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Fertilizers and Food Production

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INTRODUCTION

Fertilizers provide plants with the nutrients they need for their growth and development. Plants live, grow, and reproduce by taking up water and nutrients, carbon dioxide from the air, and energy from the sun. Apart from carbon, hydrogen, and oxygen, which collectively make up 90–95 percent of the dry matter of all plants, other nutrients needed by plants come essentially from the media in which they grow—essentially in the soil. The other nutrients are subdivided into primary nutrients (nitrogen, phosphorus, and potassium) and secondary nutrients (calcium, magnesium, and sulfur). In addition, plants also need other nutrients in much smaller amounts, and they are referred to as micro-nutrients (boron, chlorine, copper, iron, manganese, molybdenum, and zinc).

To maintain soil fertility and productivity and prevent land degradation, nutrients taken up by crops must be replenished through the application of fertilizers. The use of fertilizer results in many benefits to producers, consumers, and the environment, starting with increased agricultural outputs (mainly food and fiber) to contributing to soil organic matter maintenance, water-holding capacity, biological nitrogen fixation, soil erosion control, other physical and chemical properties, and less extensive land use. These benefits contribute to increased agricultural growth and agribusiness activities, which are catalysts for broadly based economic growth and development in most developed and developing economies; agriculture's links to the nonfarm economy generate considerable employment, income, and growth in the rest of the economy.

A commercial fertilizer is a material that contains at least one of the plant nutrients in chemical form that, when applied to the soil, is soluble in the soil solution phase and assimilable or "available" by plant roots. Most often, this implies chemical forms that are water soluble. However, in the case of phosphorus, solubility in special reagent solutions (citric acid, neutral ammonium citrate, or alkaline ammonium citrate) often is used as a guide for availability to plants. In the case of nitrogen, slow solubility in water may be more desirable from an environmental and efficiency standpoint than easy solubility.

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Fertilizer products are customarily designated by a series of numbers separated by dashes. This set of numbers is called "grade" of the fertilizer product. Each of the numbers indicates the amount of a nutrient that the manufacturers guarantee is contained in the fertilizer product. This number includes only the amount of nutrient found by accepted analytical procedures, thereby excluding any nutrient present in a form that is deemed to be unavailable for plant nutrition. The content of each nutrient, expressed as a percentage of total weight, is the guaranteed minimum rather than actual, which is usually slightly higher.

Usually, three numbers are used when giving the grade of a fertilizer product, and these three numbers always refer in order to the content of the primary nutrients: nitrogen, phosphorus, and potassium. If other nutrients are present, their content can also be indicated in the grade of the fertilizer product; each extra number is followed by the chemical symbol of the nutrient it represents. Many countries indicate the content of phosphorus and potassium not in the elemental form but in the oxide form, P_2O_5 and K_2O. Thus, a fertilizer product with a grade of 12–6–22– 2MgO is guaranteed by the manufacturer to contain: 12 percent N, 6 percent P_2O_5, 22 percent K_2O, and 2 percent MgO.

The beginning of our dependence on inorganic fertilizer can be traced back to the nineteenth century when Justus von Liebig articulated the theoretical foundations of crop production and when John Bennett Lawes began producing fertilizers containing phosphorus.[1] However, only since the 1960s when global starvation became a real possibility have fertilizers assumed a predominant role in increasing agricultural productivity. Fertilizer was an integral part of technological trinity—seed, water, and fertilizer—responsible for bringing about the "Green Revolution" that helped many densely populated countries, including India, China, and Indonesia, achieve food self-sufficiency in a short span of 20–25 years.

Since the 1960s, global cereal production has more than doubled, increasing from 866 million metric tons (mt) in 1961 to nearly 2200 million mt in 2005, with developing countries accounting for nearly 60 percent of the increase (Fig. 24.1). Most of the increased cereal production in South Asia was through

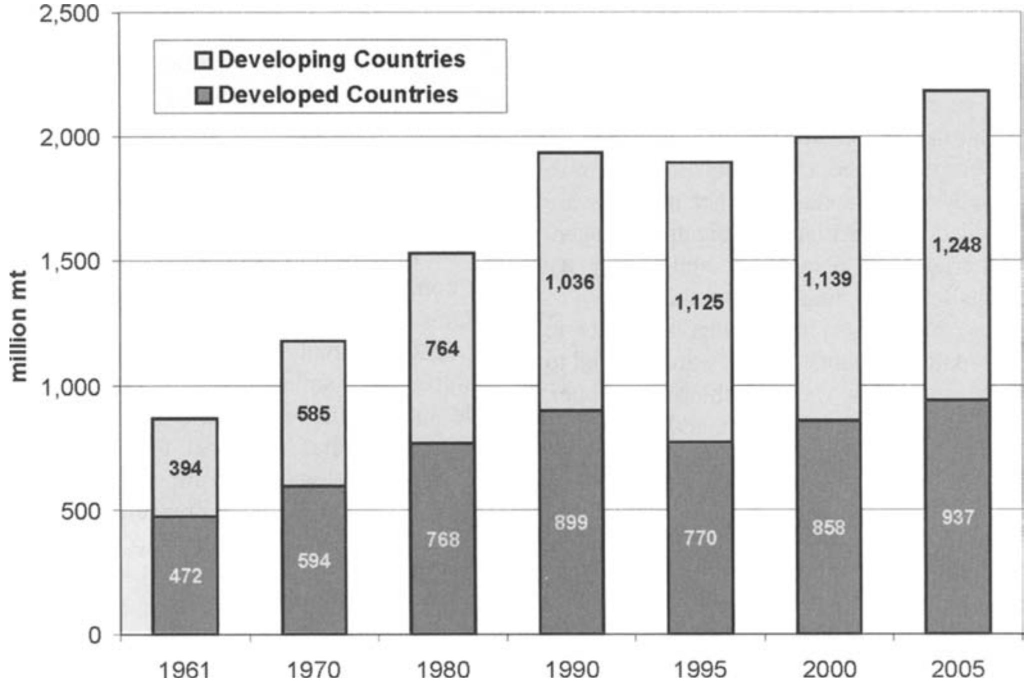


Fig. 24.1. Cereal production in developed and developing countries, 1961–2005.

