AGENCY FOR INTERNATIONAL DEVELOPMENT
WASHINGTON D. C. 20523

BIBLIOGRAPHIC INPUT SHEET

FOR AID USE ONLY

1. SUBJECT CLASSIFICATION

A. PRIMARY: Agriculture — AF25-0000-0000

B. SECONDARY: Soil fertility, fertilizers, and plant nutrition

2. TITLE AND SUBTITLE

Trends in fertilizer production

3. AUTHOR(S)

Hignett, T.P.

4. DOCUMENT DATE: 1972

5. NUMBER OF PAGES: 52p.

6. ARC NUMBER: ARC

7. REFERENCE ORGANIZATION NAME AND ADDRESS

TVA

8. SUPPLEMENTARY NOTES (Sponsoring Organization, Publishers, Availability)

(Presented at UNIDO meeting,Bucharest)
(NFDC circular,Z-38)

9. ABSTRACT

10. CONTROL NUMBER: PN-RAA-176

11. PRICE OF DOCUMENT

12. DESCRIPTORS

Estimates

13. PROJECT NUMBER

14. CONTRACT NUMBER: PASA TA (QA) 6-69 GTS

15. TYPE OF DOCUMENT

AID 890-1 (4-74)

Z-38

TRENDS IN FERTILIZER PRODUCTION

By

Travis P. Hignett
Director of Chemical Development
Tennessee Valley Authority
Muscle Shoals, Alabama 35660, USA

Paper Presented at UNIDO Meeting
Bucharest, Romania
July 10-14, 1972

TRENDS IN FERTILIZER PRODUCTION

By

Travis P. Hignett
Director of Chemical Development
Tennessee Valley Authority
Muscle Shoals, Alabama 35660, USA

The purpose of this paper is to examine current trends in fertilizer manufacturing, to analyze the reasons for these trends, and to project them into the future.

Increased Use of Fertilizer

Fertilizer use has increased sharply in recent years. Figure 1 shows that the world consumption of $N + P_2O_5 + K_2O$ reached 68 million metric tons in 1971 and has approximately doubled in just 8 years, and tripled in 14 years. In other words, more fertilizer tonnage has been added in the last 8 years than in all previous history, a trend that obviously cannot continue indefinitely. Nitrogen use has increased more rapidly than that of the other elements; it has doubled in the last 6 years and quadrupled in the last 14. The largest tonnage increases have been in the developed regions of Europe and North America, but the percentage increases have been greatest in the less developed regions of Asia, Africa, and Latin America.

TVA's latest projection of fertilizer consumption (Fig. 1) indicates that total consumption of the three major nutrients will reach 86 million tons in 1975 and 105 million tons in 1980.

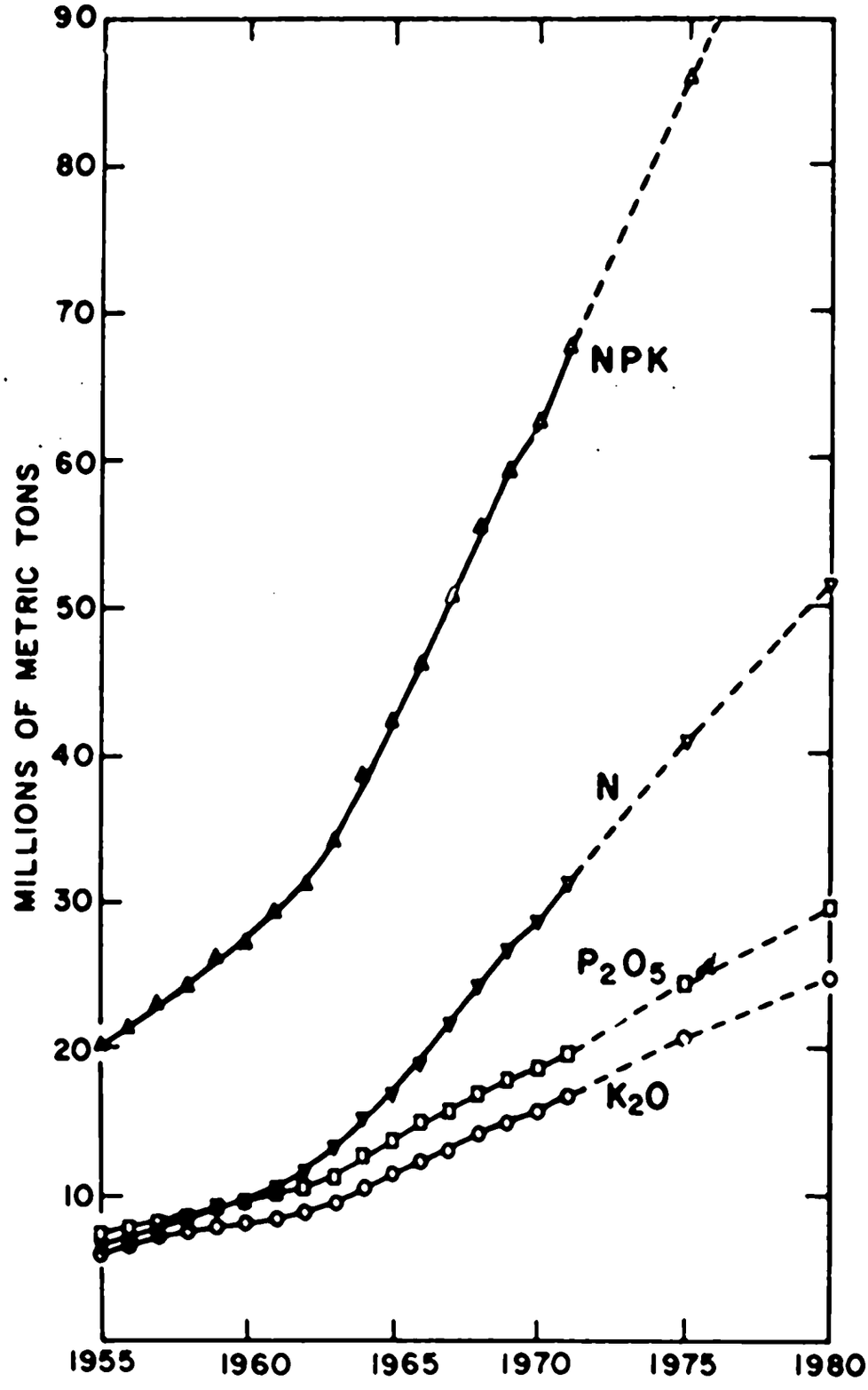


FIGURE I
WORLD COMSUMPTION OF FERTILIZER

The principal reason for the increased use of fertilizer is the need for more and better food for the world's growing population. It is possible to maintain a low to medium level of crop production with little or no fertilizer by utilizing the native fertility of the soil, returning crop residues and wastes, and utilizing the small amount of nitrogen brought down with rainfall or fixed by legumes. But this level of crop production is no longer adequate to feed the growing population of the world.

A second reason is economics; in contrast to the rising cost of labor and machinery, fertilizer costs in most countries have declined. Even in countries that have a surplus of food crops, a farmer cannot afford to neglect a substantial fertilizer application. In the past, many farmers have relied on growing legumes in a crop rotation to supply nitrogen, a sound practice when chemical nitrogen fertilizers were expensive and labor was cheap. Now the practice has become uneconomical in many areas.

TVA's latest projection of fertilizer consumption involves a slower rate of growth than our previous forecast (1), particularly in the developing countries of Asia, Africa, and Latin America. Numerous problems have slowed the growth rate in these areas. Production facilities have operated at only about 60% of capacity, leading to high production costs. Marketing and transportation of increased quantities of fertilizer have been difficult. High fertilizer costs and low prices for farm products have provided little incentive for farmers to increase fertilizer use rapidly in some countries. If TVA's forecast of fertilizer consumption is correct, food production in developing areas will fall short of the needs of the rising population. Per capita food production, which is already inadequate, will decline. While

these statements apply to developing continents as a whole, there is a wide variety of situations in individual countries; some of them have made substantial progress toward improved quantity and quality of food supplies.

In the developed countries the rate of population growth has declined and per capita food production has increased to the point that surpluses exist in several areas. This is another factor that will tend to slow the growth of fertilizer use.

Concentration

An important trend in fertilizer technology is increase in concentration of N, P_2O_5, and K_2O. Figure 2 shows this trend for four countries where the concentration of compound fertilizers has increased at rates ranging from 0.7 to 1.0% per year during the last decade. Of the four countries, the United Kingdom has attained the highest average concentration, nearly 42%, while Japan shows the greatest rate of increase. The reason for this trend lies in economics; bagging, storage, handling, and transportation often account for more than half of the cost of fertilizer delivered to the farmer. So increasing the concentration can markedly decrease the cost per unit of nutrient content at the farm.

Precise data are lacking for many developing countries, but the trend toward high concentration is evident in the increased emphasis on higher analysis materials. For instance, in South Korea, diammonium phosphate is granulated with potassium chloride to produce a 14-34-14 grade, which is blended with urea to make a variety of grades; 22-22-11 is

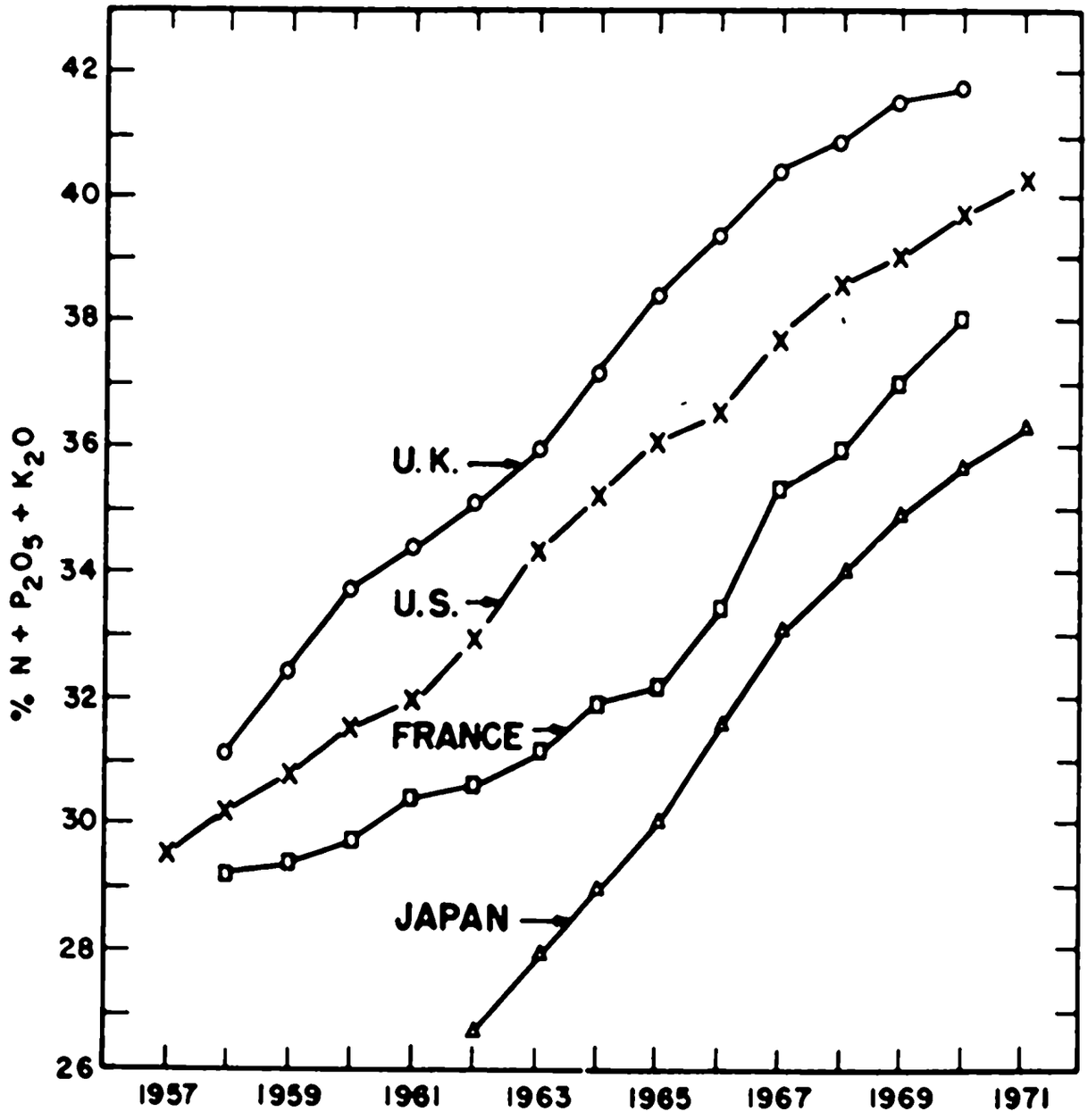


FIGURE 2
TRENDS IN CONCENTRATION OF COMPOUND FERTILIZERS

typical. Likewise, some new plants in India produce urea - ammonium phosphate compound fertilizers containing more than 50% nutrients.

