizer made by the Haber-Bosch process, produced by the reaction of ammonia with sulfuric acid. In contrast with the nitrate salt, it is chemically stable, not highly hygroscopic. It also supplies supplemental sulfur to soils that may be deficient in this element, but this is of minor value when it is used on soils receiving applications of ordinary superphosphate. The disadvantages of the material are its relatively low nitrogen content, which increases storage and transportation costs, and its marked tendency to cause soil acidification, which is greater than that of any other nitrogen fertilizer material.

Ammonium Phosphates. Ammonium phosphates include mono- and diammonium orthophosphates (see Table 3) and ammonium polyphosphates. As discussed below, these are made directly by reaction anhydrous ammonia with orthophosphoric acid or superphosphoric acid. Both are dry crystalline materials with good handling properties.

Calcium Nitrate. Calcium nitrate, made by neutralization of nitric acid with ground limestone, is mainly used in Europe. The calcium content reduces the tendency of the fertilizer for soil acidification and makes the material desirable for use where there is any tendency for soil salinization. Calcium ammonium nitrate, a related material made by mixing ground limestone with concentrated ammonium nitrate solution, has a higher nitrogen content, between 21% and 27.5%. In the 1990s this material supplied about 80% of the nitrogen fertilizer use in Holland but has since been declining in the world market (4).

Urea. Urea is a stable highly water-soluble compound of high nitrogen content (47%), with good storage properties that make it the most commonly used nitrogen fertilizer. The synthesis process has remained essentially unchanged since it was first developed by the BASF Corporation in 1922. In this process, liquid ammonia is reacted with carbon dioxide to produce ammonium carbamate, which is then dehydrated to form urea. The reactions are:

$$2\ NH_3 + CO_2 \Longrightarrow NH_2 \cdot CO_2 \cdot NH_4$$

$$NH_2 \cdot CO_2 \cdot NH_4 \Longrightarrow (NH_2)_2CO + H_2O$$

The high analysis and good handling properties of urea have made it the leading nitrogen fertilizer, both as a source of nitrogen alone or when compounded with other materials in mixed fertilizers. Although an excellent source of nitrogen, urea can present problems unless properly managed; due to its rapid hydrolysis to ammonia, significant volatilization loss of this may occur if prilled or granular urea is applied to and left on the soil surface without timely incorporation. Mixtures of urea and ammonium nitrate for use in mixed fertilizers are also more highly hygroscopic than ammonium nitrate itself.

Urea-Formaldehyde (38% N) and Isobutylidene Diurea. Urea-formaldehyde (38% N) and isobutylidene diurea (IBDU, 31% N) are specialized materials developed as "slow-release" nitrogen fertilizers. Both are polymeric compounds made by reacting urea respectively with formaldehyde and isobutyraldehyde. Both are insoluble in water, and, in the soil, both hydrolyze to release urea at a rate that depends upon the granule size, which can be varied to control the rate of nitrogen release. The category of "slow-release" materials also includes sulfur-coated urea (36% N), made by spraying urea granules with molten sulfur followed by a light coating of wax sealant. Here the rate of release is controlled by physical factors that delay the entry of water into the granule; once this occurs, osmotic forces cause rapid release of the solution. The slow overall rate of release reflects differences in the lifetimes of individual granules rather than any chemical reaction.

3. Phosphate Fertilizers

3.1. Source Materials. Mineral deposits of phosphate rock are the primary source material for phosphate fertilizers. These occur worldwide, but the dominant sources are in the United States, Morocco, and Russia. Estimates of the world reserves and resources are presented in Table 4. The wide and complex range of deposits of different quality and characteristics are described in an

Table 4. **World Phosphate Rock Reserves and Resources, $\times 10^6$ t**[a]

	Reserve	Resource
World Total	11,000	33,000
Morocco	5,900	21,000
USA	1,200	4,400
Other	1,810	7,920

[a] Ref. 1.

extensive technical literature (5). The principal phosphate mineral is apatite or fluorapatite, $Ca_{10}(PO_4)_6(OH,F)_2$. Secondary minerals include silica, silicates, and carbonates, usually as calcite or dolomite ($CaCO_3$); these must be removed by beneficiation treatment before the rock is processed (6). Beneficiation processes may differ depending upon the character and composition of different deposits; two steps are usually required in which the ore is first crushed and the phosphate fraction then separated by washing, screening, or flotation.