higher yields, but increases in sub-Saharan Africa were mostly through area expansion (Fig. 24.2). It is estimated that fertilizers accounted for 56 percent of the rise in average yields per hectare and about 30 percent of the total increase in production. Consequently, cereal production closely parallels fertilizer use in developing countries (Fig. 24.3). The only exception is sub-Saharan Africa where per capita food production has decreased

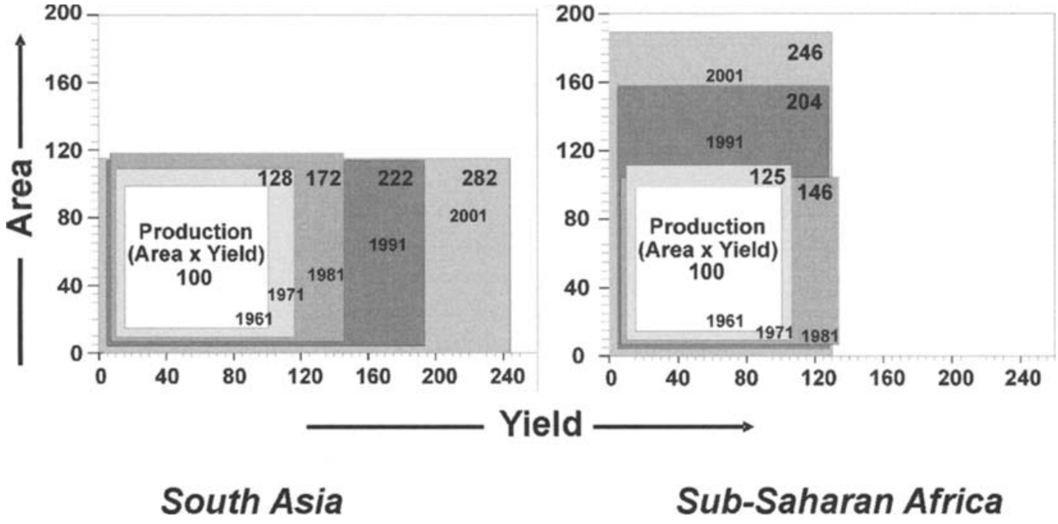


Fig. 24.2. Growth of cereal yield and area in cereal production in South Asia and Sub-Saharan Africa between 1961 and 2001 (1961 = 100 for yield and area).

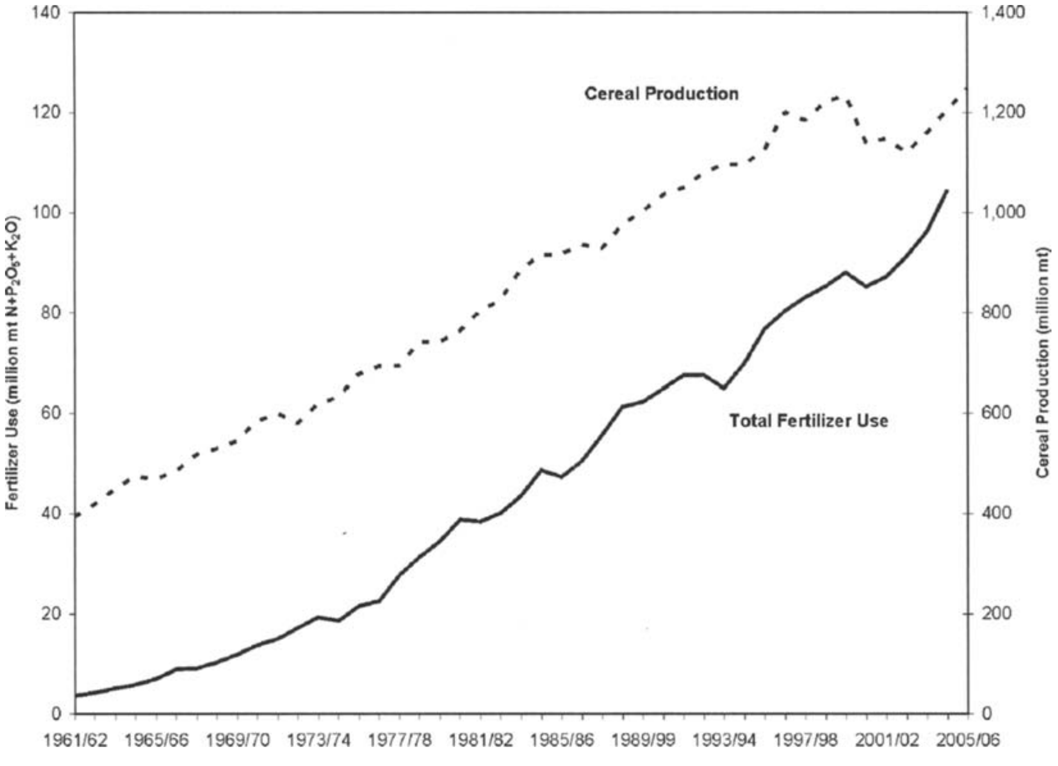


Fig. 24.3. Developing countries: total cereal production and total fertilizer use, 1961/62–2005/06.