In the next decade the concentration of fertilizers will continue to increase and may reach an average of 50% in some countries. Planned new facilities indicate that urea and diammonium phosphate will be favorite materials. With these materials and high-grade potassium chloride, compound fertilizers containing nearly 60% N + P_2O_5 + K_2O are possible. However, a growing realization of the frequent importance of including secondary and micronutrient elements in fertilizers may slow the growth in concentration of the primary elements. Also, lower analysis materials are likely to be more economical for local use in some areas.

Trend Toward Compound[1] Fertilizers

Another trend we see is toward greater use of compound fertilizers. Compound fertilizers have always been popular in the United States, but in many European countries and Japan, straight fertilizers have been more popular. During the period 1958 to 1968, compound fertilizers in Western Europe increased from 35 to 52% of all fertilizers. In Japan the increase was from 56% in 1962 to 77% in 1969. In the United Kingdom, 97% of the P_2O_5 (other than basic slag), 92% of the K_2O, and 63% of the N are supplied in compound fertilizers. Comparable figures are not available for

[1] The term "compound fertilizer" is used in this paper to apply to all fertilizer containing more than one of the three primary nutrients, N, P_2O_5, and K_2O.

the United States partly because some of the materials sold as straight fertilizers are actually compounds or are subsequently mixed by blenders to form compounds. A rough estimate indicates that in 1963, 35% of the N, 87% of the P_2O_5, and 86% of the K_2O were supplied to the farmer in compound fertilizers.

The reason for the trend toward compound fertilizers is that farmers no longer have the time or inclination to apply several fertilizers separately nor do they have the equipment to mix them. Supplemental dressings of nitrogen are often applied separately for reasons of efficiency or economy, but the basic application is preferred in the form of compound fertilizer.

Larger Factories

Another trend we see is the concentration of manufacturing operations in large factories. Plants geared to turn out 1000 or more tons per day of ammonia, urea, ammonium nitrate, phosphoric acid, ammonium phosphate, triple superphosphate, or potassium chloride are becoming commonplace. Some European plants now produce as much as 2 million tons of fertilizers per year. The reason for this trend lies in economics; as the scale of the operation is increased, the cost per unit decreases.

No doubt the average size of plants that produce basic fertilizer materials will continue to increase during the next decade. It is doubtful whether there will be much advantage in increasing plant size beyond that of some of the largest ones that have been built recently because of the cost of transporting the products over a wide area, and because further increase in scale will result in only minor decrease in production cost.

On the other hand, there is a need for smaller plants, not to manufacture basic materials, but to combine them into compounds that will satisfy local needs, as will be discussed later.

The growing pressure to control pollution of the air, rivers, and lakes increases the complexities of manufacturing operations. These problems can be dealt with more economically in a few large plants than in many small plants. Some small plants have been closed because it was uneconomical for them to comply with pollution control regulations, and probably more will do so in the future. So we can expect that pollution control regulations will accelerate the trend toward larger factories.

Complexity of Formulation

A rather wide range of $N:P_2O_5:K_2O$ ratios is needed for various crops and soils. Moreover, it is known that ten other elements are equally necessary to plant growth--the secondary elements, calcium, magnesium, and sulfur; and the micronutrients, manganese, iron, boron, copper, zinc, molybdenum, and chlorine.[1] The time is approaching and has already arrived in many areas when the industry can no longer limit its concern to the primary nutrients. The farmer has a right to expect that agronomists will prescribe and technologists will supply compound fertilizers containing the elements needed in the correct proportion for economical crop production on his farm. Already in the United States a great many compound fertilizers contain one

[1] Although chlorine was established as an essential micronutrient element in 1954, no case of naturally occurring deficiency is known, perhaps because of the abundance of the element (2).

or more of the "other ten" elements; in 1970, well over 100,000 tons of micronutrient materials were used in fertilizers plus unknown amounts of materials supplying secondary elements.

In Japan in 1970, 842,000 tons of fertilizer contained boron, magnesium, or manganese.

The trend toward more complex formulations is likely to continue because (1) more adequate fertilization with primary nutrients often results in one of the other ten elements becoming a limiting factor, (2) increased crop yields more rapidly exhaust soil supplies of these elements, (3) improved diagnostic techniques and accelerated research will result in identification of more cases of needs, and (4) increasing concentration of the three primary plant nutrients in fertilizers has been attained at the expense of eliminating some of the other ten.

Thirteen years ago in a lecture to The Fertiliser Society in London, Howard Cunningham (3) comments on the growing complexity of farmers' needs. He said:

> N, P and K must always be the main preoccupation of The Fertiliser Society but their very success in producing bigger yields of crops and stock is taxing the supply of other elements and leading to problems for farmers. Fertiliser manufacturers should apply to the solution of these problems as much skill and determination as they have applied with such success to the three major ingredients.

At the same time he was aware that the size and complexity of a granulation plant imposed serious limitations on flexibility in formulation, for he said:

> It is not easy to reconcile low cost production and special mixtures for a customer, a crop or even a district.

Farmers in many areas demand a combination of herbicides or other pesticides with fertilizer, which further increases the complexity of formulation. The advantage to the farmer is that application of fertilizer and pesticide together saves time and labor. Slow-release nitrogen is desirable in some situations and may be provided by incorporation of slowly soluble nitrogen materials or nitrification inhibitors in compound fertilizers.

Increased Use of Intermediates

In order to take advantage of the economics of large-scale manufacture and still provide for flexibility of formulation of compound fertilizer, various new systems are being developed. The general characteristics of these systems are (1) production of fertilizer intermediates in large plants where raw material costs are low, (2) transportation of the intermediates in concentrated form to the various market areas, and (3) production of the final mixture in small local plants that may combine the functions of manufacturing and retailing.

The principal intermediates are ammonia, ammoniating solutions containing free ammonia and ammonium nitrate or urea, urea - ammonium nitrate solution, monoammonium or diammonium phosphate, ammonium polyphosphate solution, triple superphosphate, phosphoric acid, and potash salts.

The local plants using these intermediates fall into three categories--dry mixing, liquid mixing, and granulation. Dry mixing plants merely make mechanical mixtures from dry fertilizer materials. The materials may be either granular or pulverized; however, most farmers prefer granular products because of superior storage and handling properties.

Dry mixing of granular materials is known as "bulk blending." Favorite materials for bulk blending are diammonium phosphate, triple superphosphate, potassium chloride, ammonium nitrate, and urea. All materials should be of about the same particle size, usually in the range of 1 to 3 mm. The materials usually are received in bulk by rail, barge, or ship. They are often stored in bulk and mixed to the farmer's order in accordance with soil test data. The mixtures may be either sold in bulk or in bags according to the farmer's preference.

Bulk blending plants are often quite small and inexpensive. A typical plant is shown in Figure 3. The output often is marketed within a radius of 20 kilometers. The average annual output of about 5000 such plants in the United States may be about 2000 tons. However, large bulk blending plants may be useful and economical, particularly when located at or near a port where materials may be received by ship or barge. One such plant in the United States has an annual output of over 200,000 tons.

One problem in bulk blending is the tendency of the materials to segregate during handling and application (4). Segregation can best be prevented by having all materials of closely matched particle size. Particle shape and density are relatively unimportant. When the particle size is not closely matched, segregation can be minimized by careful distribution in filling bins, trucks, or hoppers (5). Filling from one spot causes "coning" and promotes segregation.

Micronutrients may be added to bulk blends in several ways. Powdered micronutrient materials may be coated on the surface of the granules by use of oil or other binder. Alternatively, granular micronutrient materials

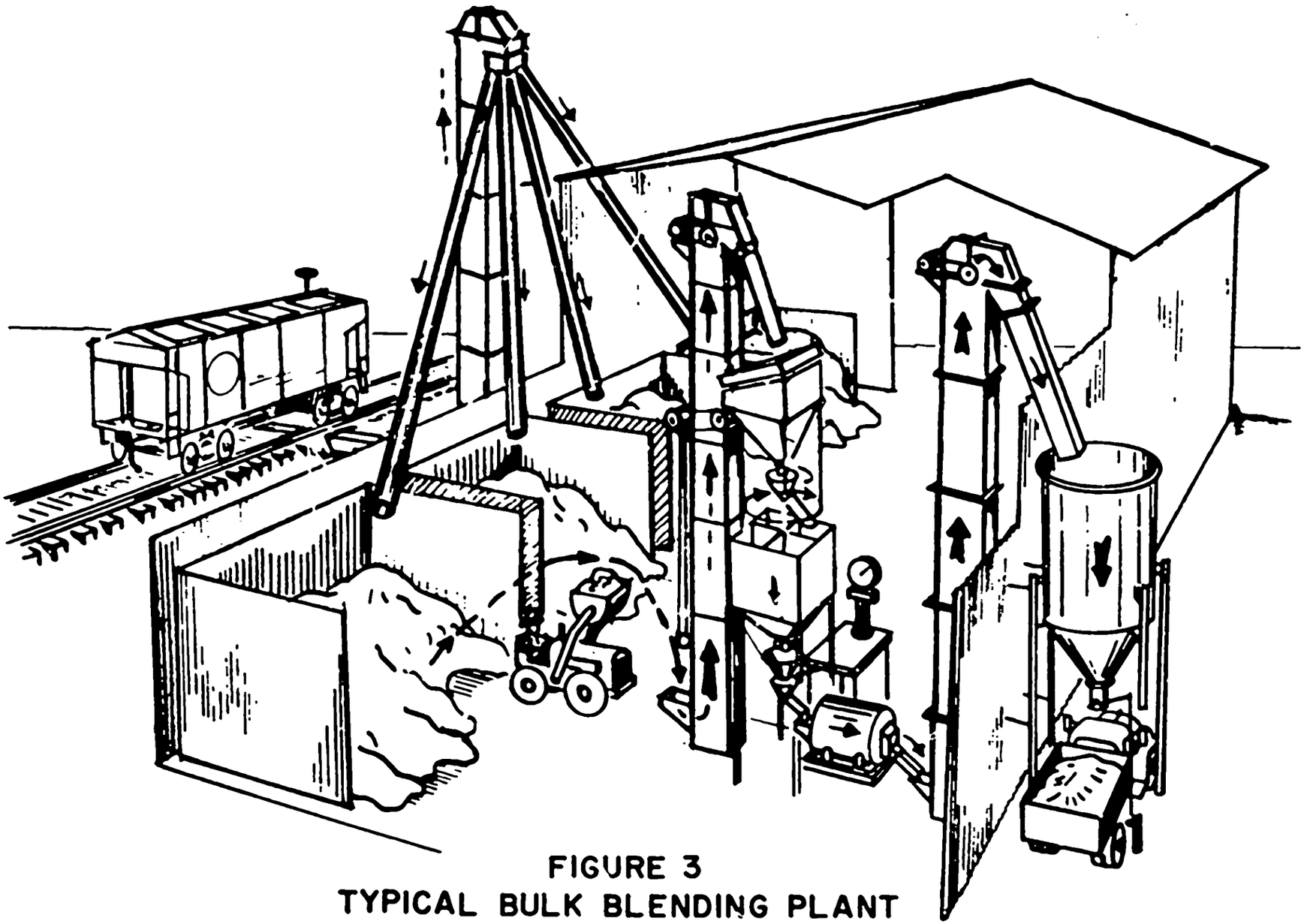


FIGURE 3
TYPICAL BULK BLENDING PLANT

may be used in the blend. Addition of pesticide to blends may be in the form of a powder (with a binder) or in the form of a concentrated liquid.

