

## *Our Changing Fertilizer Technology*

**A**BOUT 100 years ago, nitrogen, phosphorus, and potassium were identified as essential plant nutrients. Previously, fertilization was practiced on an empirical basis. Substances such as bone, wood ashes, and organic materials were used because they were found to be beneficial to crop yields, but it was not known why they were beneficial.

Nitrogen, phosphorus, and potassium became known as the primary plant nutrients. Although many other elements have been found since to be essential to plant growth, the three primary nutrients continue to be the main concern of the fertilizer industry. Other elements usually are present in adequate quantities in the soil or may be supplied more economically by means other than inclusion in fertilizer mixtures. For instance, large quantities of limestone, dolomite, and gypsum are applied directly to the soil to supply calcium, magnesium, and sulfur. Elements needed in smaller quantities are sometimes included in mixed fertilizers. They are often applied separately, since soil deficiencies in these elements are not often widespread enough to warrant inclusion in fertilizer mixtures that are offered for general use.

Although the fertilizer industry has been classified for many years as a chemical industry, it was, until the early 1950's, primarily mechanical in nature. Phosphate rock was mixed with sulfuric acid to make superphosphate. Superphosphate was mixed with potash salts and organic materials to make mixed fertilizer. Chemists and chemical engineers were conspicuously absent from many fertilizer manufacturing establishments.

But the fertilizer industry is changing rapidly. It is fast becoming a full-fledged chemical industry. New processes are being studied and adopted. New forms of fertilizer and new chemical compounds are appearing. The chemical industry is noted for its progressiveness and the avidity with which it seeks and adopts new processes. Many more changes in the fertilizer industry in the near future may be expected.)

### Trends in Quantity and Cost of Fertilizers Used

Fertilizer production and consumption have increased very rapidly in the United States, particularly since 1945. Table 14.1 and figure 14.1

TABLE 14.1. U. S. Fertilizer Consumption and Composition

Year	Thousands of Tons of Primary Plant Nutrients				Percent of Total Primary Plant Nutrients Supplied as Mixed Fertilizers	Concentration of Mixed Fertilizer, % N + P <sub>2</sub> O <sub>5</sub> + K <sub>2</sub> O
	(N)	(P <sub>2</sub> O <sub>5</sub> )	(K <sub>2</sub> O)	(Total)		
1910 <sup>a</sup>	+46	499	211	856	59	14.80
1920	228	660	257	1145	49	13.90
1925	279	680	282	1241	62	16.00
1930	377	793	354	1524	66	17.90
1935	312	597	306	1215	68	18.32
1940	419	912	435	1766	62	19.90
1941	458	993	467	1918	62	20.22
1942	399	1131	546	2076	67	20.32
1943	508	1238	643	2389	72	20.68
1944	635	1405	649	2689	68	21.12
1945	641	1435	753	2829	71	21.74
1946	759	1671	854	3284	73	21.50
1947	835	1775	878	3488	74	21.58
1948	841	1842	956	3639	75	22.14
1949	911	1884	1065	3860	72	22.78
1950	1126	2073	1215	4414	70	23.58
1950-51 <sup>b</sup>	1238	2107	1383	4728	72	24.19
1951-52 <sup>c</sup>	1422	2199	1581	5203	72	24.86
1952-53 <sup>c</sup>	1637	2271	1738	5646	72	25.85
1953-54 <sup>c</sup>	1847	2242	1806	5896	71	26.87
1954-55 <sup>d</sup>	2126	2286	1841	6253		

<sup>a</sup>From 1910 through 1950: USDA, Agricultural statistics, table 710, p. 705 (1952).

<sup>b</sup>W. Scholl and H. M. Wallace, 1955 (USDA). Commercial fertilizer consumption in U.S.

<sup>c</sup>\_\_\_\_\_, \_\_\_\_\_, and E. I. Fox 1955 (USDA). Domestic fertilizer consumption, Commercial Fertilizer and Plant Food Industry 90:35.

<sup>d</sup>A. L. Mehring and C. A. Graham, 1955 (USDA). Fertilizer situation for 1954-55, Commercial Fertilizer and Plant Food Industry 90:44.

present statistics showing this rapid increase. The quantity of primary plant nutrients used in the form of commercial fertilizers more than doubled during the period 1945-1955; it quadrupled during the period 1930-1955.