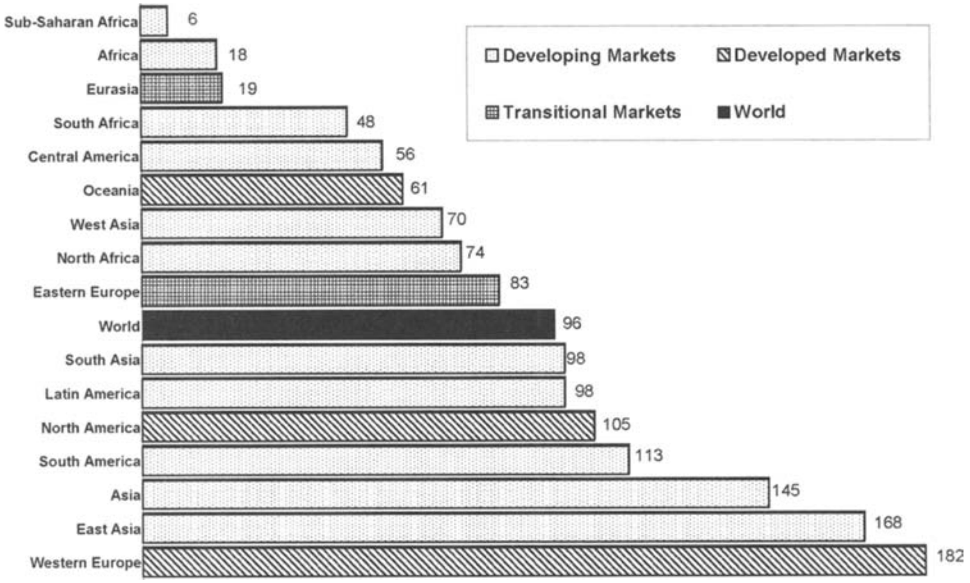


Fig. 24.4. Per hectare fertilizer use by regions and markets, 2003/04 (kg/ha).

since the 1970s. This decline can be attributed to several factors, including low soil fertility, agroclimatic conditions, and low fertilizer use. Compared with a world average of 96 kilograms of nutrients per hectare, sub-Saharan Africa uses only 6 kilograms of nutrients per hectare, resulting in a significant mining of inherent nutrients from soils that are already low in nutrient status (Figs. 24.4 and 24.5).

Growth in the future demand for food and feed will be influenced by changes in a number of forces, but mainly by growth in population, income levels and economic development, and changes in the food preferences of consumers. Although the United Nations recently adjusted downward its estimates of population growth, still during the next 20 years approximately 75 million people will be added to the world's population each year, increasing it from about 6.6 billion in 2007 to over 8 billion by 2025 (Fig. 24.6). Much of this increase will occur in the cities of the developing world, which will account for most of the increased demand for food, including meat products. The recent drive toward renewable energy sources, particularly biofuels, will also increase demand. Enthusiasm for biofuels is because of dramatically higher energy prices, geopolitical tensions, and uncertainties about future availability and access to petroleum. Also, farmers must produce more crops from existing farmland if forests and wildlife habitats are to survive. This will require increased crop yields through use of improved seeds and fertilizer. This increased fertilizer use has to be balanced against the environmental and human health concern stemming from intensive fertilizer applications, particularly in industrialized countries.

OVERVIEW OF THE FERTILIZER INDUSTRY

Since medieval times, farmers have realized the need to maintain the productivity of soil to achieve improved crop yields. Until the last 200–300 years, however, the approach was highly empirical; only by accident or by trial and error was it found that applications to the soil of various organic wastes or naturally occurring mineral substances such as manure, compost, fish, ashes, saltpeter, and other