After beneficiation, the phosphate rock is reacted with strong acid to form more soluble phosphate compounds. Sulfuric and phosphoric acids are used for the manufacture of superphosphates and nitric acid for "nitric phosphates."

3.2. Phosphate Fertilizer Materials. The principal phosphate compounds present in fertilizers are listed in Table 5.

Table 5. **Compounds Present in Fertilizer Materials, with Representative P_2O_5 Content and Water-Soluble Fraction**[a]

Fertilizer material	% P_2O_5	% P_2O_5 Water-soluble	Compounds present
superphosphates			
ordinary	21	85	$Ca(H_2PO_4)_2$, $CaSO_4$
triple	45	87	$Ca(H_2PO_4)_2$
ammoniated superphosphates			
ordinary	14	35	$(NH_4)H_2PO_4$, $CaHPO_4$, reprecip. apatite, $CaSO_4$
triple	48	50	$(NH_4)H_2PO_4$, $CaHPO_4$, reprecip. apatite,
ammonium phosphates			
monoammonium	52	100	$(NH_4)H_2PO_4$
diammonium	46	100	$(NH_4)_2HPO_4$
polyphosphate	43	100	$(NH_4)_2HPO_4$, $(NH_4)_3HP_2O_7$ and other polyphosphates
urea-ammonium phosphate	28	100	$CO(NH_2)_2$, $(NH_4)H_2PO_4$, $(NH_4)_2HPO_4$
nitric phosphate	9	40	$CaHPO_4$, $(NH_4)H_2PO_4$, $Ca(NO_3)_2$, reprecip. apatite,
dicalcium phosphate	48	3	$CaHPO_4$

[a] Ref. 1.

Phosphate Rock. Despite the very low water solubility of phosphate rock, it has been found to be an economically useful fertilizer in some acid tropical soils of high phosphate fixing capacity. This is probably due to slow dissolution under the acid conditions to give a low phosphate concentration in the soil solution; this does not produce the rapid reaction with the soil minerals characteristic of the high concentrations released during the dissolution of more water-soluble phosphates. The effectiveness of the rock varies considerably depending upon its character and composition and the soil conditions. The effectiveness declines rapidly where the soil pH is higher than about 5.0 or 5.2, and its usefulness is, therefore, confined to acid-tolerant crops that can grow in soils of this pH or less (8). Because most of the major crops of the temperate region require soil pH values above this limit, phosphate rock is not a major fertilizer material in such areas.

Ordinary Superphosphate. Ordinary superphosphate is produced by the treatment of apatite rock with concentrated sulfuric acid to give a mixture of monocalcium phosphate and calcium sulfate. The ideal reaction is:

$$\mathrm{Ca_{10}(PO_4)_6(OH/F)_2 + 7\ H_2SO_4 \rightarrow 3\ Ca(H_2PO_4)_2 + 7\ CaSO_4/F_2 + H_2O}$$

Water, CO_2 (from any carbonate present), and some fluorine (as fluosilicate) are lost as gases during the reaction, but the calcium sulfate and other residual minerals remain in the dry product, which has a P_2O_5 content of about 21%. This acidulation of phosphate rock to make ordinary superphosphate was the original process developed for the manufacture of effective phosphate fertilizers, dating from the first successful industrial production by Lawes in England in 1842. It remained the dominant phosphate fertilizer material until the introduction of triple superphosphate in the 1950s. Despite the disadvantage of a relatively low phosphate content, which increases transportation and handling costs measured on a unit P_2O_5 basis, ordinary superphosphate possesses some economic advantages. These include lower energy requirements in processing, the possible use of by-product sulfuric acid, the avoidance of the need for calcium sulfate waste disposal, and the retention of insoluble iron and aluminum phosphates and calcium fluoride without significant reduction in the amount of water-soluble phosphate content. This latter consideration is likely to become of increased future importance as supplies of higher-grade phosphate rock are depleted and lower grade material is increasingly used (9).