As shown in table 14.1, the use of nitrogen and potash increased more rapidly than the use of phosphate fertilizers during the period 1945-1955. Nitrogen use tripled during this period; potash use more than doubled, and phosphate use increased by about 60 percent. The ratio of plant nutrients (N:P<sub>2</sub>O<sub>5</sub>:K<sub>2</sub>O) was about 1:2:1 for many years prior to 1945; in 1955, this ratio approached 1:1:1. It appears likely that nitrogen use will exceed that of either of the other plant nutrients.

The price of fertilizers decreased considerably when compared on a basis that takes into account the decreased purchasing power of the dollar. The adjusted cost per unit of the primary plant nutrients in terms

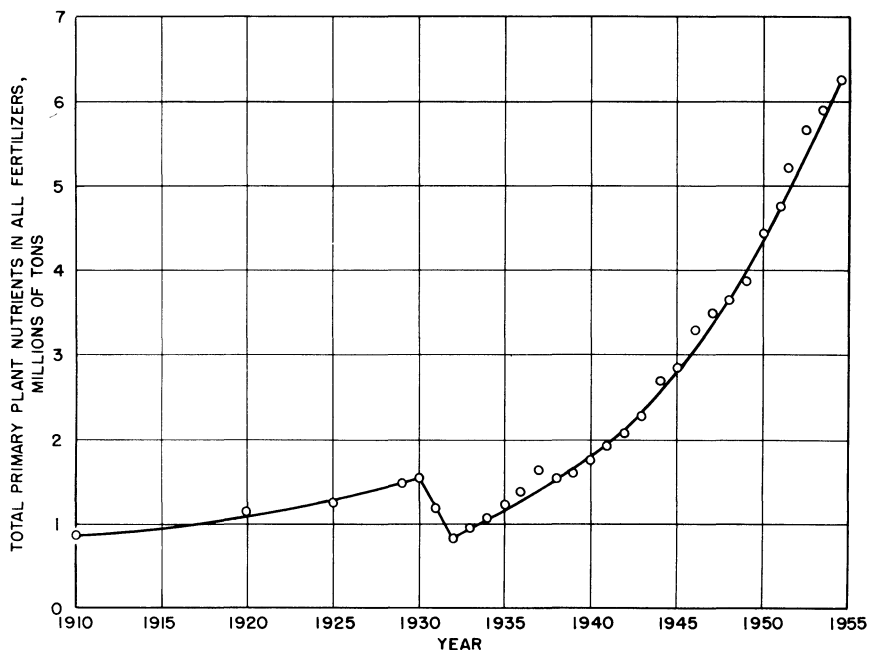


Fig. 14.1 — Annual U. S. consumption of primary plant nutrients in fertilizer.

of the 1955 dollar is presented in table 14.2. Past prices were adjusted by the Bureau of Labor Statistics wholesale price index. The basis for these data was wholesale market prices of the principal fertilizer materials, in bulk carload lots, f.o.b. point of production.<sup>1</sup> In calculating an average price of a unit of one of the nutrients (such as nitrogen), an average of the principal forms of that nutrient was taken and weighted in proportion to the quantities of these forms that were used.

The data in table 14.2 indicate that the 1954-1955 price of a unit of nitrogen in fertilizer materials was only about one-third of the adjusted 1920 price. A unit of potash cost only one-fifth of the adjusted 1920 price. The adjusted price of a unit of  $P_2O_5$  decreased about 27 percent.

The decrease in the relative price of two of the three primary plant nutrients has probably been an important factor in the increased use of fertilizer and in the shift in proportions of plant nutrients. Changes in costs of plant nutrients also may result in changes in optimum farm practices. For instance, in 1920 when one unit of nitrogen cost about four times as much as one unit of  $P_2O_5$ , the use of phosphate fertilizer on nitrogen-fixing crops would yield a quite different return, in

<sup>1</sup>These price relationships may not accurately reflect the relative costs of the plant nutrients to farmers because of locational factors, especially differences in transportation costs.