Bulk blending is particularly popular in North America. In 1971 it was estimated that bulk blends accounted for 58% of all dry compound fertilizers in the United States. Several other countries recently have started bulk blending operations, and the practice may grow.

Successful use of bulk blending in small local plants requires dependable transportation, such as a network of railroads and a supply of rail cars that protect bulk fertilizer from the weather. Covered, hopper-bottom cars are preferred for ease in unloading. In many developing countries, rail cars suitable for transporting bulk fertilizer are lacking. A blending operation may be located at a port where bulk materials may be received by ship. In this case there must be sufficient storage at or near the port for bulk materials to match the size of shipments, and mechanical equipment for unloading ships is desirable to minimize the time that ships must stay in port. The unloading equipment should be such as to avoid undue degradation of the granular material and protection from the weather. In very humid climates, dehumidified bulk storage is desirable. There are several blending facilities of this type both in developing and developed countries. The blends usually are bagged for inland transportation.

Another system which provides for flexibility of formulation in small local plants is liquid mixed fertilizers. Like bulk blending, production of liquid mixed fertilizers utilizes very simple, inexpensive equipment and depends on shipped-in intermediates. Liquid fertilizers have some special advantages which will be discussed in a later section of this paper.

A small granulation plant based mainly or entirely on shipped-in intermediates is another solution to the problem of maintaining flexibility of formulation. Although granulation plants do not have as much flexibility as bulk blend or liquid mix plants, a small local plant can produce formulations that are needed by farmers in the area for their crops and soils.

A typical small granulation plant may use superphosphate produced at the site. It may also use a higher analysis phosphatic intermediate--triple superphosphate, ammonium phosphate, or phosphoric acid. Nitrogen may be supplied by ammonia, ammoniating solutions, urea, or some combination of these materials. Potash is supplied as the chloride or sulfate.

Most small granulation plants attempt to operate with a formulation such that drying is accomplished mainly by the heat generated in chemical reactions. Several small plants have operated successfully without any dryer at all.

Superphosphoric acid has been used in small batch granulation plants (6), and more recently in a small, continuous granulation plant without a dryer (7), to promote granulation at low moisture contents. Grades were 12-18-18-3MgO and 15-15-15-4MgO. Formulations containing about 200 pounds of superphosphoric acid and 70 to 100 pounds of sulfuric acid per ton of product gave good results. The acids were neutralized with ammonia - ammonium nitrate solutions. The granular products were hard and dry (less than 1.0% moisture) and had good storage properties.

Another approach to a simplified granulation system is to use a powdered monoammonium phosphate with special properties that are well suited to granulation. Several low-cost processes are available for

producing this material (8, 9, 10). The monoammonium phosphate may be used to supplement and upgrade superphosphate or to replace it. Granulation may be promoted through use of steam, ammonia or ammoniating solution, or a combination of these practices. A typical grade of the powdered monoammonium phosphate is 10-50-0; it may be produced at low cost and shipped in bulk to granulation plants (11). In most cases it may be preferable to manufacture monoammonium phosphate at the plant where phosphoric acid is produced rather than to deal with the problems of shipping the acid.

Some granulation plants use only dry materials; the mixture is granulated by addition of water or steam or both. In some cases, heating the mixture with a flame in the granulator may generate enough liquid phase for granulation. Granulation at elevated temperature is preferable to granulation by water addition alone, as the water added during granulation must be subsequently evaporated by drying, and the dried granules are likely to be porous and weak.

Granulation with formulations including urea and superphosphate in several small British plants has been described (12). Additional materials included in the formulation were ammonium sulfate, monoammonium phosphate, and potash. Recently a granulation plant in Brazil started operation using urea-ammonia solution shipped in from Europe. Initial operation was quite satisfactory.

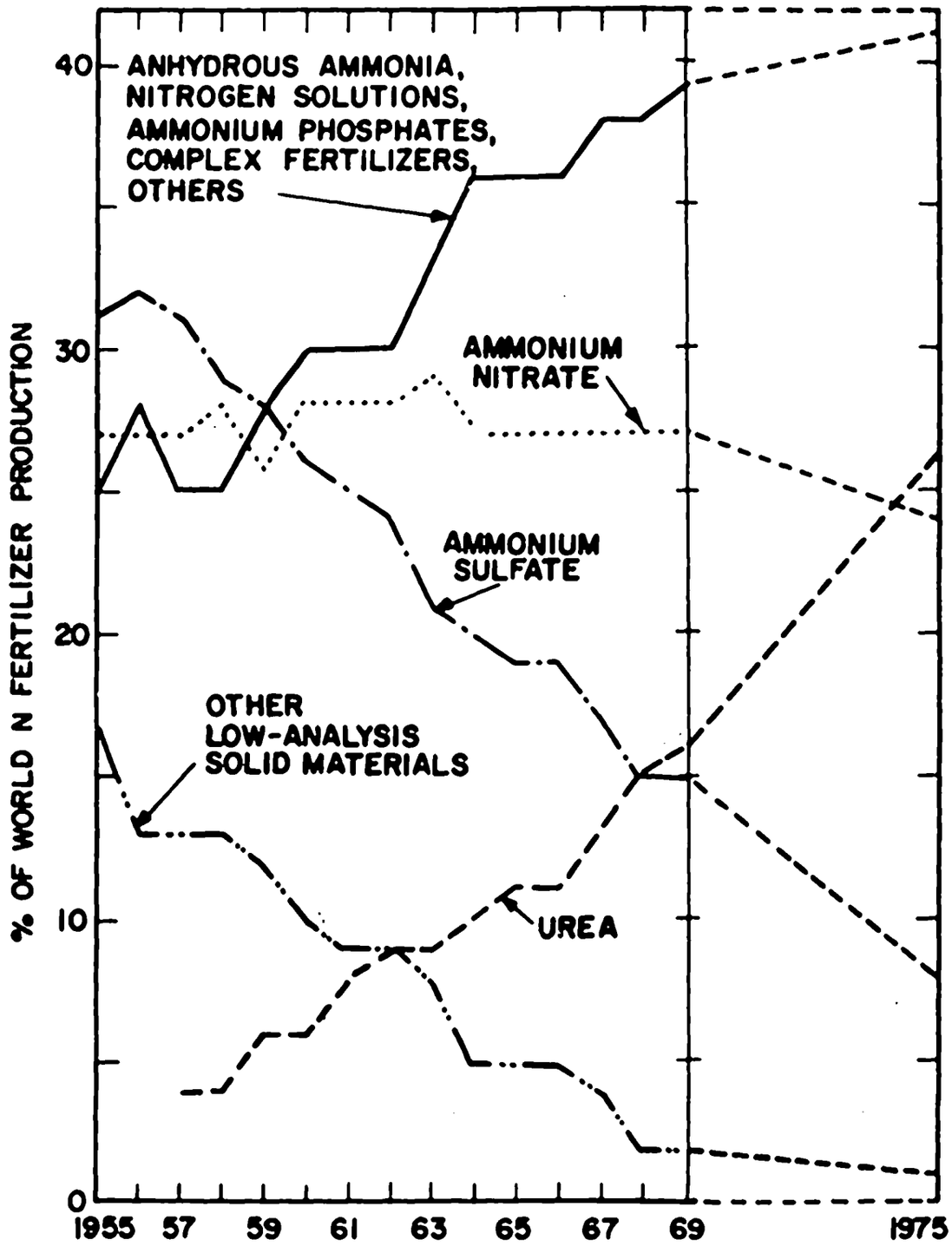
Many granulation plants use phosphoric acid as an intermediate, either to supply all the phosphorus or to supplement superphosphate. Ammonia may be supplied as such or as ammoniating solution.

As in the case of blending, granulation with shipped-in intermediates requires suitable, dependable transportation and storage facilities. Solid materials should be protected from the weather, although prevention of deterioration is less critical than in blending.

Granulation in large plants adjacent to the plants where basic intermediates are produced is sometimes the best arrangement even though large granulation plants cannot economically prepare small lots of special grades. In large granulation plants (20 to 50 tons/hr) the usual practice is to produce a limited number of grades, ordinarily three to six, as the time and expense involved in clearing the equipment of one grade before beginning the production of another make short runs or frequent changes uneconomical. Some companies that operate large granulation plants also have smaller plants (6 to 10 tons/hr) that granulate special grades. Also, special grades may be made by blending or by addition of micronutrients as a coating after granulation.

Trends in Types of Nitrogen Materials

A prominent feature of the world nitrogen industry is the rapid rise in popularity of urea, as shown in Figure 4. Data for Figure 4 through 1969 are from FAO reports; TVA projections to 1975 take into account planned capacity. Urea's share of the world nitrogen fertilizer market has risen from less than 5% in 1955 to 16% in 1969 and is expected to increase to about 26% by 1975. These figures are for solid urea only, and do not include the urea content of solutions. In the United States, about half of the urea used for fertilizer goes into solutions.



WORLD TRENDS IN TYPES OF
NITROGENOUS FERTILIZER MATERIALS
(FAO DATA; DOES NOT INCLUDE USSR OR COMMUNIST ASIA.)
FIGURE 4

The largest group of nitrogen fertilizer materials consists of anhydrous ammonia, nitrogen solutions, the nitrogen content of ammonium phosphates and complex fertilizers, and miscellaneous other materials. Ammonium sulfate, once the dominant nitrogen material, supplied only 15% of the world market in 1969 and may decline to 8% by 1975. Other low-analysis materials include calcium nitrate, sodium nitrate, and calcium cyanamide--a group now supplying only 2% of the market. Ammonium nitrate now supplies 27% of the market; in future years the percentage may decline slightly.

Nearly 40% of the 1975 world fertilizer nitrogen capacity will be for production of urea (including solutions and the urea content of complex fertilizers). In the developing countries of Africa, Asia, and Latin America, urea is expected to constitute 62% of nitrogen capacity.

The growing demand for urea is attributed to its high analysis and to improvements in technology that have lowered its cost. At present, urea is less expensive than ammonium nitrate per unit of nitrogen both in capital and production costs. Manderson (13) estimates the production cost of urea to be about 12% less than ammonium nitrate; when distribution and application costs are included, urea's cost advantage is about 20% under U. S. conditions. In comparison with ammonium nitrate, which has been the leading form of nitrogen since about 1960, urea has advantages of freedom from fire and explosion hazards; also, it is agronomically preferable for rice.