Triple Superphosphate. Triple superphosphate is made by the reaction of phosphate rock with phosphoric acid to produce monocalcium phosphate. The ideal reaction, assuming the rock is pure hydroxyapatite, is:

$$\mathrm{Ca_{10}(PO_4)_6(OH)_2 + 14\ H_3PO_4 \rightarrow 10\ Ca(H_2PO_4)_2 + 2\ H_2O}$$

The presence of a fluorapatite fraction reduces the monocalcium phosphate yield. The resulting products have P_2O_5 contents of about 46%, of which about 90% is usually water-soluble. The insoluble fraction comprises fluorite and iron and aluminum phosphates derived from impurities present in the original rock and phosphoric acid used in the reaction.

Because the production of triple superphosphate is dependent upon phosphoric acid, this must be made as a preliminary step in the overall process. The "wet process" phosphoric acid, which is the material usually used, is made by an extension of the reaction of sulfuric acid with phosphate rock used in ordinary superphosphate manufacture:

$$\begin{array}{c} Ca_{10}(PO_4)_6(OH/F)_2 + 10\ H_2SO_4 \\ \downarrow \\ 6\ H_3PO_4 + 10\ Ca(SO_4, F_2) + H_2O \end{array}$$

After removal of the calcium sulfate by filtration of the reaction slurry, the acid is concentrated to about 52% to 54% P_2O_5 content by evaporation before it is used in triple superphosphate production. The calcium sulfate represents a major waste by-product, which has limited uses, being of inferior quality to regular commercial gypsum, due to phosphate contamination and impurities derived from the original phosphate rock.[2]

Both ordinary and triple superphosphates are produced in granulated forms that have good handling storage and spreading qualities and are satisfactory for use in the production of granulated compound fertilizer formulations also containing nitrogen and potassium materials (10).

Ammoniated Superphosphates. Because ordinary and triple superphosphate contain the acidic monocalcium salt, both react readily with ammonia to form multinutrient "ammoniated" superphosphates. These can be used to make dry "bulk-blended" granular compound fertilizers with a wide range of NPK compositions. The addition of ammonia results in the reduction of the water-soluble fraction of the phosphate content from about 85% to 90% to about 50%, depending on the degree of ammoniation, due to the conversion of the monocalcium phosphate to a mixture of monoammonium and dicalcium phosphates:

$$Ca(H_2PO4)_2 \rightarrow (NH_4)H_2PO_4 + CaHPO_4.$$

The dicalcium phosphate is only slightly water-soluble. While it is less effective as a source of phosphorus for plants than monocalcium phosphate when in the granular form, dicalcium phosphate is of significant value as a fertilizer because the phosphate it contains reacts much less readily with phosphate-fixing materials in the soil matrix; its long-term value is similar to that of the water-soluble fraction.

Ammonium Phosphates. Since their introduction in the 1960s, when granular ammonium phosphate fertilizers were first made by the reaction of anhydrous ammonia with phosphoric acid, these have become one of the leading forms of water-soluble phosphate fertilizer on the world market. Both can be readily produced in granular form with low moisture content and good storage and handling properties; the monoammonium form can also be made as a powdered material (10). Diammonium phosphate is a major material in the world market where the high analysis (18-46-0) offers favorable unit transportation and handling costs for the supply of both nutrients. It is also widely used as a source of nitrogen in both dry and fluid fertilizers.

One disadvantage of the diammonium form is the possible loss of nitrogen from the soil to the air as ammonia if the fertilizer is spread on the soil surface without incorporation. For this reason, the monoammonium product is favored in regions where the soil pH is above 7.0 or more; with an analysis of 11-52-0, this form is economically equal to the diammonium source. Both materials can be readily incorporated in bulk blended formulations and are used in the production of liquid fertilizers.

Ammonium Polyphosphates. Ammonium polyphosphates are liquid fertilizers with compositions up to 11-37-0, manufactured by the reaction of anhydrous ammonia with superphosphoric acid. Superphosphoric acid is made by the concentration of regular wet-process acid up to P_2O_5 concentrations of 78%. Granular polyphosphates suitable for bulk blending are made by reacting ammonia with regular wet process acid of 52% P_2O_5 content and using the heat of reaction to drive off water to produce a phosphate melt of 10-43-0, with about 40% of the phosphorus in the polyphosphate form. These materials are, however, not suitable for bulk blending due to their “sticky” nature (10).