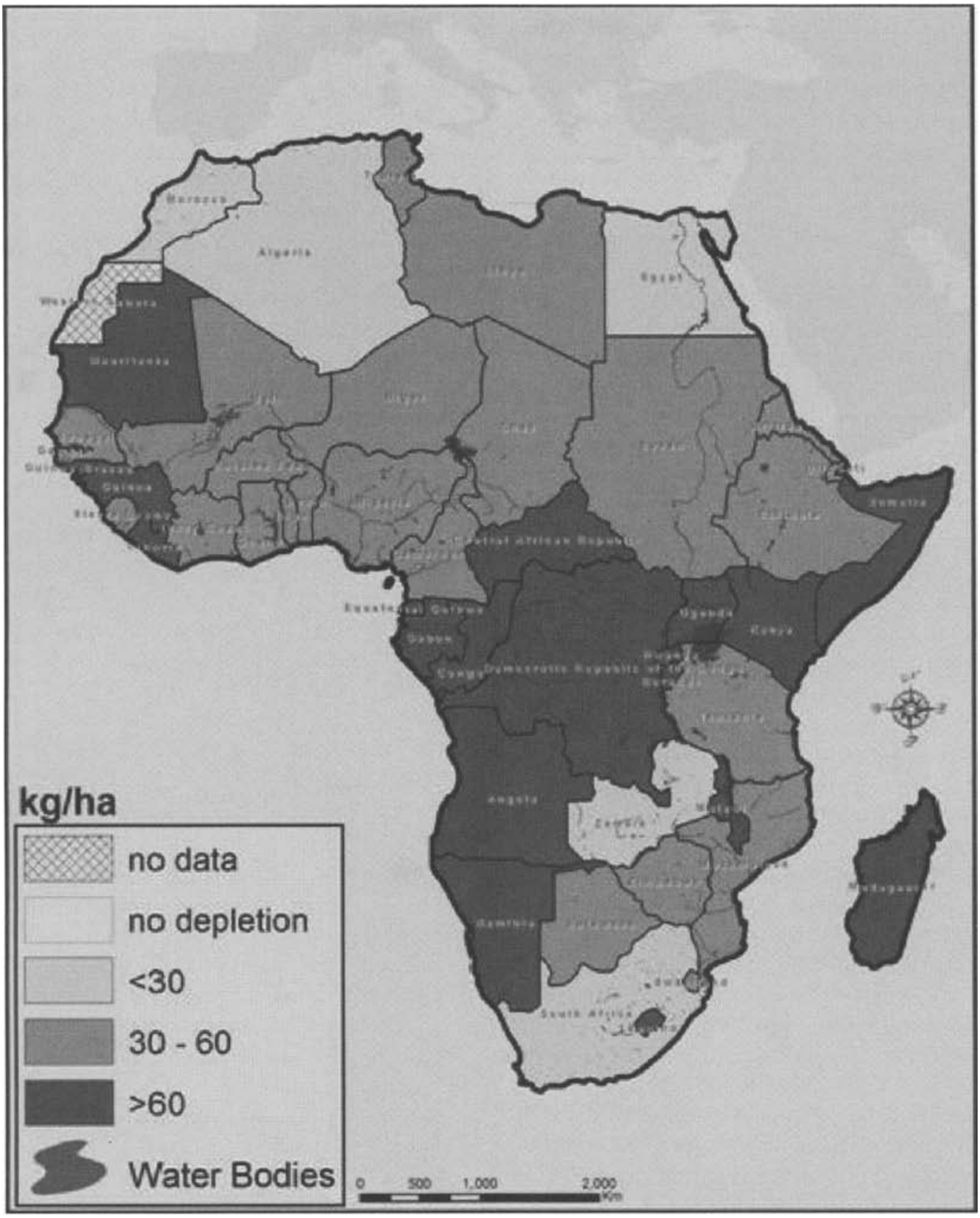


Fig. 24.5. Average nutrient depletion (NPK) in Africa for 2004.

substances would sometimes increase yields or apparently restore productivity to fields that were considered "worn out."

As more and more chemical elements were identified, scientists became interested in determining the amounts and relative importance of various elements in plants. The German scientist Liebig clarified the value of elements derived from the soil in plant nutrition and stressed the necessity of replacing

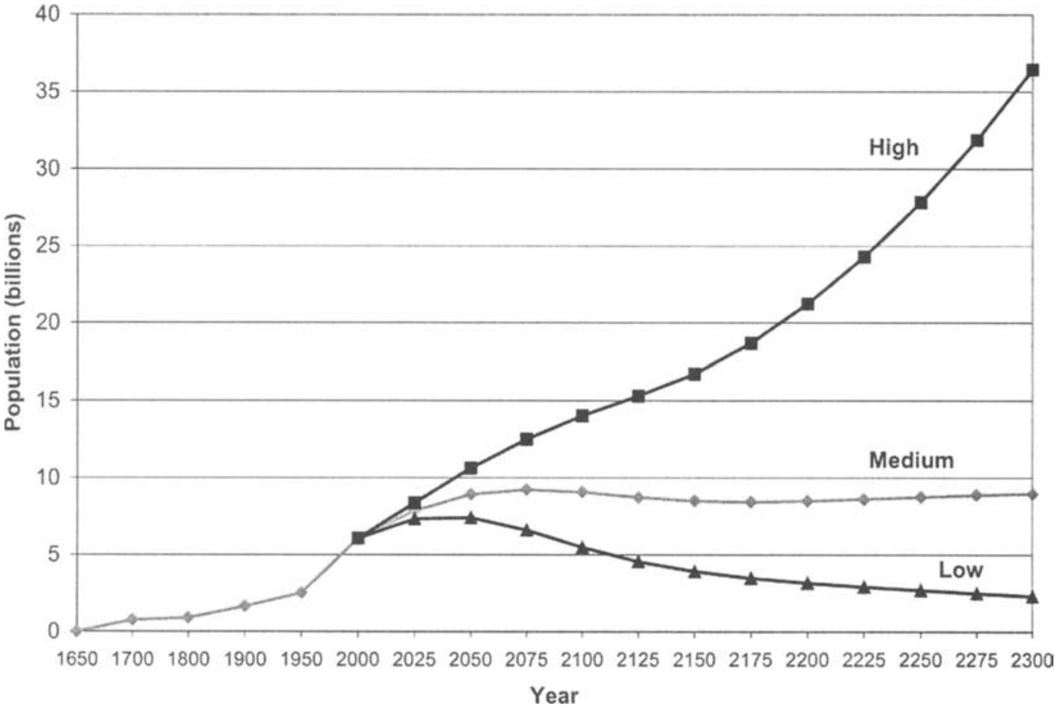


Fig. 24.6. World population projection.

those elements to maintain soil fertility. He usually is credited with initiating the fertilizer industry. Liebig recognized the value of nitrogen but believed that all plants could get nitrogen from the air, a concept that unfortunately is not true. He envisioned a fertilizer industry with nutrients such as phosphate, lime, magnesia, and potash prepared in chemical factories. In 1840 Liebig published a recommendation that pulverized animal bones be treated with sulfuric acid to make the phosphate more readily available to plants. This practice was accepted, and the production of fertilizers by chemical processing thus began.

Natural organic materials and various chemical byproducts represented a large proportion of the total world fertilizer supply until about the middle of the twentieth century; in the later years of the century, however, the dependence shifted almost entirely to synthesized or chemically processed materials. Only by this means has it been possible to keep up with increasing populations, increased farm acreage, and increased plant food needs of new and improved crop varieties. Today, the fertilizer industry utilizes many facets of highly sophisticated chemistry and engineering in the manufacture of fertilizers, and in pollution control, including disposal of waste products. The procuring and handling of raw materials and the distribution and marketing of products also involve the latest technology and many innovations. In addition, the agronomic aspects of fertilizer usage engage the efforts of many individuals and organizations worldwide. The development and introduction of "high-yielding" varieties of seed required more concentrated and efficient fertilizers. Many organizations and private companies worldwide have carried out extensive research and development on improving fertilizer production, developing new products, and increasing efficiency of usage. The most notable among them include the U.S. Tennessee Valley Authority, the International Fertilizer Development Center, and the Rothemstadt Experiment Station.