The usual commercial prilled urea has several faults. The particle size is too small for use in bulk blends. The small particle size also increases caking tendency and rate of moisture absorption. Also, some types of broadcast spreaders operate less efficiently with small particle size prilled urea. The usual prilled urea is weak; it has a low crushing strength and poor resistance to abrasion. This weakness may lead to excessive fines formation in bulk shipments and in some types of applicators. In view of the extensive development that has taken place in improving the efficiency and economy of the urea synthesis process, it seems odd that so little study has been given to improving the quality of the final product.

One company in Canada (Cominco Ltd.) is producing urea by a spray-drum granulation process in a plant located in Calgary. Two sizes are produced--one size, about 1.7 to 3.3 mm, is used for direct application and bulk blending; a larger size, 4 to 6 mm, is used for forest fertilization by aerial application. The granules are harder and more resistant to abrasion than prilled urea. The cost of granulation is said to be about the same as prilling.

TVA has developed a pan granulation process for urea through a pilot-plant stage. The process has proved capable of producing closely sized, well-rounded granules in any desired size range. Crushing strength and resistance to abrasion were quite satisfactory. Larger scale development is planned.

Although some urea is marketed without conditioner, most of it is now conditioned by coating with an inert material, such as kaolin clay, or by treatment with formaldehyde or other organic chemicals. These treatments prevent caking while stored in moistureproof bags, but they do not retard the rate of moisture absorption when the material is in contact with air above the critical humidity which is 75% relative humidity at 30°C. In many areas where the climate is hot and humid, there is a need for a conditioning treatment that will significantly retard moisture absorption. TVA is conducting research on this problem; some promising results have been obtained. In any conditioning treatment it is helpful to have larger granules to decrease the surface area.

In view of the plentiful supply and low cost of urea, consideration of ways of using it is appropriate. With the world trend toward farmer preference for mixed (compound) fertilizer, use of urea in granular mixtures is receiving attention in many countries. The high analysis of urea is useful in offsetting the low analysis of cheaper nitrogen sources in mixtures. A 50-50 mixture of urea and ammonium sulfate, for example, would contain 33.4% nitrogen--nearly as much as ammonium nitrate. So substitution of urea - ammonium sulfate mixtures for ammonium nitrate might be a good way to move low-cost byproduct ammonium sulfate into a high-grade product.

The technology of utilizing urea in granular compound fertilizers, with or without ammonium sulfate, is well advanced in Great Britain (14) and and Japan (15). There are some technical problems, but ways of dealing with them have been developed.

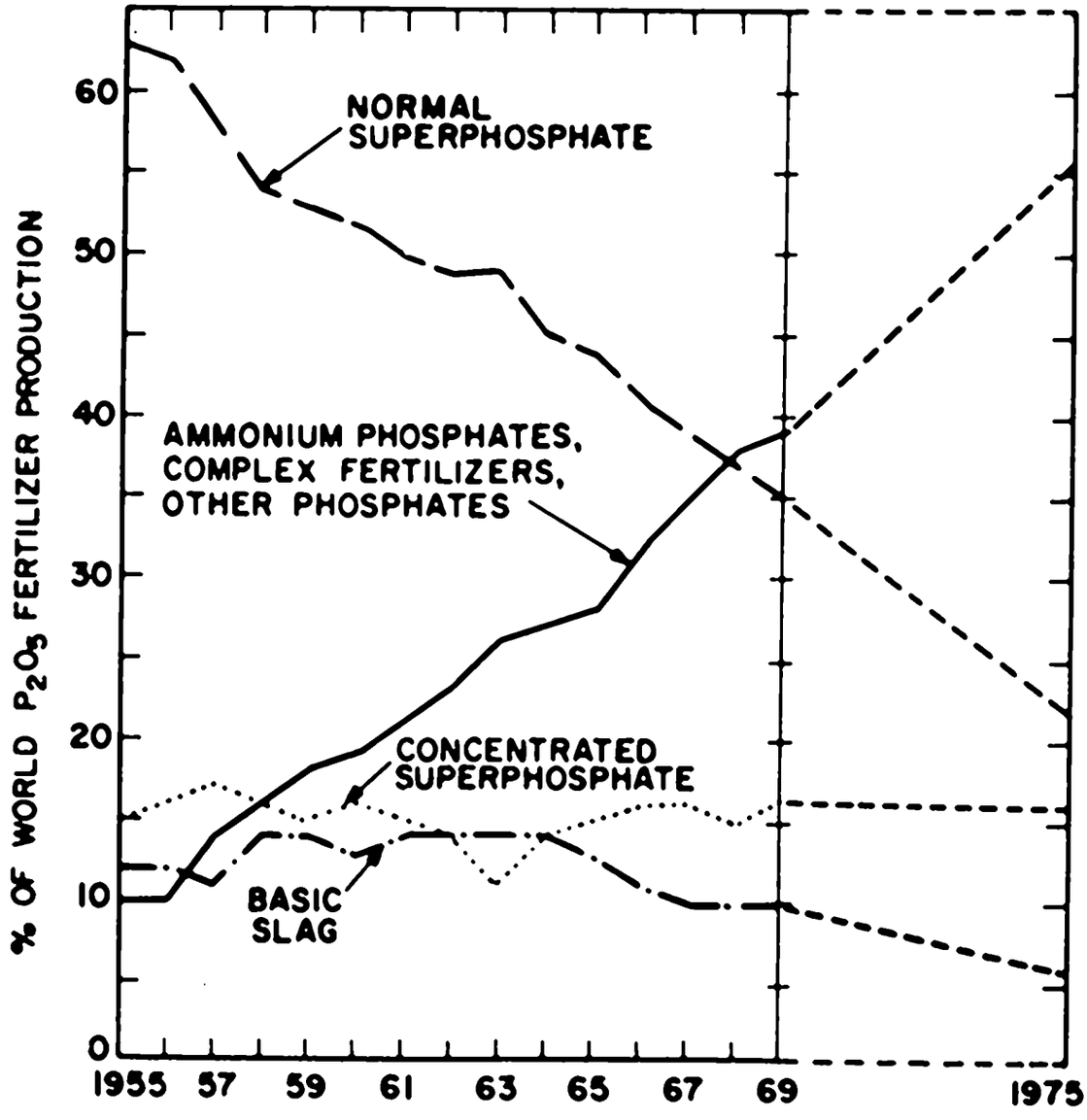
Compounds containing urea must be dried at a relatively low temperature to avoid hydrolysis of urea (forming ammonia and carbon dioxide) and to avoid softening or melting in the dryer. Rather large dryer capacity is required to attain adequate drying at low temperature.

When the compounds contain urea and single or triple superphosphate, a urea - monocalcium phosphate forms, releasing water of hydration and causing the mixture to become wet and sticky. Ammoniation of the superphosphate helps to prevent this condition, but reduces the water solubility of the P_2O_5. Addition of ammonium sulfate helps by reacting with the superphosphate preferentially. The most prevalent method of dealing with the problem is very light ammoniation plus inclusion of ammonium sulfate in the formulation and careful drying.

Granular compound fertilizers containing urea and superphosphate should be cooled to about 30°C before storage, as slow hydrolysis of urea releases ammonia which reacts with the superphosphate, causing a decrease in P_2O_5 water solubility. This reaction occurs to an appreciable extent even at temperatures as low as 40°C during several months' storage.

Trends in Types of Phosphate Materials

Figure 5 shows world trends in types of phosphate materials with projections to 1975. A striking feature is the decline in relative importance of single superphosphate from 63% of the total P_2O_5 supply in 1955 to 35% in 1969. A further decline to 22% in 1975 is forecast. The decline in actual tonnage has been small. In fact, 1966 was the year in which the largest tonnage of single superphosphate was produced, and the 1970 tonnage exceeded that of 1960. However, most of the expansion in the phosphate



WORLD TRENDS IN TYPES OF PHOSPHATIC FERTILIZER MATERIALS
(FAO DATA; DOES NOT INCLUDE USSR OR COMMUNIST ASIA.)
FIGURE 5

industry has been in higher analysis products, particularly triple superphosphate, ammonium phosphate, and other complex fertilizers. Concentrated superphosphate has maintained a nearly steady level of 15% of the total. The group, ammonium phosphates, complex fertilizers, and other phosphates, has risen from 10% in 1955 to 39% in 1969; further increase to 56% in 1975 is predicted. Probably as much as three-quarters of this group consists of ammonium phosphate, including straight ammonium phosphate and that formed in complex fertilizers. Most of the remainder is the P_2O_5 content of nitric phosphates. Basic slag is expected to supply a declining percentage of fertilizer P_2O_5 in the future.

Decline in use of single superphosphate (and ammonium sulfate) may bring about a need for alternative sources of sulfur. Substantial responses to sulfur have been noted in some parts of nearly all states of the United States and in at least 47 other countries, including many developing countries (16). Most soils in tropical and subtropical regions are inherently deficient in sulfur. Sulfur-deficient areas become more numerous and serious when heavy rates of nitrogen and other primary nutrients are applied. Much sulfur is supplied by rainfall in highly industrialized areas where it originates from burning of coal and oil. In these areas, sulfur is seldom needed in fertilizers. However, as plans for prevention of atmospheric pollution materialize, much more need for supplying sulfur in fertilizers can be expected.

Ideally, sulfur should be supplied in fertilizers only when it is needed. To attain this ideal, an alert, efficient agricultural advisory service should be available to every farmer. Even in the most developed

countries, this service is often lacking for many farmers. In developing countries, little may be known about the need for sulfur. Sulfur deficiencies may become evident only after several years of cropping with sulfur-free fertilizers.

In some cases, single superphosphate may be the most economical source of sulfur. However, elemental sulfur has been proved to be economical and effective in many cases. Elemental sulfur can be incorporated in granular fertilizer by spraying it in liquid form in the granulator.

There is a growing trend toward use of phosphoric acid as an intermediate, rather than converting it to finished fertilizer at the point of manufacture. In the United States, possibly as much as 1 million tons of P_2O_5 is shipped as phosphoric acid from the point of manufacture (near phosphate mines) to market areas for conversion to fertilizer. "Superphosphoric" acid (70 to 72% P_2O_5) may comprise about half of the shipments; the remainder is usually shipped at a concentration of 54% P_2O_5. The acid is used at the destination in granulation plants, in liquid mixed fertilizer plants, or for direct application.

Shipment of phosphoric acid is attractive in the United States partly because of long distances between phosphate mines and market areas. For the same reason, international shipments can be logical, and several phosphoric acid plants are either in operation, under construction, or planned which are intended primarily to supply phosphoric acid to international trade.

There is some interest in partial purification of phosphoric acid, especially in areas where the phosphate rock contains more than the usual amount of impurities. The impurities form a sludge that is troublesome in

shipping, and some types of impurities detract from the quality of liquid fertilizer. Calcining the phosphate rock removes organic impurities. Concentration of the acid followed by settling or centrifuging removes some of the sludge. Concentration to superphosphoric acid volatilizes most of the fluorine and silicon. Some companies remove part of the magnesia from superphosphoric acid for liquid fertilizer production. One company in Mexico practices partial purification by solvent extraction. Phosphoric acid produced by the hydrochloric acid route, as in the Israel Mining Industries process, has a low impurity content.

Liquid Fertilizers

Consumption of liquid fertilizers has grown rapidly in the United States, as shown below.