Urea-Ammonium Phosphates. Urea-ammonium phosphates are mixed fertilizers made by the addition of urea to diammonium phosphate during the granulation stage of the process. The urea is added as a solution or as granules or prills. The basic formulation is 28-28-0, but compositions up to 35-17-0 can be made with up to 25% of the phosphorus as polyphosphate. The materials have excellent spreading and storage properties (10).

Nitric Phosphates. Nitric phosphates are produced by the acidulation of phosphate rock with nitric acid. One manufacturing advantage they offer is that they do not contain or require the removal of calcium sulfate because no sulfuric acid is used to make them. However, unless supplementary phosphoric acid is used in the acidification, the water-soluble fraction of the product is low. For this and other reasons, the use of nitric phosphates has greatly declined since the introduction of ammonium phosphates (10).

3.3. Agronomic Effectiveness of Phosphate Fertilizers.

The effectiveness of phosphate fertilizers depends on a number of factors, including their chemical composition, their physical state, the way in which they are used, and the crop and farming systems in which they are employed. Two chemical indices have been found to be broadly useful in relating their relative agronomic effectiveness to their chemical composition. These are the size of the water-soluble phosphate fraction and the overall solubility in neutral ammonium citrate solution. The latter includes the water-soluble fraction but also serves as an additional index of the value of the water-insoluble fraction. It has been adopted as a standard chemical definition of the “available phosphate” used in fertilizer quality control laws in the United States and other countries.

The relative agronomic effectiveness of different fertilizer materials is usually evaluated in greenhouse trials or small-plot experiments using the soil type, management practices, and cropping systems in which they will be used. The relation between chemically defined availability and agronomic effectiveness of phosphate fertilizer materials is complex, being affected by a range of management factors. Among others, these include particle size, composition, application method, soil phosphate status, soil pH and texture, and the kind of crop being grown. While no comprehensive survey of these effects is possible in this article, some general statements can be made.

The initial rate of growth of many crops can be increased by the use of larger sized granules of water-soluble materials. This is of particular importance for such crops as corn, where the early growth stages are important in the development of a mature stand, although this, of course, also depends on other factors. For fertilizer granules up to about 6 mm in diameter, the effectiveness is directly related to the amount of water-soluble phosphate in each granule because this, in turn, determines the volume of the surrounding soil into which the phosphate is moved by capillary forces acting on the dissolving fertilizer particles. The amounts of water-soluble phosphate in a number of representative fertilizer materials are presented in Table 5.

The availability of water-insoluble compounds is determined by the surface area of the granules; these are more effective when used as small granules or fine powders of less than 1 mm diameter and are well mixed with the soil matrix. In some cases, the solubility and effectiveness of less water-soluble forms can be increased by granulation with ammonium compounds. These effects may not be observed when fertilizers are applied to fertile soils of high phosphate status because the immediate crop response may be small, the object of the fertilizer application being to maintain the soil fertility by replacement of the phosphate removed by the crop or that fixed by reversion to less available forms in the soil (7).

The fixation of a significant fraction—sometimes as high as 70%—of the applied phosphate almost invariably requires the addition of amounts in excess of that taken up by the crop. Because this “fixed” phosphate is retained in the fertilized soil horizon by adsorption on soil minerals, continued applications result in increases in the available soil phosphate and a reduction in the response to the added fertilizer. The fixation reactions cause a slow reversion to less available forms that takes place over several years.

4. Potassium Fertilizers

Potassium fertilizers are produced by the refinement of mineral deposits of soluble potassium salts found in salt lakes or underground deposits. The principal deposits are in North America—with large deposits in Canada—and the former Soviet Union; these represent about 85% of the world total. The principal ore is sylvinite, a mixture of crystals of sylvite (potassium chloride) and halite (sodium chloride). The potassium salt is separated by flotation or fractional crystallization to give a product containing about 50% K or 60% K_2O. The mineral langbeinite ($K_2SO_4 \cdot 2MgSO_4$) is also used to produce potassium sulfate by treatment with KCl and removal of the magnesium chloride by fractional crystallization. The fertilizer grade of K_2SO_4 contains about 41% K or 49% K_2O.