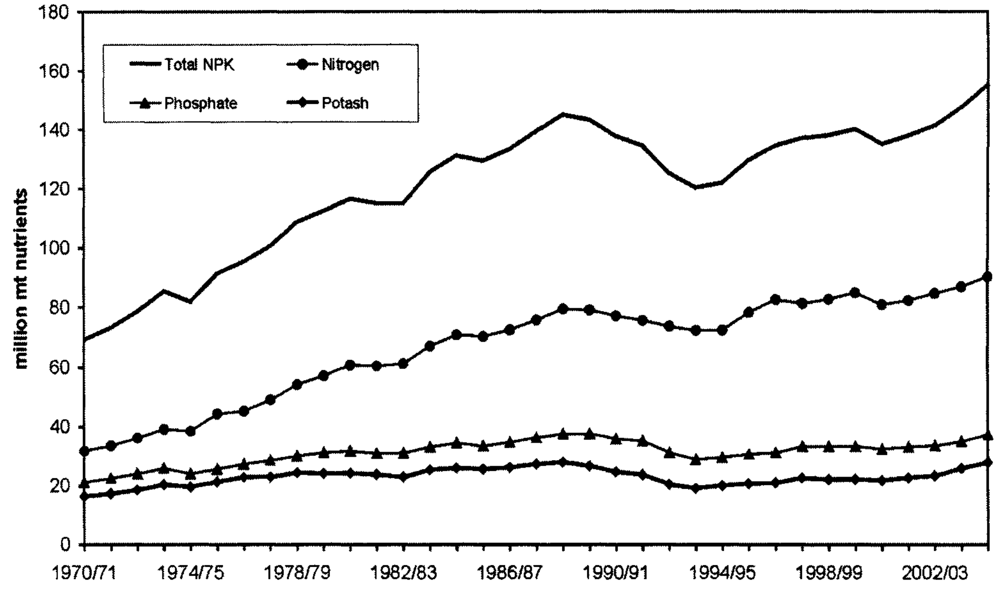


Fig. 24.7. World: nitrogen, phosphate, potash, and total NPK consumption, 1970/71–2004/05.

The fertilizer industry is a large-volume producer, one that falls within the basic industrial structure of a country. The magnitude of this industry is apparent from Fig. 24.7, which shows the yearly global consumption of primary plant nutrients (N, P_2O_5, and K_2O) since 1970/71. For 2002/03 the total consumption of N, P_2O_5, and K_2O was 152.5 million mt. Of this amount, China, the United States, and India consumed 39.6 million mt, 19.3 million mt, and 16.1 million mt, respectively. Collectively, these three countries accounted for about 50 percent of the world consumption. Assuming an average nutrient content of all fertilizers for that period of about 40 percent shows that some 358 million mt of fertilizers was produced and handled by the industry during that year.[2] In general, the industry includes a number of "basic producers" each of which typically concentrates on producing large amounts of single-nutrient or high-nutrient fertilizer products, usually at locations near raw materials. Numerous other components of the industry concentrate on locating close to local farmers and distributing the basic products either in the form received from basic producers or after various secondary-processing operations such as granulation, blending, or conversion to fluids. In the United States, fluid mixtures account for more than 20 percent of the total fertilizer sales. To a lesser extent, fluid mixtures have been introduced into Europe, North America, and South America. Fluid mixtures are used on high-value crops in some middle eastern countries, particularly Israel, where efficient use of water is as important as the efficient use of plant nutrients.

RAW MATERIALS FOR FERTILIZER PRODUCTION

The primary raw materials for nitrogen fertilizers are natural gas, naphtha, fuel oil, and coal. The manufacturing of phosphate fertilizers most often requires phosphate rock. Naturally occurring potassium salts form the basis of the production of most potash fertilizers.

Natural gas, naphtha, fuel oil, and sulfur have fairly definable specifications. In contrast, phosphate rock and coal are products that can vary significantly in composition and other characteristics. These variations can affect the processes used to upgrade the "as-mined" ores or the processes for manufacture of fertilizers from beneficiated products. Potash ores also vary greatly in composition depending on origin; however, the end products of mining, beneficiation, and processing generally have relatively constant compositions.

Adequacy of requisite raw materials is the most obvious concern when facing a substantial increase in future demand. Two separate yet intertwined issues in the case of fertilizers are: sufficiency of raw materials and availability of energy to convert them into final products. Potassium is of least concern among the three primary nutrients. Not only is this element abundantly present in the earth's crust, but also it can be found in conveniently concentrated deposits in both deeply buried and near-surface sediments. Potassium deposits in descending order of known reserves are in North America (Canada and the United States), Germany, Russia, Belarus, Brazil, Israel, and Jordan. Even the most conservative reserve base estimates indicate a reserve on the order of 500 years at the level of the late 1990s production.[3] Mining, crushing, and beneficiation of potassium usually amount to about 10 gigajoules (GJ)/t of the nutrient, energy demand comparable with that required in making cement.

Phosphate deposits are not as abundant as those of potassium minerals; recently published totals range between 1.5 and 3.5 billion tons of P reserves, 4.7–9.5 billion tons of potential reserves, and about 13 billion tons of resources.[4] Phosphate deposits in the descending order of known reserves are in Morocco and Western Sahara, United States, South Africa, Jordan, and Tunisia. At the current rate of extraction, global reserves would last about 80 years, and the estimates are that resources could support the recent rate of application for nearly 250 years. This time horizon can be extended by tapping less accessible (but plentiful) deposits at a higher price. Depending on the final product, energy costs of phosphatic fertilizers range from about 18 to 32 GJ/t P.