	Liquid fertilizers[a] used in U.S., millions of metric tons			
	1965	1967	1969	1971
Anhydrous ammonia	1.4	2.2	2.8	3.4
Aqua ammonia	0.7	0.8	0.6	0.7
Nitrogen solutions	1.7	2.3	2.5	3.2
Liquid mixed fertilizers	0.9	1.7	2.0	4.0[b]

[a] In addition to these materials, direct application of phosphoric acid (50 to 60% P_2O_5) amounted to 50,000 to 70,000 tons per year.
[b] Estimated.

Including anhydrous ammonia, liquids comprised 26% of all fertilizer in 1971. The data for liquid mixed fertilizer use in 1965-69 may be incomplete due to incomplete reporting; a recent survey by TVA in cooperation with the National Fertilizer Solutions Association indicated a 1971 consumption of about 4 million metric tons, or about 20% of all compound fertilizers (17).

Growth in use of anhydrous ammonia is mainly attributable to its low cost, which more than offsets increased storage, transportation, and application costs. The average prices paid by farmers in the United States in 1970 for various nitrogen fertilizers are shown below (18).

	Price, $/kg of N
Anhydrous ammonia	0.10
Urea	0.20
Ammonium nitrate	0.20
Nitrogen solution	0.19
Ammonium sulfate	0.28

Liquid mixed fertilizers are more expensive than bulk blends, but are comparable in cost to granular compound fertilizers. Their popularity is due to advantages other than price.

Liquid fertilizers are dependably free flowing, free from dust or caking problems, and unaffected by humid atmosphere. Convenience of handling and application is a primary advantage from the farmer's viewpoint. Labor saving, rapid application, and adaptability to mechanical handling are all part of the convenience factor.

Even distribution and precise placement are easier with liquids than solids. Liquid mixing is readily adapted to prescription formulation. Herbicides or pesticides are often mixed with liquid fertilizers, avoiding separate application. Liquid fertilizers are especially popular in irrigated areas, as the fertilizer may be added to the irrigation water.

From the viewpoint of manufacture, a primary advantage is the simplicity and low cost of the equipment for production, storage, handling, and transportation. Economical manufacture does not require large plants. Dust and fume problems are practically nonexistent. Losses are very small.

Control of composition is simple. Problems of hygroscopicity, dustiness, and caking are absent. Storage, loading, and handling are not expensive because pumps and piping are cheaper than conveyors, elevators, power shovels, and cranes, both in capital cost and in operating cost.

The usual nitrogen materials for liquid mixed fertilizer are urea - ammonium nitrate solutions (28 to 32% N) and solid urea. Urea - ammonium nitrate solutions are preferred because they are cheaper, more convenient, and give high solubility in grades containing little or no potash. Solid urea gives higher solubility in most NPK grades.

Ammonium polyphosphate solution is the most popular phosphatic material. Solid ammonium polyphosphate also may be used. The ammonium polyphosphate materials are prepared by reaction of superphosphoric acid with ammonia. The superphosphoric acid may be made from elemental phosphorus (thermal process) or by concentrating wet-process phosphoric acid. At present, most of the liquid products are made from wet-process superphosphoric acid. The usual solution grade is 10-34-0 or 11-37-0. At present, only the Tennessee Valley Authority (TVA) produces the solid material. Its grade is 15-62-0 (made from thermal acid). "Soluble" refined potassium chloride (62 to 63% K_2O) is the usual potash source.

Use of liquid fertilizer is increasing rapidly in some European countries, including the United Kingdom, France, and Belgium. The use in France is the most advanced.

While the advantages of convenience and labor saving may not be very important in developing countries, there are other advantages that should be considered. Manufacturing facilities for liquids generally are

simpler and less expensive than for granular solids. Liquids lend themselves well to production of homogeneous mixtures in local distribution centers to meet local needs--a segment of the fertilizer production and marketing system that has been sadly neglected in many developing countries. Many developing countries are located in very humid, tropical areas where even relatively nonhygroscopic solids give trouble. Hygroscopicity is never a problem with liquids. Application equipment for liquids need not be expensive; it may even be primitive.

Foreseeable improvements in liquid fertilizer manufacture include production of ammonium polyphosphate solution directly from orthophosphoric acid without the intermediate production of superphosphoric acid. This has already been accomplished in France (19) and in some U. S. plants, and should result in reduced cost.

Agronomic advantages of liquid fertilizers have been reported which may be due to more precise placement or to the presence of polyphosphates, as discussed below.

Suspension Fertilizers

A disadvantage of clear liquids is the low analysis of grades that contain a substantial proportion of K_2O. For instance, the average analysis of liquid mixed fertilizer (including a small proportion of suspensions) in the United States in 1970 was 8.4-16.4-7.6 as compared with 9.2-17.7-12.7 for all mixed fertilizer. This disadvantage is minimized by the marketing system; the final mix is seldom transported far. Nevertheless, the relatively low analysis often has a significant effect on the cost of transportation and application.

Suspension fertilizers are a means for overcoming the disadvantage of low analysis. They are liquids containing solids--usually soluble salts in their saturated solution. The mixtures are treated to minimize settling by inclusion of 1 to 3% of a gelling-type clay in their formulation. In 1971, about one-third of all liquid mixed fertilizers were suspensions.

With suspensions, the analysis can be on a level comparable with granular solid or bulk blended fertilizers. Popular grades of suspension fertilizers are 7-21-21, 3-10-30, 10-20-20, and 15-15-15--about twice the nutrient content obtainable in clear liquids with these ratios.

Another advantage of suspensions is greater flexibility in formulation; the materials need not all be soluble. This is a particular advantage when secondary elements or certain micronutrients must be supplied; magnesium and manganese compounds, for example, are only slightly soluble in liquid mixed fertilizer.

Some of the advantages of liquids may be lost in going to suspensions. Handling and application of suspensions, in their present state of development, are not as simple, convenient, and trouble-free as for clear liquids.

Ammonium Polyphosphate

The term "ammonium polyphosphate" is used in fertilizer parlance to denote materials containing condensed phosphates. As discussed previously, solutions or solids produced by ammoniation of superphosphoric acid are favorite intermediates for compounding liquid fertilizers. Typical compositions of the three most popular polyphosphate materials are given below.

	Phosphate species in ammonium polyphosphate, % of total P_2O_5		
	10-34-0 solution	11-37-0 solution	15-62-0 solid[a]
Ortho	49	20	41
Pyro	42	37	54
Tripoly	8	23	4
Tetrapoly and higher	1	16	1

[a] Made from electric-furnace phosphoric acid.

Ammonium polyphosphates may also be made directly from orthophosphoric acid by a process that utilizes the heat of reaction of the acid with ammonia to dehydrate the ammonium phosphate. This process is in an advanced stage of pilot-plant study.

Chemically, ammonium polyphosphates are the ammonium salts of polyphosphoric acids. The general formula for polyphosphoric acid is $H_{n+2}P_nO_{3n+1}$. The specific ammonium polyphosphates most abundant in fertilizers are triammonium and tetraammonium pyrophosphate, $(NH_4)_3HP_2O_7$ and $(NH_4)_4P_2O_7$, and pentaammonium tripolyphosphate, $(NH_4)_5P_3O_{10}$.

Ammonium polyphosphates are particularly useful in liquid fertilizers because they sequester the impurities normally present in wet-process phosphoric acid, thus avoiding precipitation of insoluble iron, aluminum, and other compounds when the acid is ammoniated. Also, the ammonium polyphosphates are more soluble than the orthophosphates, permitting production of higher analysis solutions.

Terman and Engelstad (20) summarizing studies in the United States concluded that ammonium polyphosphate usually was equal or slightly superior to monoammonium phosphate. Both were usually superior to concentrated superphosphate for early growth response. Fourcassie and Gadet (21)

concluded from experiments in France that ammonium polyphosphate supplied as liquid fertilizer was consistently superior to other phosphorus sources as the result of better phosphorus utilization. Most of these tests were made on calcareous soil. Field tests at six locations in Japan indicated that response to solid ammonium polyphosphate was generally greater than to ammonium orthophosphate, although early growth was sometimes slightly delayed. There was some suggestion that better utilization of native or applied micronutrients may have been a factor in the favorable results with polyphosphates.

Gourny and Conesa (22) reported that liquid fertilizer containing 34 to 82% of its phosphate as nonorthophosphate was slightly inferior to ammonium orthophosphate on acid soil, but markedly superior on calcareous soil.

Conesa (23) demonstrated that plants can take up polyphosphate without previous hydrolysis.

Singh and Dartigues (24) reported that polyphosphate was superior to ammonium orthophosphate on two zinc-deficient calcareous soils.

Soubies and Baratier (25) emphasize the advantage of band placement of ammonium polyphosphate solution near the seed as compared with broadcast solid orthophosphate. They claimed that the band placement used with liquids was not possible with solids.

Mortvedt and Giordano (26) reported that liquid polyphosphate fertilizers were effective carriers of iron sulfate in greenhouse tests for crops grown on iron-deficient soils, whereas application of iron sulfate alone or in several granular fertilizers was ineffective.

In a recent series of field tests in the United States (27), ammonium polyphosphate solution gave higher yields of maize, wheat, and milo than orthophosphate fertilizer in either liquid or solid form.

Nitric Phosphates

Nitric phosphate-type processes are particularly attractive for countries with limited raw material resources for fertilizer manufacture. The only feed materials required are ammonia and phosphate rock--either or both of which can be imported. Economics is more favorable for nitric phosphates when sulfur prices are high.

The approximate location of nitric phosphate plants in the world is given in Figure 6 (28). About sixty plants are believed to be producing solid nitric phosphates--with about two-thirds of these located in Europe.

Recent process improvements have made the nitric phosphate process more versatile and have removed some of the earlier objections to these products. It is now possible to produce high-analysis grades such as 20-30-0 and 23-23-0 with over 80% of the P_2O_5 water soluble in large, efficient plants (29).

Estimates usually indicate that nitric phosphate processes are more economical than production of equivalent amounts of nitrogen and phosphate fertilizers as ammonium phosphate and ammonium nitrate or urea. When compared with the urea plus ammonium phosphate, the cost advantage is small and may be offset by higher transportation costs if the products are shipped very far (28)