While the KCl product is economically preferable because of the higher analysis and reduced transport costs, the presence of the chloride ion is of no positive agronomic significance but has disadvantages for application to crops such as tobacco and potatoes, which are sensitive to it, and where the sulfate form must be used. Where mixed fertilizers containing triple superphosphate or ammonium phosphates are used, the sulfate salt may provide supplemental sulfur in areas where there is a shortage of soil sulfur.

5. Fertilizer Use

Fertilizer applications include a very wide variety of usage patterns and materials with a considerable range of compositions. Because no extended survey of these is possible within the scope of the present article, the following discussion is confined to the broad aspects of the types of materials produced and how these are used. More detailed information on use patterns found in the various crops and agricultural systems of the world can be sought in the agricultural literature.

Fertilizers are applied as fluids, dry bulk, or bagged granulated materials. Considerable amounts of nitrogen are used as “direct applications” of this single nutrient, either by surface applications of urea, ammonium nitrate, or sulfate or by the injection of gaseous ammonia or “aqua ammonia” solution into the soil. The use of these latter high nitrogen content fluid materials has steadily increased due to their ease of handling and application to row crops; they are also well suited for use by contract suppliers and applicators who formulate and apply fertilizers to the field as requested by the farmer.

Mixed formulations containing two or three nutrients are used as dry materials made by the blending of granular materials in bulk or in fluid forms made by blending fertilizer solutions3. About one-half of the fertilizers used in the United States are applied as mixed formulations, and about three-fourths of these are used as bulk materials or in solution. The fraction used as dry bagged materials—as opposed to those supplied and used in bulk—has steadily declined over the last 30 years, reflecting the reduced transport costs of bulk materials and the growth of the contract applicators as part of the farm support industry (10,11).

The availability of the number of high analysis components has made possible the supply of mixed materials with a wide range of composition. This is of particular importance for the supply of fluid fertilizers by contract applicators who are able to prepare and apply materials whose composition is adjusted to meet the needs of individual farmers. Such arrangements also eliminate the need for application equipment and fertilizer storage facilities on the farm and permit the development of application schedules that can be fitted to weather and other farm operations.

The forms of nitrogen in “conventional” fertilizers discussed above all dissolve rapidly in moist soil to give a large amount of readily available nitrogen. This may be much greater than the immediate needs of young plants, and the excess will then enter the general nitrogen cycle of the soil, with reduced availability to the older maturing crop, or be leached out of the soil profile. While this loss can be remedied by supplemental applications, some special ‘slow-release’ formulations have been developed in attempts to provide a more controlled nitrogen supply to the crop over more extended periods. These formulations are of two kinds: those containing less soluble or more stable forms of nitrogen and those where the regular granules are enclosed in a protective coating to slow their dissolution and nitrogen release. Slow-release formulations have been found most useful on crops other than corn or small grains whose early rapid growth is promoted by substantial amounts of readily available nitrogen. Sulfur coated urea has been shown to be an effective source of nitrogen in rice culture where fertilizer must be applied to the flooded crop, when significant amounts of nitrogen can be lost by denitrification or volatilization of ammonia. Some success has been reported for sugarcane and pineapples, where crop growth extends over more than one growing season, in turfgrass production, and the management of greens on golf courses and permanent grass in parkland. A technical discussion of the possible value of slow-release fertilizers has been presented by Allen (12).

5.1. Application Techniques. Fertilization practices depend upon a number of factors including crops grown, soil types, and weather conditions in a region or area. The timing of applications in relation to rainfall events and the rate of crop growth is always of major importance. Practices vary greatly between regions with different rainfall patterns, with major differences between temperate and tropical regions. These cannot be summarized here, and information must be sought from surveys and recommendations for local practices, but some general comments are possible.

There are several principal techniques for fertilizer application in the field. These include: 1) surface broadcasting without incorporation into the soil, 2) surface application with immediate incorporation and placement in the soil by an attachment to the plow or cultivator, and 3) the injection of liquids and gaseous formulations by pumping through cultivator knives. Applications are also made in irrigation water for crops grown with such water supplies.