Nitrogen fertilizers via ammonia synthesis account for more than 90 percent of the world's nitrogen fertilizers. Nitrogen supply for ammonia synthesis is truly inexhaustible since the atmosphere contains 3.8 quadrillion tons of the element. Various feedstocks can be used to obtain hydrogen, and during the last several decades the focus has been to improve the energy efficiency of ammonia synthesis. Natural gas is the preferred feedstock and the best natural gas-based plants now use less than 33 GJ/t N. The global mean, which is affected by more energy-intensive reforming of heavier hydrocarbons (naphtha and fuel oil) and coal, is now between 49 and 55 GJ/t N, roughly half of the level prevailing during the early 1950s.

Even if all of the energy needed to fix the fertilizer nitrogen were to come from natural gas, it would still be less than 7 percent of the recent annual global consumption of the fuel and less than 2 percent of all energy derived from fossil fuels.[5] Clearly, there is little reason to be concerned about either the current needs or the future supplies of energy for producing nitrogenous fertilizers via the ammonia synthesis route. Moreover, there is no doubt that higher absolute energy needs for nitrogen fertilizers will be partially offset by improved efficiency of ammonia synthesis and by higher efficiencies of fertilizer use. Because today's low-income countries will experience much faster growth of energy needs in sectors other than the fertilizer industry, the share of global fossil fuel consumption for ammonia synthesis by the middle of the twenty-first century may be only marginally higher than it is today.

The global natural gas resources are considered abundant, and they are conservatively estimated to be between 1.1 and 1.7 times as large as all the natural gas that has already been extracted or found in proven reserves.[6] In the absence of natural gas, naphtha, or fuel oil, ammonia synthesis could proceed easily (albeit more costly) by tapping the world's enormous coal deposits or using a variety of biomass feedstocks.

NITROGEN FERTILIZERS

Nitrogen is a component of amino acids that make up proteins; chlorophyll (the molecule that captures the sun's energy); enzymes; and the genetic material, nucleic acids. Therefore, this nutrient is required in large amounts by all plants and forms one of three primary nutrients. Although nitrogen is available in abundance

(79% by volume) in the earth's atmosphere, only a very limited number of plant varieties, chiefly legumes, can utilize this nitrogen directly from the air. For most plants, including such important cereal crops as rice, wheat, and corn, the nitrogen must be in a chemical form dissolved in the soil solution. Atmospheric phenomena, including lightning discharge, convert nitrogen to nitrogen oxides, which then is absorbed in rain water and enters the soil. However, this contribution is quite small and the resultant nitrogen content of soils is normally very low (less than 0.3%). Continuous cropping without replenishment quickly depletes the soil of this important nutrient.

Until about the early 1950s, the more widely accepted method of supplying nitrogen was through the application of manures/organic waste and the use of crop rotation. Crop rotation entailed growth of a nitrogen-fixing legume crop such as peas, clover, or alfalfa, which then was plowed into the soil to provide nitrogen for a subsequent non-legume crop, for example wheat and corn. This method gives the added bonus of improving soil organic matter status. Such a crop rotation is relatively inefficient with regards to land usage and labor requirement. Modern, high-yield agriculture cannot, under most conditions, be sustained by such a system. Nevertheless, the use of crop rotation is being promoted in many countries of sub-Saharan Africa, particularly land-locked countries where natural soil fertility is very low and the price of fertilizers relatively high.

Natural Organics

Animal and human wastes have long been used as fertilizers, especially in Europe and Asia, particularly China. Even some American Indians are said to have planted a dead fish in each corn hill to increase yields. Such materials contain small percentages of nitrogen and other plant nutrients that are assimilable by plants. Today, the use of raw sewage on crops persists in Asia and Europe, but volumewise is not of great significance. In the United States and most European countries, the use of raw sewage is not considered acceptable, but some municipal sewage plants employ special sterilization, heavy metals removal, and drying processes that yield acceptable fertilizers of low nitrogen content. The volume of such output is small, however. Other organic materials traditionally employed as fertilizers of usable nitrogen content include guano (deposits of accumulated bird droppings), fish meal, and packinghouse wastes including bone meal and dried blood. However, the cumulative importance of all such natural nitrogen sources in modern agriculture is minor. Less than 1 percent of the total fertilizer nitrogen now used comes from such sources. These products for the most part are not chemically altered prior to use. Processing is mainly physical in nature to improve handling and distribution properties.

Nitrogen Fertilizers from Synthetic Ammonia

The development of a practical ammonia synthesis process in the early years of the twentieth century was a profound scientific achievement of great social significance in view of the subsequent dependence of the world on fertilizer for support of its growing population.

Both the historical background and detailed technical descriptions of modern ammonia synthesis processes are covered in Chapter 22. These processes are all refinements of the original one conceived and developed by Fritz Haber and Carl Bosch in Germany during the period 1904–13. Basically, a gaseous mixture of nitrogen and hydrogen, in proper proportions to form ammonia, is compressed to very high pressure in the presence of an activated iron catalyst. Ammonia forms and is removed by cooling and condensation. The nitrogen feed is obtained from air by any of several routes that remove the oxygen. Likewise, there are several routes by which hydrogen feed is obtained, most of which involve decomposition of water by reaction with a carbon source such as natural gas, naphtha, or coke. The preparation and the purification of the synthesis gas and the synthesis itself are highly sophisticated modern processes