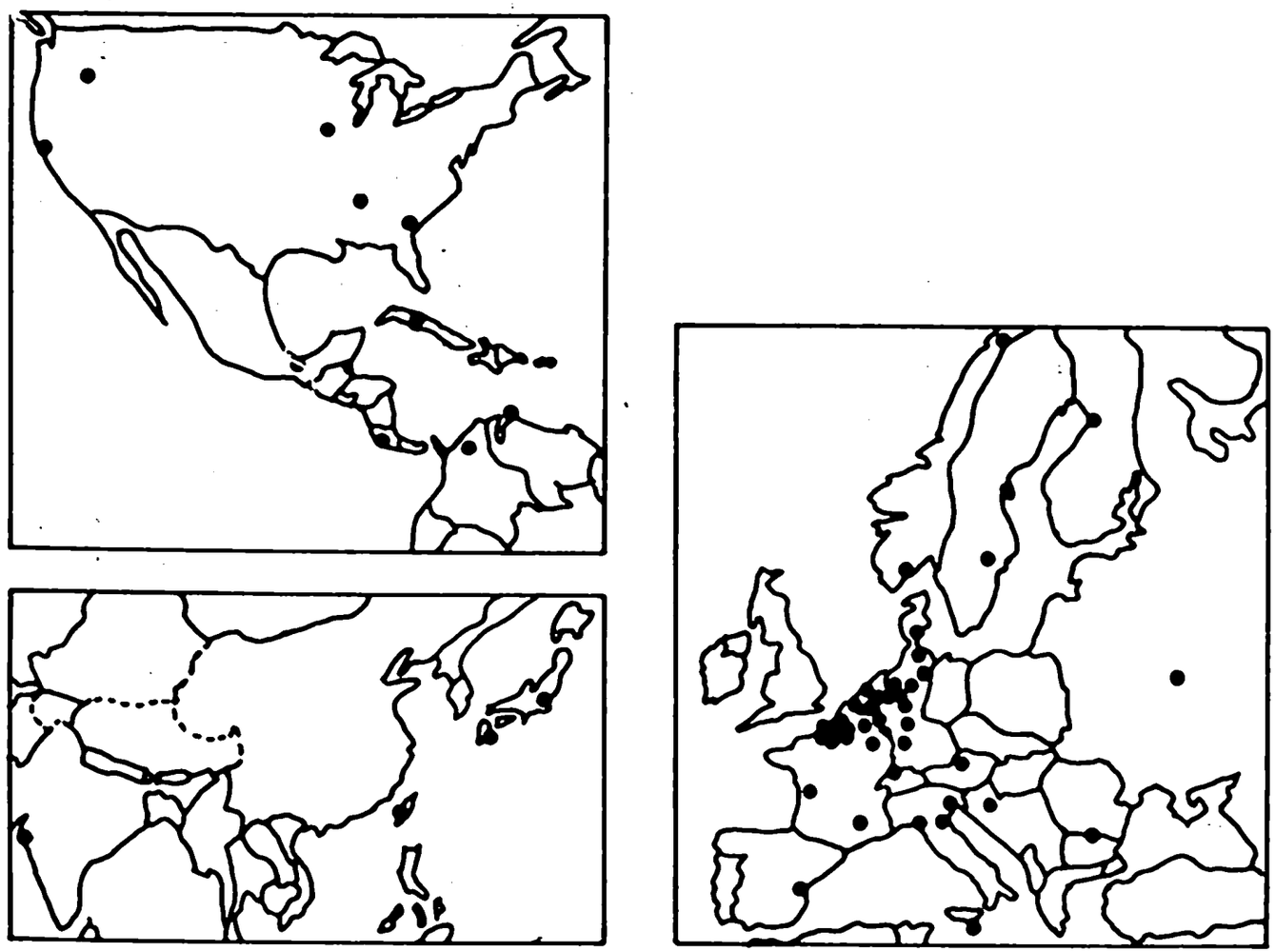


FIGURE 6
APPROXIMATE LOCATION OF NITRIC PHOSPHATE PLANTS
IN THE UNITED STATES, ASIA, AND EUROPE

The principal disadvantages of nitric phosphates are that about 2 tons of nitrogen is produced for each ton of P_2O_5, and that most of the nitrogen is in the form of ammonium nitrate. Also, it is not easy to produce a wide range of grades.

Potassium Phosphates

There has been much interest in potassium phosphates because of their very high analysis and good agronomic properties. The potassium phosphates under consideration include the orthophosphates, KH_2PO_4 and K_2HPO_4, and the polyphosphates ranging from pyro and tripoly to long-chain polyphosphates commonly called "metaphosphate." The orthophosphates and short-chain polyphosphates are quite soluble, whereas the metaphosphates may be either soluble or insoluble, depending on their method of preparation and impurity content.

There is some small use of potassium orthophosphate in specialty fertilizers to make water-soluble mixes for foliar application or transplanting solutions. There is also some use in liquid fertilizers for farm use; one company in the United States produces a 0-26-27 potassium polyphosphate solution for use in liquid mixed fertilizers. All of these materials are produced from potassium hydroxide or carbonate, and hence they are too expensive for general use.

Many research projects have been aimed at producing potassium phosphates from potassium chloride, the cheapest source. Most of these projects have not proved economical because of the difficulty of utilizing

or disposing of the byproduct hydrochloric acid. Even if the hydrochloric acid is utilized to react with phosphate rock, calcium chloride becomes a byproduct which is difficult to dispose of in many locations.

Recently a process was developed in Ireland by Goulding Fertilisers on a pilot-plant scale that produces KH_2PO_4 and anhydrous HCl gas (30). A similar process was developed in the United States by Pennzoil, and the two companies have agreed to pool their information. It is claimed that anhydrous HCl can be utilized in certain organic oxychlorination processes where its value will be comparable with that of elemental chlorine. It was recently announced that a small plant in California would be adapted to production of potassium phosphates by the Goulding-Pennzoil process.

Controlled-Release Fertilizers

Fertilizers that release plant nutrients slowly throughout the growing season or even several growing seasons continue to attract the attention of technologists and agronomists. Potential advantages claimed for controlled-release fertilizers are increased efficiency of uptake by plants; minimization of losses by leaching, fixation, or decomposition; reduction in application costs through reduction in number of applications; elimination of luxury consumption; and avoidance of burning of vegetation or damage to seedlings. This is an impressive list of potential advantages.

The term "controlled-release fertilizers," as used in the following discussion, refers to fertilizers that for any reason release their nutrient content over an extended period. Even a simple choice among materials inherently slow to dissolve is viewed as a measure of control.

Controlled-Release Phosphate Fertilizers

Numerous controlled-release phosphorus compounds have been tested, and some are in use. Prominent among them are ground phosphate rock, calcined aluminum phosphate ore, basic slag, defluorinated phosphate rock (tricalcium phosphate), fused calcium magnesium phosphate, Rhenania phosphate, bone meal, dicalcium phosphate, magnesium ammonium phosphate, calcium metaphosphate, and potassium metaphosphate. (The so-called metaphosphates are more properly designated as polyphosphates.)

Ground phosphate rock containing about 1.8 million metric tons of P_2O_5 was applied to the soil in 1969-70 (31). This probably represented some 6 million tons of rock. About half was used in the U.S.S.R., and the remainder was widely distributed among many countries.

The effectiveness of ground phosphate rock varies widely with variation in its reactivity. A good indication of reactivity is solubility in neutral ammonium citrate. The effectiveness of the most reactive rocks, such as those from Gafsa and North Carolina, may approach the effectiveness of water-soluble phosphates on some soils and with certain crops. The least reactive rocks, such as igneous apatite and Udaipur (India) rock, are quite ineffective on all soils. Effectiveness depends on soil pH and is greatest on acid soils; on high-pH soils, even highly reactive rocks are quite ineffective. As an exception, calcined aluminum phosphate ores, such as those from Senegal or Christmas Island, are more effective on neutral or alkaline soils.

Basic slag containing about 1.3 million metric tons of P_2O_5 was applied in 1969-70 (31). Gross weight of the slag probably was about 8 million tons. Basic slag is generally regarded as quite effective except

on calcareous soils. It is also valued for its content of the secondary nutrients calcium and magnesium and for its micronutrient content.

Calcined aluminum phosphate ore is used mainly in France. It tends to be more effective on high-pH than acid soils. The main source of aluminum phosphate ore is Senegal. However, several other occurrences are known, and some is now being mined on Christmas Island. Its effectiveness depends on the calcination temperature and on fine grinding, and may be indicated by solubility in neutral or alkaline ammonium citrate. It is more soluble in the alkaline reagent.

Straight dicalcium phosphate is manufactured for fertilizer use in relatively small quantities in France and Belgium. However, substantial amounts are present in nitric phosphates and ammoniated superphosphates. It is fully soluble in neutral ammonium citrate and is generally considered to be an effective fertilizer, particularly on acid soils when broadcast in fine particle size and incorporated with the soil.

Fused calcium magnesium phosphate is manufactured mainly in Japan. It is effective on acid soils when finely ground. It supplies magnesium and silica, which may be quite helpful in some soil-crop combinations.

Most of the insoluble or slightly soluble phosphate materials are used either because they are less expensive than soluble phosphates or because they supply other elements. Very seldom if ever can any agronomic superiority be attributed to their slow release of nutrient in the soil. In fact, the slightly soluble materials often give inferior results, particularly in the first year of application. However, some of them are valued for specialty uses because they may be safely placed in contact with seeds or roots, whereas soluble phosphates might damage seedlings or roots in some situations.

Soluble phosphates react rapidly with the soil to form relatively insoluble products (32). So even fully soluble phosphates become slow-release fertilizers in the soil. The main effort has been to find ways to increase the release rate. When soluble phosphates are applied in granular form, the reaction with the soil is delayed, and pockets of relatively soluble phosphate may persist at the granule sites for several weeks. Thus, good results usually are obtained by placement of soluble granular phosphate fertilizers near the seed.

Controlled-Release Nitrogen Fertilizers

Slightly Soluble Materials: One group of controlled-release nitrogen fertilizers comprises chemical compounds that are only slightly soluble. It may be noted that the rate of release of nutrient from most of these slightly soluble compounds is not directly related to water solubility. Instead, the release rate is related to microbiological attack which converts the nitrogen to forms that can be utilized by plants. However, the rate of attack is related to the rate of solution, which depends, in turn, on solubility, particle size, and other factors.

Urea-aldehyde compounds are the principal representatives of this group that are produced commercially. Isobutylidene diurea (IBDU) is produced in Japan through the reaction of urea with isobutyraldehyde in 2:1 mole ratio. When pure, it contains 32.18% N. Hamamoto (33) reported methods for its preparation and discussed its usefulness as a fertilizer. Crotonylidene diurea (CDU), also called cyclodiurea, is produced in Japan and Germany through the reaction of urea with crotonaldehyde or acetaldehyde. The pure compound contains about 32% N.

Ando (15) reported a Japanese consumption of 1800 tons of N as IBDU and 1400 tons as CDU in 1968--a total of 3200 tons of N or 10,000 tons of the two slow-release materials. This was more than twice the 1966 use. The materials were used to prepare compound fertilizers in which about half of the nitrogen was in slow-release form.

Hamamoto (33) discussed agronomic studies made in Japan with IBDU and other slow-acting nitrogen materials. The release rate from these slightly soluble materials is a function of the particle size. Under Japanese conditions, use of these materials was often advantageous in improving yields and in saving labor by decreasing the number of applications. Hamamoto stated that the cost of IBDU to farmers was over twice that of conventional nitrogen fertilizers per unit of nitrogen. Compound fertilizers of 1:1:1 ratio with half of the nitrogen supplied as IBDU cost about 20% more than conventional fertilizers. For this reason they were used mainly on vegetables and cash crops and not so much on grains.

Urea-formaldehyde reaction products, usually called "ureaform," are produced by about six manufacturers in the United States and in several other countries. Unlike IBDU and CDU, ureaform is not a definite chemical compound. It contains methylene ureas of different chain lengths; the solubility increases with decrease in chain length. It usually contains about 38% N.

Perhaps the most useful component of ureaform as a slow-release nitrogen material is trimethylene tetraurea; shorter chain lengths are too rapidly decomposed, and longer chains are highly resistant to decomposition. Unfortunately it is very difficult to produce commercially a pure trimethylene tetraurea; ureaform contains both shorter and longer chains.

A typical ureaform may contain 30% of its nitrogen in forms that are soluble in cold water (25°C). The quality of the remaining 70% is judged by the percentage that is soluble in hot (boiling) water as determined by prescribed analytical procedures. At least 40% of the nitrogen insoluble in cold water should be soluble in hot water for acceptable agronomic response; typical values are 50 to 55%.

The consumption of ureaform in the United States is approximately 50,000 tons per year. Most of the production goes into mixed fertilizer for specialty uses, such as for lawns, flower gardens, and golf courses. The wholesale price of ureaform per unit of nitrogen is about three times that of urea, ammonium nitrate, or ammonium sulfate.

In TVA's tests of many other organic nitrogen-containing compounds as fertilizers, some proved readily available, some slowly available, some inert, and some toxic. Among those that showed promise as slow-release fertilizers were oxamide, glycouril, cyanuric acid, ammeline, and ammelide. For lack of a practical process, none of these materials has been manufactured commercially for fertilizer use.