TABLE 14.2 Adjusted<sup>a</sup> Wholesale Price, Bulk, F.O.B. Works or Ports, 1955, Dollars per Unit of N, P<sub>2</sub>O<sub>5</sub>, or K<sub>2</sub>O

Year	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	Average
1920	4.63	1.23	2.18	2.68
1930	4.30	1.06	1.39	2.25
1940	3.42	1.26	1.17	1.95
1950	1.79	0.82	0.40	1.00
1955	1.56	0.90	0.40	0.95

<sup>a</sup>Wholesale price index of Bureau of Labor Statistics, U. S. Department of Labor: Monthly Labor Review, Feb. 1952 and May 1955, and Statistical Abstracts of the United States, 1937 and 1954.

comparison with the use of nitrogen fertilizer, than by the mid 1950's when chemical nitrogen was relatively cheaper.

#### Sources of Nitrogen

Typical wholesale prices for the various forms of nitrogen during a 35-year period (1920-1955) are shown in table 14.3. Prior to 1920, natural organics were the principal sources of nitrogen, and generally the cheapest. Ammonium sulfate, a by-product from the steel industry, was an important source of nitrogen in 1920. This material came into use with the adoption of by-product coke ovens around 1900. The quantity of available ammonium sulfate increased as the by-product ovens replaced the older beehive ovens and as the steel industry expanded. Nitrate of soda was a principal source of nitrogen from 1920 to 1950, but this source supplied a much smaller percentage of the total nitrogen used in 1955.

Since 1920 the use of organics has declined. In many instances, new uses have been found for these materials in which they are processed into products of higher value.

The first successful synthetic ammonia plant was started in 1921. Several other plants were built in the next few years. These plants supplied nitrogen materials to both chemical and fertilizer markets. About one-third of the fertilizer nitrogen consumption was supplied from synthetic ammonia in 1930, and about the same proportion in 1940. After 1945, greatly increased proportions of nitrogen fertilizer were derived from synthetic ammonia, and in 1955, it was estimated that about 88 percent of the nitrogen fertilizer used was derived from this source. Nitrogen fertilizer materials supplied from synthetic ammonia include anhydrous ammonia, ammonium nitrate, ammonium sulfate, urea, ammonium phosphates, sodium nitrate, and nitrogen solutions which are composed of ammonia, water, and either ammonium nitrate or urea.

Ammoniation of superphosphates was started in 1928 and increased slowly at first. In 1940, 60,000 tons of nitrogen was used for

TABLE 14.3. Estimated Consumption and Adjusted Wholesale Prices of Fertilizer Nitrogen, Phosphate, and Potash by Sources<sup>a</sup>

Fertilizer	Consumption in 1000 Tons of N, P <sub>2</sub> O <sub>5</sub> , or K <sub>2</sub> O, Adjusted Wholesale Prices (in parentheses) in Dollar per Unit				
	1920	1930	1940	1949-50	1954-55
<b>Nitrogen</b>					
Ammonium sulfate	78 (4.49)	128 (3.58)	137 (3.02)	179 (2.39)	382 (2.10)
Ammonia	-	(in "others")	60 (1.16)	107 (0.95)	502 <sup>b</sup> (1.04)
Nitrogen solutions	-	(in "others")		252 (1.20)	470 <sup>c</sup> (1.30)
Ammonium nitrate	-	-	-	154 (1.72)	484 (1.94)
Sodium nitrate	47 (4.88)	71 (4.98)	119 (3.63)	100 (3.17)	(in "others")
Organics	77	60 (5.00)	48 (4.00)	42	33
Others	26	118	55	199	255
Total nitrogen	228	377	419	1033	2126
<b>Phosphate</b>					
Normal superphosphate	528 (1.23)	690 (1.06)	675 (1.21)	1601 (0.81)	1521 (0.88)
Concentrated superphosphate	13	40	155 (1.51)	272 (0.88)	471 (0.98)
Others	119	63	82	187	294
Total phosphate	660	793	912	2060	2286
<b>Potash</b>					
Muriate, 60%	-	28	291 (1.17)	866 (0.40)	1675 (0.40)
Muriate, 50%	69 (2.67)	149 (1.48)	69 (1.17)	96 (0.43)	
Manure salts	72 (1.71)	85 (1.24)	18 (1.27)	21 (0.21)	1 (0.19)
Others	116	92	57	86	165
Total potash	257	354	435	1069	1841

<sup>a</sup>Data for 1920, 1930, and 1940 from Fertilizer Technology and Resources in the United States, Academic Press, Inc., New York, 1953. Data for 1949-50 from "Commercial Fertilizer Yearbook," Walter W. Brown Publishing Co., Inc., Atlanta, Georgia, Sept. 1950. Data for 1954-55 from "fertilizer situation for 1954-55," Commercial Fertilizer and Plant Food Industry 90: No. 6, p. 44, June, 1955.  
<sup>b</sup>390,000 tons were used for direct application.  
<sup>c</sup>75,000 tons were used for direct application.

ammoniation as ammonia and as solutions. In the 1954-1955 season, about 507,000 tons of nitrogen was used as ammoniating materials. This amount is over eight times the 1940 usage and about 24 percent of the total nitrogen used in the 1954-1955 season.