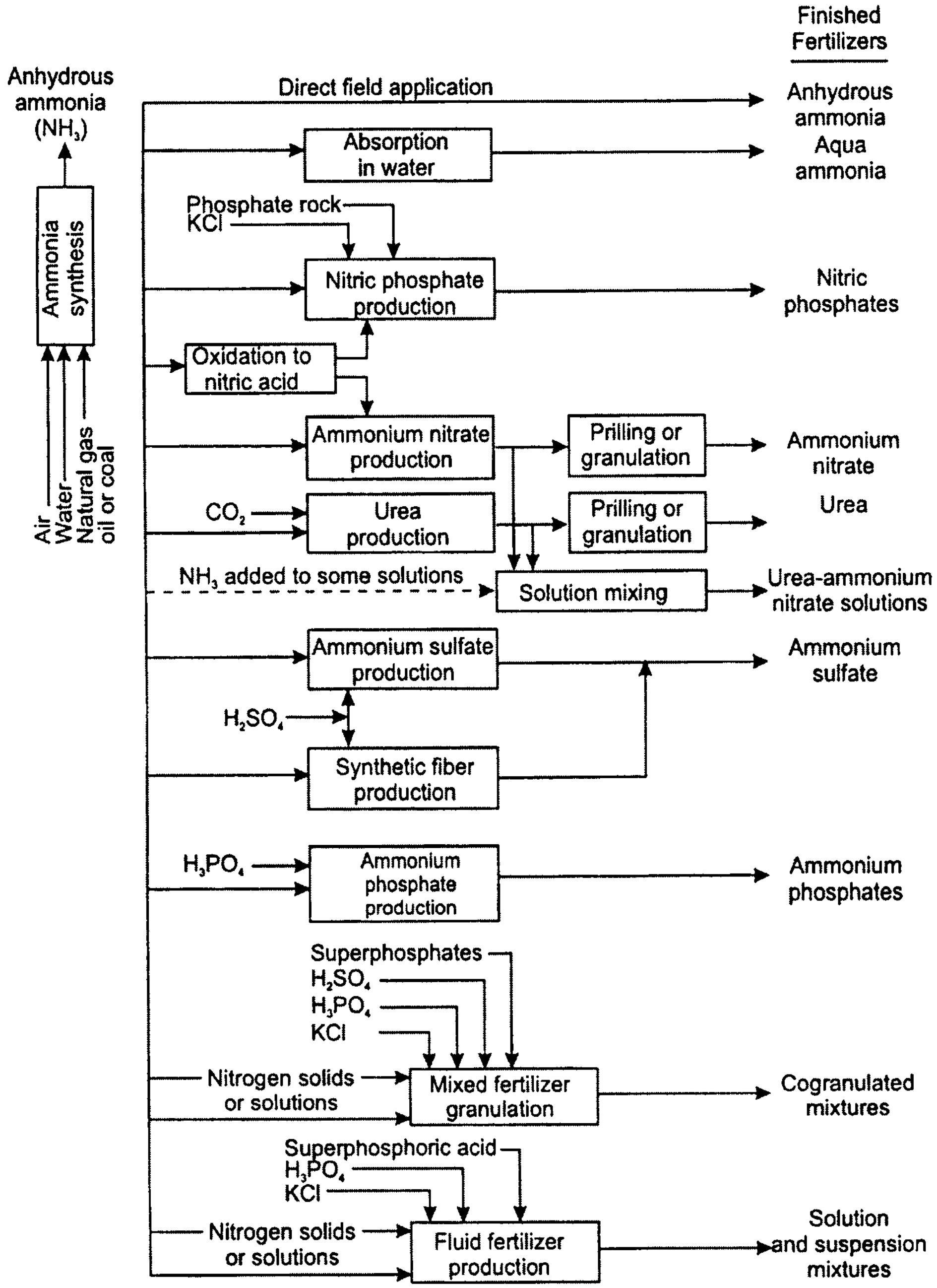


Fig. 24.8. Major routes of synthetic ammonia into finished fertilizers. *(Courtesy TVA.)*

that require great skill and know-how in design, construction, and operation of plants.

There are many processing routes by which synthetic ammonia subsequently finds its way into finished fertilizers. The major routes are outlined graphically in Fig. 24.8 and are discussed in some detail below.

Anhydrous Ammonia. Anhydrous ammonia, without further processing, is an excellent nitrogen fertilizer when properly injected in gaseous form below the surface of many soils. Such direct injection first came into farm use in the early 1940s and rapidly became accepted. Anhydrous ammonia is an important nitrogen fertilizer in the United States, Canada, Denmark, and Mexico, but in some other countries, for various reasons it is a relatively minor nitrogen source.[3]

Anhydrous ammonia injection is popular for economic reasons. Ammonia is naturally the cheapest form of fixed nitrogen at the point of production because no further processing is required. Also, the nitrogen content of anhydrous ammonia (82.4% N) is almost twice that of the next most concentrated nitrogen fertilizer (urea: 46% N); this high nitrogen content reduces shipping and handling weight proportionally.

From production to field application, ammonia is handled in liquefied form. Because ammonia is a gas at normal atmospheric pressure and temperatures, its maintenance in liquid form requires either pressurization or refrigeration. Although such handling requires specialized equipment and considerable safety precautions, there are advantages and economies inherent in the handling of a fluid rather than a solid.[3]

In order to maintain ammonia in liquid form at atmospheric pressure, it is necessary to refrigerate it to at least −33°C. In storage and handling without refrigeration, rather high pressures must be contained when atmospheric temperatures reach high levels. For example, a pressure of 19 kg/cm^2, which for safety reasons has been set as the upper limit allowable for storage vessels at retail locations, will maintain the liquid form only up to a temperature of 46°C. Safety pop-off valves are set to vent ammonia at higher pressures.

Facilities for handling liquid ammonia from points of production to points of use are highly developed in the United States. A considerable amount of ammonia is moved hundreds of miles through interstate pipelines. Major pipelines run from points of production in Texas, Oklahoma, and Louisiana oil fields all the way to the intensively farmed midwestern area of the United States. Storage at the points of production and at large terminals sometimes is in pressurized vessels (spheres), but more often it is at atmospheric pressure in large, insulated, refrigerated vessels. Refrigeration is effected simply by allowing vaporization of some of the contained ammonia, compressing the resulting vapor, and recondensing it in a water-cooled condenser. Barges with similar self-sustaining refrigeration systems commonly move large amounts of anhydrous ammonia on rivers and on the high seas. Also, specially designed railroad tank cars ranging in capacity from 24 to 73 tons are used widely for ammonia transport. These cars typically are nonrefrigerated, instead depending on pressure retention to maintain the liquid form. Large pressurized tank-trucks also are used. At retail depots in farming areas, storage normally is in pressure vessels, often with some compressor capability to recondense vapor and to facilitate transfers. Movement of ammonia to farm fields is via wheeled pressure tanks known as "nurse" tanks. Application equipment, usually tractor-drawn, is equipped with pressure tanks that are filled by transfer from nurse tanks.