In some cases the use of high analysis fertilizer materials may cause problems if the risks associated with their physical or chemical properties are not understood. Where surface applications of formulations containing urea or some ammonium salts are not plowed or cultivated into the soil and the fertilizer is not rapidly washed into the soil by rain, they may lose a significant fraction of their nitrogen to the atmosphere; the risk of such losses is particularly high on calcareous or more alkaline soils. Where row crops are fertilized with injections or subsurface placement of soluble materials, correct placement of the fertilizer band below or to the side of the seed or emerging plant is important because high concentrations of salt and ammonia are toxic to young roots or germinating seeds.

5.2. Application Rates. Rates of fertilizer applications are often based on field and greenhouse experiments designed to measure the response of the chosen crop to applications of nutrients under soil and management conditions representative of local practices. Such experiments require multiple replications of each treatment to give data suitable for statistical analysis. The measurement of crop response to individual nutrients, where each must be measured where the supply of other nutrients is fully adequate, can require very elaborate experimental designs. The most precise measurements of crop response can be made in greenhouse experiments where growth conditions can be fully controlled.

Recommendations for fertilizer usage by farmers are, however, usually based on results from field experiments designed to use the actual farm practices of the region, including application and cultivation methods and crop management. It is frequently found that the application rates required to reach maximum yields are so high that the fertilizer cost is not met by the value of the crop obtained. For this reason, the recommended rates of application are close to those at which the response curve shows the highest return for the unit cost of the fertilizer applied. This point, which is essentially that at which the effectiveness of an incremental addition of fertilizer is greatest, is almost invariably below the maximum potential yield.

The amounts of nutrients applied may differ considerably from those taken up by the crop or removed in the harvest. The increase in soil fertility by the addition of nitrogen results in increased biological activity and consumption of nitrogen by the soil biomass. This may result in increased losses of nitrate by leaching or of gaseous losses to the atmosphere by denitrification. Increases in the availability of soil phosphate are almost inevitably made at the expense of some fixation of phosphate by the soil minerals. This phosphate is not, however, lost from the soil profile, and successive additions of fertilizer phosphate tend to slowly increase availability of the soil phosphate reserve, so that, while the response of later crops to the fertilizer may be initially reduced, continued economic crop production will require continued, but perhaps smaller, fertilizer applications. The level of these applications must then be determined by soil tests measuring the availability of the residual soil phosphate coupled with records of crop yields and local knowledge of the soil conditions and crop requirements.

Soil tests are of great value in making recommendations for application rates. Owing to the complexity of the soil nitrogen cycle and its sensitivity to soil temperature and soil moisture levels, soil testing for nitrogen requirements has lagged behind that for phosphate and remains more limited in scope. The most successful are based on measurements of early nitrogen uptake by the crop or measurements of available soil nitrogen early in the growing season. In the United States, a recent development of this approach for the estimation of nitrogen requirements of corn has been the introduction of the "Pre-Side Dress Nitrate Test" (PSNT) to measure the amount of available soil nitrogen after the emergence of the crop early in the growing season. This is used as an index of the amount of nitrogen that should be applied as a supplemental side-dressing to meet the high nitrogen demand of the maturing crop. This approach has been found to give more consistent results than applications based on estimates of the mineralization rates of soil nitrogen (14).

Soil tests for phosphate are almost invariably based on the extraction of soil samples with dilute acids that also contain a reagent—often an ammonium salt—for complexing or sequestering the calcium and aluminum ions released with the phosphate during the reaction. The various tests used in different places reflect the differences in soil, climate, and crops in the regions where they have been developed. Each one provides an estimate of the available phosphate in the soil that can be correlated with the crop response measured in greenhouse or field experiments. The amounts of phosphate extracted are only a fraction of the total phosphate in the soil, and different fractions may be removed from the same soil in different tests; interpretations of such soil test data are, therefore, based, in some degree, upon experience and judgment (13).

Potassium fertilizer requirements are based upon the amount of "exchangeable potassium" measured in the same soil extractant, again calibrated against the results of field experiments interpreted in the light of local experience. In many soils, the readily available or "exchangeable" potassium is naturally replenished over the growing season by release of less readily available potassium held within the crystal structure of the soil minerals and soil clays, but this may not occur fast enough to meet the demand of the growing crop. The addition of fertilizer potassium then serves to replenish the readily available soil potassium and to prevent depletion of the overall reserve as this is used by successive crops.