The use of ammonia and nitrogen solutions for direct application and the use of solid ammonium nitrate have grown spectacularly since 1945, and by mid 1950's accounted for about 22 and 23 percent of the total nitrogen use, respectively. Large-scale production of ammonium sulfate from synthetic ammonia was started in 1945 and, 10 years later, ammonium sulfate production from this source was about equal to the production of the by-product material. Ammonium sulfate from both sources accounted for about 18 percent of the nitrogen fertilizer consumption.

The production of urea was increasing sharply by mid 1950's, and processes that produce compound fertilizers such as ammonium phosphates and nitric phosphates also were coming into increased use.

### Phosphates

Normal superphosphate, made from phosphate rock and sulfuric acid, has been and continues to be the principal form of phosphate fertilizer. It contains about 20 percent available  $P_2O_5$ . However, the use of concentrated superphosphate has been increasing rapidly, as shown in table 14.3. This material is made from phosphate rock and phosphoric acid and contains 45 to 50 percent available  $P_2O_5$ . Either electric-furnace or wet-process phosphoric acid may be used. In the 1954-1955 season, about twelve times as much concentrated superphosphate was used as in 1930, with the use of this material increasing more as new plants come into production. In 1930, normal and concentrated superphosphate supplied 87 and 5 percent of the available  $P_2O_5$  consumed; in the 1954-1955 season, the proportions were 66 and 21 percent, respectively. Although concentrated superphosphate is slightly more expensive than normal superphosphate at the point of production, the savings in transportation costs make the concentrated product less expensive in many consumer areas. TVA has contributed significantly to the farmer's acceptance of concentrated superphosphate and of high-analysis mixtures made from it. Test-demonstration and educational-sales programs have helped to create a market for these products.

The development of the electric-furnace process, in which TVA has been active, has permitted the use of low-grade phosphate rock that otherwise might not be economically usable. The quantity of low-grade rock in our reserves far exceeds the high-grade rock. Much of the low-grade rock cannot be beneficiated economically by presently known processes.

Except for TVA's operations, there has been little production of phosphate fertilizer by electric-furnace methods, although large quantities of phosphorus compounds for other uses are made by this process. However, by the mid 1950's there was an important quantity of commercial electric-furnace phosphoric acid used in the production of fertilizer.

Fertilizer processes using significant amounts of electric-furnace phosphoric acid are the production of nitric phosphates, liquid fertilizers, diammonium phosphate, and enriched superphosphate. Calcium metaphosphate is made from phosphorus produced in the electric furnace. Whether the electric-furnace route will become a much greater factor in the production of phosphate fertilizers depends on a large number of factors that cannot be predicted; however, conditions appear favorable for some expansion.

Companies that produce most of the wet-process phosphoric acid use it to make concentrated superphosphate and ammonium phosphates. There are indications that wet-process phosphoric acid may become more generally available to other fertilizer manufacturers. Reductions in freight rates on fertilizer-grade acid should encourage this trend. The increased availability of wet-process acid may encourage its use in mixed fertilizers in conjunction with ammoniation, in enriched superphosphate, and in liquid fertilizers.

Noteworthy advances have been made in the technology of mining and beneficiating phosphate rock. More efficient techniques have helped keep the price of phosphate rock at a reasonably low level and have greatly increased the recovery of usable phosphate from our reserves.

#### Potash

Prior to 1933, the United States was dependent principally on European sources for potash materials. The large New Mexico deposits were discovered in 1925, and production started in 1931. Domestic production has increased rapidly, until only about 2 percent of our potash is imported.

There have been excellent advances in methods of mining, beneficiation, and refining of potash salts, which have been reflected in increased use of high-grade salts and decreased cost. The data of table 14.3 show that, in 1930, only 9 percent of the fertilizer potash was in the form of the 60 percent  $K_2O$  muriate of potash; 41 percent was in the 50 percent  $K_2O$  grade; and 50 percent was in the form of lower-grade salts such as manure salts, which contain about 25 percent  $K_2O$ . In contrast, in 1953 about 90 percent of the fertilizer potash was supplied in the form of potassium chloride containing at least 60 percent  $K_2O$  (6).