Coated Soluble Materials: A wide range of materials and techniques have been explored with the object of making controlled-release fertilizers by coating soluble fertilizer materials with plastic films, resins, waxes, asphaltic materials, or other barriers. The only known commercial production of coated controlled-release fertilizer utilizes a process developed by Archer Daniels Midland Company (ADM). The main component of the coating is a copolymer of dicyclopentadiene with a

glycerol ester (34). Applied in several layers that vary in composition, the coating releases fertilizer solution by osmotic exchange with moisture from the soil. The coated granular fertilizer was manufactured by ADM under the trade name Osmocote starting in 1964. It now is produced and marketed by Sierra Chemical Company under exclusive license from ADM. Three grades of Osmocote are available: 14-14-14, 18-9-9, and 36-0-0. The nitrogen in the first two grades is supplied by ammonium nitrate and ammonium phosphate; the third grade is coated urea. The weight of the coating ranges from 10 to 15% of the gross weight.

Osmocote products are recommended for turf, floriculture, nursery stock, and high-value row crops. The retail price was reported to be about $0.55 per kilogram in 1965.

Sulfur-coated urea (SCU) is a controlled-release material that has been under development by TVA for 10 years. Sulfur was selected as the coating material on the basis of economy and efficiency after several coating materials were tried. Urea was selected as the material to be coated because of its high nitrogen content, low cost, and commercial availability.

Initial studies indicated that sulfur alone was not adequately resistant to moisture penetration. The discovery that an oily wax sealant was required with the sulfur provided the breakthrough to a successful coating. The wax was subject to microbial attack in the soil, however, with deterioration of its sealing properties. Need for addition of a microbicide was evident. Coal tar, in the proportion of 0.2%, proved effective and economical.

In early laboratory work, 2- to 15-pound batches of urea were coated in small drums. The development then was shifted to a small continuous pilot plant with a production rate of about 300 pounds per hour. The process is now being developed further in a large pilot plant with a capacity of about 1 ton per hour.

A schematic flow diagram of the pilot plant is shown in Figure 7. Granular urea is preheated in the first rotating drum to 80°C with electric radiant heaters to prevent the sulfur from freezing too rapidly on the granules. The molten sulfur is air-atomized and sprayed onto the rolling bed of granules in the second drum. Wax and coal tar are applied in the third drum. The coated granules are then cooled in a fluidized bed cooler, and a powdery conditioner is applied in a fourth drum to eliminate the tacky condition of the wax.

Most of the work was done with commercial granular urea (1.7 to 3.3 mm) produced by the spray-drum granulation process. Some tests were made with prilled urea, but its smaller particle size results in greater surface area per unit weight of urea; this greater surface requires a coating that is higher in percentage by weight of the product for a given coating thickness. For this reason, large, well-rounded granules are preferred for coating.

The rate of dissolution of coated urea can be varied by varying the thickness of the coating. As an indication of the dissolution rate, a laboratory test is used in which the percentage of the urea that dissolves in 7 days in water at 38°C is measured. Current agronomic information indicates that in general the best results are obtained with materials that

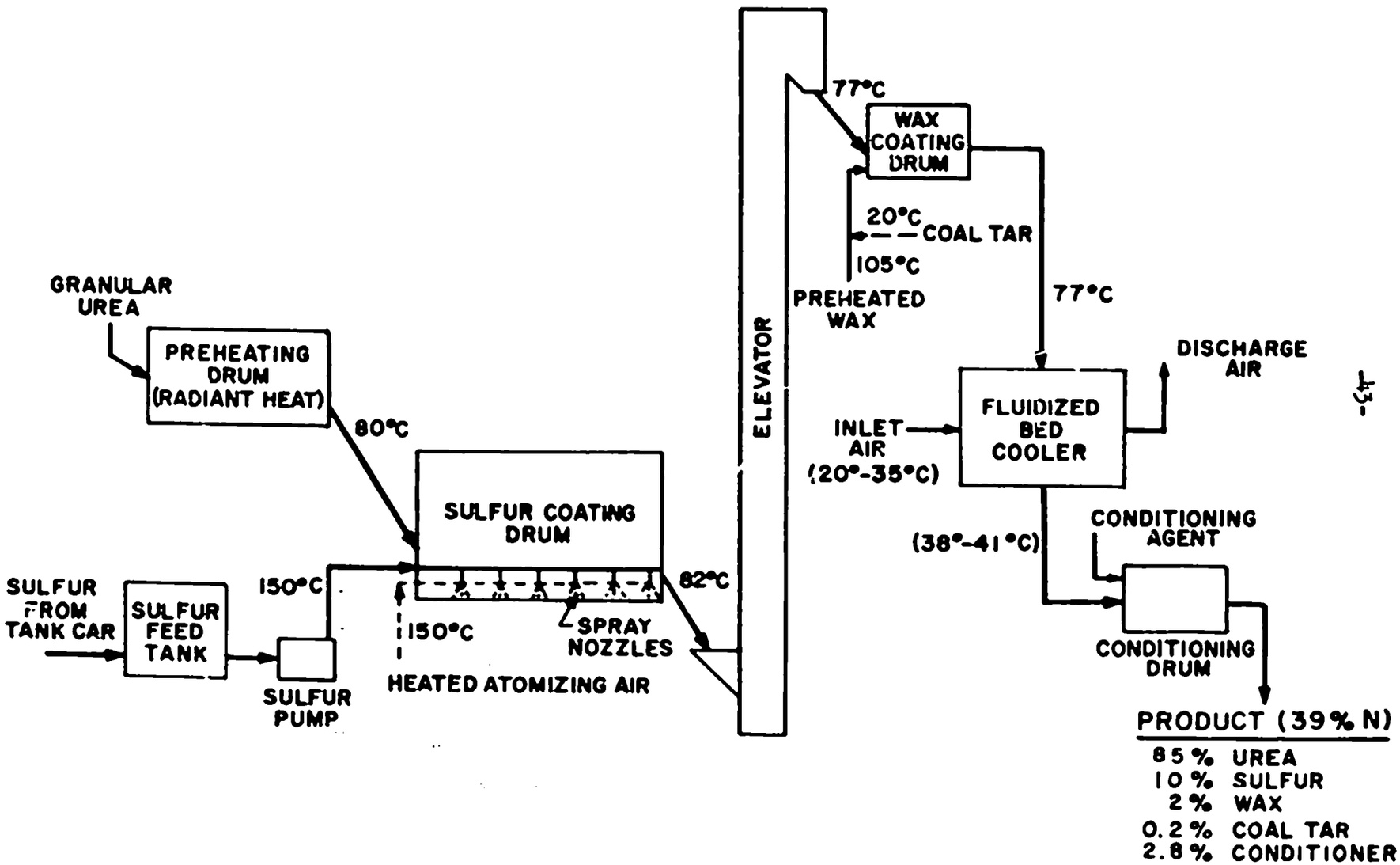


FIGURE 7
FLOW DIAGRAM FOR SULFUR-COATED UREA PILOT PLANT

have a 7-day dissolution of 20 to 30%. Such material can be produced with a total coating weight of as little as 15% (10% sulfur, 2% wax and coal tar oil, and 3% conditioner).

Typical dissolution patterns in water are shown in Figure 8. These tests were made with early products; in subsequent work, improved coating technique provided similar dissolution patterns with lighter coatings. However, the figure illustrates the relative effect of coating weight and the effect of water temperature on dissolution. It also shows that the dissolution rate decreases with time of immersion. Soil dissolution rates are not necessarily the same as dissolution rates in water. Allen et al. (35) have published data on the rate of dissolution in the soil as affected by coating weight, temperature, placement, and inclusion of microbicide in the coating.

In addition to the controlled-release characteristics, coated urea has excellent storage and handling characteristics and might even be handled in bulk in humid climates. Also, it may be blended with triple or single superphosphates, which are incompatible with uncoated urea.

Agronomic tests have been completed or are in progress in 29 countries and in 36 states of the United States. Some results of TVA tests have been reported (36, 37, 38).

Coated urea was advantageous for use on sugarcane, pineapple, rice grown with delayed or intermittent flooding, and in general for long-season crops or for conditions conducive to heavy leaching or to decomposition losses.

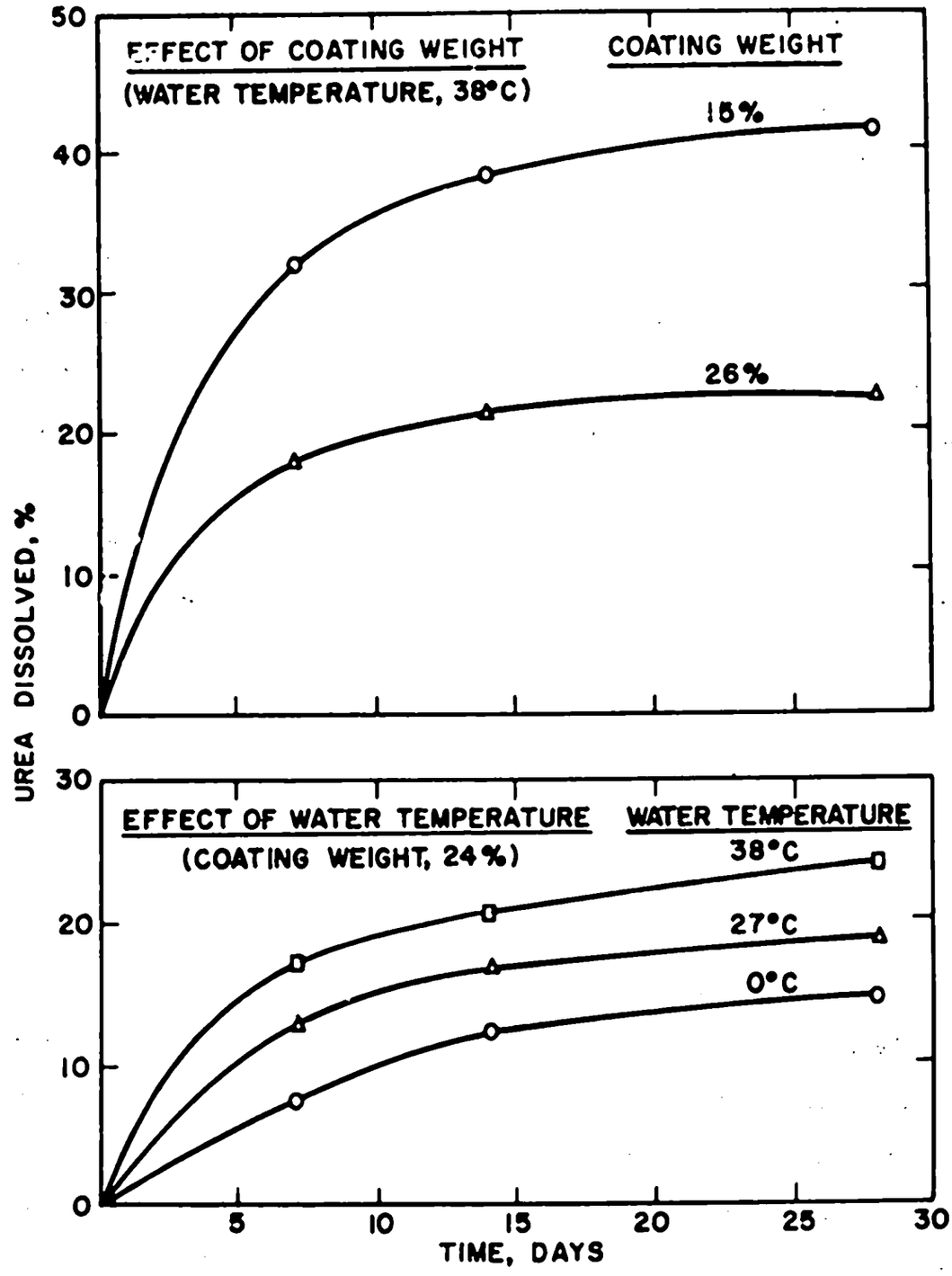


FIGURE 8
RATE OF DISSOLUTION IN WATER OF COATED UREA (1.7-3.4 MM)

The sulfur-coating technique may be applied to fertilizers other than urea. Experimental work has included coating of diammonium phosphate, potassium chloride, potassium sulfate, and various compound fertilizers.