6. Environmental Impacts

The function of fertilizer applications is to raise the level of soil fertility and biological activity in the soils and farming areas where they are used by increasing the amounts of available plant nutrients, in particular nitrogen and phosphorus. Adverse environmental impacts may occur where the amounts of these nutrients are increased to levels at which losses of nutrients carried in drainage water or air from the fertilized land cause undesirable changes in water quality and the ecological environment in wetlands, streams, rivers, and lakes that receive surface drainage and groundwater. These effects are usually eutrophic, representing undesirable increases in the biological activity of the aquatic environment, including large increases in phytoplankton production and reduction of light penetration by the algal blooms in the water column or by the growth of epiphytes on the surface of submerged aquatic vegetation. These changes result in hypoxic or anoxic conditions due to the reduction in oxygen production by photosynthesis and its consumption by the decaying excess organic matter present. Where large areas of farmland are involved, such changes, which have been observed in many parts of the world, may extend to large distances from the nutrient sources, sometimes including significant impacts on river estuaries and the oceanic coastal shelf (15).

It should, however, be noted that, while fertilizer applications represent major inputs to agricultural systems, they are not the only sources of nutrients contributing to the decay of water quality. Mineralization and nitrification of soil organic matter, biological fixation of atmospheric nitrogen, animal manures, municipal sewage wastes—both as solids and nutrients discharged from water purification plants—also contribute to undesirable nutrient loadings to drainage waters. In agricultural areas where there is high animal production, the amounts of nutrient applied to the land as animal manures are often of similar magnitude to fertilizer applications.

In recent years a large body of research has been directed towards the need to reduce the fertilizer contribution to these problems, recognizing the need to provide more detailed information on optimal fertilization rates to reduce excess amounts of nitrogen that may remain in the soil after the growing season to produce high nitrate concentrations in subsoils and with subsequent loss by leaching in drainage or groundwater. Adjustments of the recommended levels for nitrogen applications to give credit to the nitrogen contained in manure applications or remaining from previous annual applications have become a feature of the Nutrient Management Plans, which amplify the simpler recommendations of previous years. Because phosphate losses are closely associated with losses in runoff or that carried by eroding soil, they can be reduced by Best Management Practices designed to reduce erosion and runoff. Recent research has focused on the use of soil tests to identify soils where the levels of available phosphate are such that they present particular risks for the release of runoff containing phosphate concentrations that present an environmental hazard (16). Other recent work has focused on the use of hydrologic techniques and studies of drainage patterns to identify particular land areas within watersheds and drainage basins where the risks of erosion and runoff are minimal, with consequent reduced risk of adverse environmental impacts of fertilizer use (17).

7. End Notes

1. In stating fertilizer composition nitrogen is always expressed as elemental *N*, but phosphate and potassium content may be expressed in terms of either their elemental forms, P and K, or as their oxide forms, P_2O_5 and K_2O. The conversion factors are $P = 0.437\ P_2O_5$ or $P_2O_5 = 2.29\,P$ and $K = 0.83\,K_2O$ or $K_2O = 1.20\,K$. The oxide form is the most frequently encountered and will be used here.
2. "Electric furnace" acid is a much purer form of phosphoric acid, made by burning elemental phosphorus produced by the reaction of phosphate rock with silica and carbon at high temperature in an electric furnace and adsorbing the phosphorus pentoxide in water. This is, however, not economically competitive with wet process acid for fertilizer production. Because of its high purity, electric furnace acid is extensively used to make phosphates, such as dicalcium phosphate, used as animal feed supplements and in other industrial processes for which wet process acid is unsuitable.
3. Granular materials of mixed formulation are first made by feeding the desired proportions of phosphate and potassium components into ammoniator-granulator drums, where nitrogen solutions or anhydrous ammonia are added to provide the heat of reaction and the fluid necessary for the production of granules, which are then screened for uniformity of granule size. These granular materials may then be physically mixed to make bulk blends of other compositions (10).

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