#### Production of Mixed Fertilizer

Mixed fertilizer has been and continues to be the principal form of fertilizer used by the farmer. About 70 percent of the plant nutrients used are in the form of mixed fertilizer. As shown in table 14.1, there is no definite trend in the percentage of plant nutrients supplied in the form of mixed fertilizer, although the percentage was somewhat greater in the 1950's than prior to 1942.

At first, the production of mixed fertilizers was a mechanical operation consisting of dry mixing of various fertilizer materials and conditioners. Ammoniation of superphosphates as an integral part of mixed

fertilizer production was started in 1928 and has been increasing greatly. There also has been an increase in the use of sulfuric or phosphoric acid during ammoniation. These practices place increased emphasis on the chemical aspects of mixed fertilizer production.

The principal advantages of ammoniation are: (a) ammonia and nitrogen solutions are the cheapest forms of nitrogen available to the fertilizer manufacturer; and (b) since these solutions are highly concentrated forms, they facilitate the preparation of high-analysis fertilizers. These advantages have proved to be sufficient to stimulate widespread efforts by fertilizer manufacturers to use as much ammonia or ammoniating solutions in their formulations as possible. TVA has conducted pilot-plant development (10) of methods and equipment for incorporating more than the usual proportion of nitrogen in superphosphate by ammoniation. Since the extent to which superphosphate can be ammoniated imposes a limitation on the amount of ammoniating solution that can be incorporated in mixtures, many manufacturers add sulfuric or phosphoric acid to the mixture to absorb more ammoniating solution.

There has been much interest by fertilizer producers in the TVA continuous ammoniator. Over 40 companies have been given royalty-free licenses to use the process or to manufacture the equipment.

Granulation of mixed fertilizers and production of high-analysis fertilizers have been increasing rapidly. The two trends are related, since most high-analysis fertilizers contain a large proportion of soluble salts which would cause caking unless the mixture is granulated. Granulation greatly decreases the caking tendency, but does not necessarily eliminate it. Drying, curing, conditioning, and packaging in "moistureproof" bags also help prevent caking. Granulation also is effective in preventing segregation of the fertilizer ingredients. It facilitates more uniform distribution in the field and decreases dust losses of fertilizers. About 100 fertilizer plants were producing granular fertilizers of some kind by the mid 1950's. Most of these plants were above average in production capacity. TVA actively studied granulation of high-analysis fertilizers, and the majority of plants producing granular materials made at least some use of information from TVA's research and development program.

There is little standardization in the particle size of granulated fertilizer; many plants produce a partially granulated product containing some fines. Experiments sponsored by TVA have been set up to determine the agronomic effect of particle size for materials of several degrees of water solubility.

The concentration of primary plant nutrients in mixed fertilizers has increased steadily, as shown in table 14.1, and in 1954 averaged about 27 percent. In some areas the trend toward high-analysis products has been much more pronounced. For instance, in 1954 the average concentration was about 35 percent in the west north-central states as compared with 22 percent in the south Atlantic states (7).

Granulation and ammoniation have resulted in a change in the chemical character of mixed fertilizers to the extent that the chemical



compounds present in them may be far different from the compounds present in the ingredients. A few grades of typical mixed fertilizers were examined by TVA for identification of chemical compounds. The phosphate compounds identified, roughly in the order of decreasing abundance, were dicalcium phosphate, ammonium phosphate, apatite, and monocalcium phosphate. The kind of apatite was not identified, but it is probably that both fluorapatite and hydroxyapatite were present. The principal nitrogen compounds identified were ammonium chloride, potassium nitrate, ammonium phosphate, and ammonium sulfate. The principal forms of potash were potassium nitrate and potassium chloride.

### Combination Fertilizer Processes

There has been a sharp increase in combination fertilizer plants in which fertilizers containing two or three of the primary plant nutrients are produced directly, without the usual steps of first producing separate fertilizer materials and then mixing them in another operation. Most of these plants are either of the nitric phosphate type or the ammonium phosphate type.