Nitrification Inhibitors: Nitrogen fertilizers in the ammonium form are immobilized in the soil by sorption on clay particles and hence are resistant to leaching. However, the ammonium form is rapidly converted to the nitrate form in most soils by microbiological processes called nitrification. The nitrate form is more readily available to most plants, although some plants (e.g., rice) can readily use the ammonium form. Thus, some of the purposes of controlled release (resistance to leaching and delayed availability) may be attained by delaying nitrification of ammonium nitrogen.

Numerous organic chemicals have been identified as nitrification inhibitors. The inhibition is due to the toxicity of these chemicals to organisms that convert ammonium nitrogen to nitrite, which is the first step of the nitrification process.

One of the nitrification inhibitors that has received attention in the United States is 2-chloro-6-(trichoromethyl) pyridine. The Dow Chemical Company is promoting it under the trade name N-Serve. The company plans to have a manufacturing unit in operation within a year, and they are aiming for a price level that will permit the grower to use N-Serve at a cost of $6.20 to $7.40 per hectare. The minimum concentration of N-Serve in the soil for delaying nitrification at least 6 weeks is said to range from 0.5 to 10 parts per million.

Dow points out that a nitrification inhibitor is helpful only when conditions favor high nitrogen loss from the soil. Such conditions are heavy rainfall or heavy irrigation, coarse textured soil, soil in the pH range where nitrification readily occurs, and anaerobic soil conditions.

Potassium azide (2 to 6% KN_3) dissolved in anhydrous ammonia was effective in lowering the rate of nitrification in tests conducted by the U. S. Department of Agriculture in cooperation with agricultural experiment stations in the states of Louisiana (39) and Washington (40). PPG Industries, Inc., is exploring this and other agricultural uses (e.g., as a herbicide in rice culture) for the azide. They think they may have a commercial production unit in about 3 years.

Another nitrification inhibitor that has received much attention in Japan is 2-amino-4-chloro-6-methyl pyrimidine. It is manufactured by Mitsui Toatsu Chemicals, Inc., (formerly Toyo Koatsu Industries, Inc.) under the trade name AM. Japanese companies produced 15,400 metric tons of NPK fertilizers containing AM in 1968.

Controlled-Release Potash Fertilizers

Some interest has been shown in controlled-release potassium fertilizers. TVA conducted tests with potassium polyphosphates and potassium calcium pyrophosphates. Some of the materials were only slightly soluble in water by the AOAC procedure. Agronomic evaluation of the materials was reported by Engelstad (41). Their only advantage was reduced injury to germinating seeds. Most of the materials were as readily available as soluble potash salts. Some of the least soluble materials showed slow-release characteristics when applied as large particles (about 7 mm), but there was no conclusive evidence of increased efficiency.

More recently, sulfur-coated potassium chloride has been prepared by TVA for agronomic tests. Some of these tests were promising in that yields were increased in comparison with uncoated potassium chloride (42). More information is needed for agronomic and economic evaluation. The low cost of soluble potassium fertilizers tends to discourage efforts to increase their efficiency.

Conclusions About Controlled-Release Fertilizers

Controlled-release nitrogen fertilizers very probably will prove useful for some field crops in some situations. Much more study will be required, however, to determine the place of controlled-release nitrogen fertilizers in the farm economy.

Controlled-release fertilizers are most likely to prove advantageous where labor is scarce and expensive. In developing countries where labor is plentiful and inexpensive, multiple applications of soluble fertilizer can be used to attain improved yields and higher efficiency of utilization with less cost.

Prospects for improvement of phosphate and potassium fertilizers through controlled release seem remote.

Summary

Conspicuous trends in the world fertilizer situation include a rapid rate of growth in production and consumption; increasing concentration of N, P_2O_5, and K_2O; and a growing preference for compound rather than single-nutrient fertilizers. Variety and complexity of formulation of compound fertilizers are increasing to meet requirements of various crops and soils. To an increasing extent, fertilizer manufacturers will concern

themselves with secondary and micronutrient elements, as well as the three major nutrients.

Dramatic reductions in cost of producing basic fertilizer materials have been achieved through improvements in technology and increased scale of operation. There is a growing tendency to use these basic materials as intermediates in small local mixing plants that combine them into compounds that meet the needs of their area. Highly concentrated intermediates, such as ammonia, ammoniating solutions, phosphoric acid, ammonium phosphates, and refined potash salts, are being used to an increasing extent in local plants; developments in low-cost transportation of intermediates contribute to the economics of their use. The local plants are of three types--dry mixing, including bulk blending; liquid mixing; and granulation. Liquid fertilizers offer some special advantages in manufacture, distribution, and application which may increase their future popularity.

High-analysis materials, particularly urea and ammonium phosphates, will supply increasing percentages of the world's fertilizers, whereas lower analysis materials will decline in importance. Ammonium polyphosphate is an interesting new material. New nitric phosphate processes are available that provide high water solubility and higher concentration. The nitric phosphate processes are often economically attractive, but lack of versatility has limited their acceptance in some regions.

Controlled-release fertilizers are a subject of much interest. Controlled-release nitrogen fertilizers offer some definite advantages for some crops and soils. Their future will depend on technological developments to allow production costs commensurate with their advantages.

References

1. Kennedy, F. M., Harre, E. A., Hignett, T. P., McCune, D. L. Estimated World Fertilizer Production Capacity as Related to Future Needs--1967 to 1972-80. Tennessee Valley Authority, Muscle Shoals, Alabama 35660. June 1968.
2. Stout, P. R. J. Agr. Food Chem. 4, No. 12, 1000-6 (December 1956).
3. Cunningham, H. U. Proc. Fertiliser Soc. (London), No. 56. 1959.
4. Hignett, T. P. Proc. Fertiliser Soc. (London), No. 87. 1965.
5. Hoffmeister, George. Agr. Chem. 20, 42, 46, 96, 98 (February 1965).
6. Bischofberger, G., Heck, R. R. Proc. Fertiliser Soc. (London), No. 91. 1966.
7. Achorn, F. P., Lewis, J. S., Jr. Croplife, 10-1, 15 (March 1969).
8. Brownlie, I. A. Proc. 14th Annual Meeting Fertilizer Industry Round Table (Washington), 64-8. Office of Secretary-Treasurer, Glen Arm, Maryland 21057. 1964.
9. Hemsley, J. D. C. Proc. 16th Annual Meeting Fertilizer Industry Round Table (Washington), 109-13. Office of Secretary-Treasurer, Glen Arm, Maryland 21057. 1966.
10. Kearns, T. C. U. S. Patent 3,419,378. December 31, 1968.
11. Chem. Week 104, No. 20, 90 (May 17, 1969).
12. Hignett, T. P., Davis, C. H. "Urea and Superphosphate in Production of Granular Compound Fertilizers." Presented at FAI Technical Conference on Recent Advances in Fertilizer Technology, New Delhi, India, January 1972.
13. Manderson, M. C. Chem. Eng. Progr. 68, No. 4, 57-61 (April 1972).

14. Nitrogen, No. 66, 29-34 (July-August 1970).

15. Ando, Jumpei. Proc. 20th Annual Meeting Fertilizer Industry Round Table (Memphis), 85-92. Office of Secretary-Treasurer, Glen Arm, Maryland 21057. 1971.

16. Beaton, J. D., Fox, R. L. "Fertilizer Technology and Use," 2nd ed., Chapt. XI. R. A. Olsen, Editorial Committee Chairman. American Society of Agronomy, Madison, Wisconsin. 1971.

17. Achorn, F. P., Balay, H. L. Fertilizer Soln. 16, No. 30, 32, 34, 36, 38, 40, 42-3 (January-February 1972).

18. Fertilizer Situation. Economic Research Service, U. S. Department of Agriculture, Washington, D. C. March 1971.

19. Kotlarevsky, Igor. "Production of Ammonium Polyphosphate and Liquid Fertilizer from 52-54 Per Cent Phosphoric Acid." Paper No. ID/WG.99/6 presented at 2nd Interregional Fertilizer Symposium, Kiev, USSR. 1971

20. Terman, G. L., Engelstad, O. P. Com. Fertilizer 112, 30, 32-3, 36, 40 (June 1966).

21. Fourcassie, F., Gadet, R. Bull. Ass. Fr. Etude Sol. 8, 213-37 (1966).

22. Gourny, P., Conesa, A. P. "Possibilities d'Utilisation par la Plante des Polyphosphates Incorpores au Sol." Presented at VI Congres Mondial des Fertilisants, Lisbon, Portugal, October 1968.

23. Conesa, A. P. C. R. Acad. Sc. Paris, 268D, 2063-6 (April 21, 1969).

24. Singh, Y., Dartigues, A. Plant Soil 32, 397-411 (1970).

25. Soubies, L. A., Baratier, J. P. Fertilizer Soln. 12, No. 6, 48-57 (November-December 1968).

26. Mortvedt, J. J., Giordano, P. M. Fertilizer Soln. 14, No. 4, 22-7 (July-August 1970).

27. Fertilizer Soln. 15, No. 6, 88-91 (November-December 1971).

28. Slack, A. V., Blouin, G. M., Livingston, O. W. Farm Chem. 130, No. 6, 124-6, 128, 130, 132 (June 1967).

29. Hignett, T. P. Proc. Fertiliser Soc. (London), No. 108. 1969.

30. Thompson, W. H. Chem. Eng. 83-5 (April 5, 1971).

31. World Fertilizer Review, No. 1, 47 (May 1971).

32. Huffman, E. O. Proc. Fertiliser Soc. (London), No. 71. 1962.

33. Hamamoto, Masao. Proc. Fertiliser Soc. (London), No. 90. 1966.

34. Powell, Robert. "Controlled Release Fertilizers." Noyes Development Corporation, Park Ridge, New Jersey 07656. 1968.

35. Allen, S. E., Hunt, C. M., Terman, G. L. Agron. J. 63, No. 4, 529-33 (July-August 1971).

36. Allen, S. E., Mays, D. A., Terman, G. L. Crops Soils 21, 13-5 (December 1968).

37. Mays, D. A., Terman, G. L. Sulphur Inst. J. 5, No. 3, 7-10 (1969).

38. Mays, D. A., Terman, G. L. Agron. J. 61, 489-92 (1969).

39. Parr, J. F., Carroll, B. R., Smith, S. Soil Sci. Soc. Amer. Proc. 35, No. 3, 469-73 (1971).

40. Papendick, R. I., Parr, J. F., Smith, S., Smiley, R. W. Soil Sci. Soc. Amer. Proc. 35, No. 4, 579-83 (1971).

41. Engelstad, O. P. "The Role of Potassium in Agriculture," 63-77, ed. V. J. Kilmer, S. E. Younts, N. C. Brady. American Society of Agronomy, Madison, Wisconsin. 1968.

42. Allen, S. E., Mays, D. A. J. Agr. Food Chem. 19, No. 5, 809-12 (September-October 1971).