In 1943, TVA started experimental work on the treatment of phosphate rock with nitric acid for making phosphate and nitrogen fertilizers. The principal purpose of this work was to develop lower-cost processes for producing fertilizers. Four nitric phosphate processes were developed through the pilot-plant state (1, 2, 4, 5, 9). Stanfield (8) has discussed the economics of these processes in comparison with conventional processes.

Most of the TVA development work was done without knowledge of similar work in progress in Europe, since information on this work was not published until later. However, similar processes were developed in Europe and have come into extensive use, particularly in France.

In the early 1950's the sulfur shortage stimulated intense interest in the nitric phosphate processes in the United States. Sixteen companies were given certificates of necessity to build nitric phosphate plants. As the shortage of sulfur was alleviated, interest in the nitric phosphate processes waned and only two plants were built. By 1955, other companies were considering construction of nitric phosphate plants.

Combination fertilizers based on ammonium phosphate have been produced in several plants. Wet-process phosphoric acid is combined with ammonia to produce impure monoammonium or diammonium phosphate or mixtures of these salts. Sulfuric acid and additional ammonia are added to form ammonium sulfate when higher  $N:P_2O_5$  ratios are desired. Potassium chloride is added if desired. The resulting products are homogeneous, granular materials of high water solubility.

### Liquid Fertilizers

The direct application of anhydrous ammonia, aqua ammonia, and nitrogen solutions has proved very popular. According to estimates,

about 22 percent of the total nitrogen used in the 1954-1955 season was applied in these forms (3). The use of liquid fertilizer mixtures containing two or more plant nutrients has shown rapid growth. About 150 companies produced liquid fertilizer mixtures in 1955 or had them registered for sale. Although the quantity constituted a very small proportion of total fertilizer consumption in most areas, the rapid growth of liquid mixed fertilizer production may indicate important future possibilities.

Some of the advantages claimed for liquid mixed fertilizer are: greater ease of application to the soil, lower cost of preparation and handling, elimination of bagging costs, and elimination of the faults of dry fertilizer such as caking and segregation. One of the disadvantages is that the raw materials for the liquid mixes often are more expensive. Storage of raw materials or products is more expensive. Differing opinions are held regarding agronomic effectiveness. Many producers claim that liquid fertilizers are more effective than solids, at least for some crops or areas. More rapid soil fixation of the phosphorus content of liquid materials is advanced as a possible reason for lowered effectiveness. More data are needed on this point.

Most liquid fertilizer manufacturers use electric-furnace phosphoric acid as the source of phosphate. The supply of this material is limited. If an important proportion of fertilizers is to be supplied in liquid form, either electric-furnace production of phosphoric acid must be greatly expanded or an alternative source developed. Wet-process phosphoric acid is not widely used in liquid mixes because its impurities precipitate on neutralization and might cause trouble by clogging handling and distribution equipment. Perhaps this difficulty can be overcome.

Most manufacturers of liquid mixtures operate on a highly seasonal basis. The amount of raw materials obtainable during a short peak season is limited. If a large proportion of fertilizer is to be supplied in liquid form, problems of storage of raw materials or products will have to be solved.

#### Some Present and Possible Future Trends and Problems

There is an evident trend toward large-scale production of fertilizers in modern chemical plants. This type of fertilizer production offers economic advantages of lower processing costs. Processes that are too complex for small manufacturers may be carried out economically by larger manufacturers. A disadvantage of the large-scale chemical plant is that its economics usually require more nearly continuous operation than is characteristic of the mixed fertilizer industry. It is not economical to allow the large investment required to remain unproductive during the greater part of the year. Skilled operators are required, and steady employment is necessary to keep them. The need for steady operation of the manufacturing facilities and the highly seasonal demand for the product are responsible for a serious storage problem.

Another characteristic of a large chemical plant for fertilizer

production is that it usually is not feasible to make a large number of grades. As fertilizer plants grow in size and complexity, it may become desirable to decrease the number of grades.

Divergent trends are evident in the water solubility of the phosphorus content of fertilizers. Fertilizers of lower water solubility are produced by the nitric phosphate processes and by heavy ammoniation of superphosphates. The production of highly water-soluble materials such as ammonium phosphates and liquid fertilizers is also expanding.

There is a need for close coordination of the work of chemists, engineers, agronomists, economists, and others in evaluating new processes and products and determining optimum direction of change. In many cases, compromises may be necessary between manufacturing economics and the economics of fertilizer use and distribution. These points have been emphasized previously in Chapter 2.

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