Because anhydrous ammonia is gaseous at atmospheric conditions, for fertilizer use it must be injected below the surface of the soil to ensure absorption by the soil solution. Most applicators are equipped with a metering system and a series of soil-penetrating "knives"; the metered ammonia is piped through tubing down the trailing edge of each knife to a single opening at the deepest extremity. A penetration of 15–25 cm is typical. Retention of ammonia in the soil is best when abundant soil moisture is present.

Aqua Ammonia. Ammonia in a simple water solution is popular as a nitrogen fertilizer in some locations, but overall it claims less than 1 percent of the total nitrogen fertilizer market. This product is made from anhydrous ammonia in units referred to as "converters." These units simply provide cooling as ammonia and water are combined in metered proportions. Aqua ammonia normally contains 20 percent nitrogen (24% NH_3). Its chief advantage over anhydrous ammonia is its low vapor pressure; this allows handling in nonpressure equipment, which simplifies design and reduces safety hazards. The chief disadvantage of aqua ammonia as a fertilizer is its relatively low nitrogen content, which limits its shipping range and increases field handling requirements. As with anhydrous ammonia, the preferred application method is knifing below the soil surface to limit volatilization loss; however, a relatively shallow injection depth of only 7–13 cm can be used.

Ammonium Nitrate and Urea. Almost half of the total global fertilizer nitrogen application is as ammonium nitrate or urea, in either solid or solution form, although many countries are restricting the availability of ammonium nitrate because of its potential use by terrorists to make bombs. The history and the technology of ammonium nitrate and urea production from synthetic ammonia are covered in detail in Chapter 29. The production of nitric acid from synthetic ammonia, which is a prerequisite to the production of ammonium nitrate, also is covered completely in Chapter 29. The production plants for all these materials are, like synthetic ammonia plants, highly sophisticated, involving all facets of modern engineering.

The production processes for both ammonium nitrate and urea yield their products first in the form of saturated solutions. Typical ammonium nitrate solution concentration is 75–85 percent (26–30% N) at 40–75°C, and typical urea solution concentration is about 75 percent (34% N) at 93°C. To produce the solid forms of these products, the solutions first must be concentrated to extremely low water contents (1–2%) and then fed to prilling or granulation equipment. The resultant solid products that range in size between 2 and 4 mm are highly acceptable to farmers as high-nitrogen fertilizers and to "bulk blenders" as nitrogen sources in the formulation of dry-blend mixed fertilizers, as will be described later. The nitrogen content of solid ammonium nitrate is 34 percent, and that of urea is 46 percent.

The concentration and the solidification of ammonium nitrate and urea solutions to form solid fertilizers require considerable expenditure of energy and processing expense; so it is attractive to use the solutions in the formulation of liquid fertilizers, without processing them into solid form. However, neither ammonium nitrate nor urea alone is sufficiently soluble at ambient temperatures to be attractive for direct use as liquid fertilizer. With either compound alone, a solution with a salting-out temperature of 0°C would contain only about 18 percent nitrogen. Fortunately, however, the joint solubility of the two compounds in water is much more favorable than this; so the liquid nitrogen solutions marketed for fertilizer use almost invariably are joint solutions of ammonium nitrate and urea. Typical commercial solutions contain 28–32 percent nitrogen, with compositions and characteristics as shown in Table 24.1.

TABLE 24.1 Physical and Chemical Characteristics of Urea–Ammonium Nitrate Nonpressure Nitrogen Solutions

Grade, % N	*28*	*30*	*32*
Composition by weight			
Ammonium nitrate, %	40.1	42.2	43.3
Urea, %	30.0	32.7	35.4
Water, %	29.9	25.1	20.3
Specific gravity, 15.6°C	1.283	1.303	1.32
Salt-out temperature, °C	−18	−10	−2

Source: Fertilizer Manual, United Nations Industrial Development Organization and International Fertilizer Development Center, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1998.

The high-volume use of these solutions is a result of their economy of production and the safety and convenience of their handling and application. The use of nonpressure equipment and surface application (in contrast to knifing) is normal. Nitrogen solutions of other compositions also are prepared commercially, but are used primarily as intermediates in the preparation of solid fertilizers. Such solutions usually consist of various combinations of water, ammonia, ammonium nitrate, and/or urea. Because of the content of free ammonia, most of these solutions require pressurized handling.

Ammonium Sulfate. Although an excellent nitrogen–sulfur fertilizer with good physical properties, ammonium sulfate is now outranked economically by ammonium nitrate and urea. The chief reasons for the unpopularity of ammonium sulfate are its relatively low nitrogen content (21%) and its relatively low solubility in liquid fertilizers. At most U.S. locations, it is uneconomical to produce ammonium sulfate from synthetic ammonia and virgin sulfuric acid. As a result, most of the ammonium sulfate available for fertilizer use is a byproduct of other processes. A larger source now is byproduct ammonium sulfate solution from the production of caprolactum and acrylonitrile, which are synthetic fiber intermediates. This byproduct solution normally is fed to steam-heated evaporator– crystallizers to yield the solid ammonium sulfate. Additional production of byproduct ammonium sulfate is obtained from "spent" sulfuric acid, by reaction with synthetic ammonia. In this case, the production of ammonium sulfate is a method of disposing of acid that already has been partially spent in other processes. Some ammonium sulfate is produced by scrubbing ammonia-containing coke-oven effluent gas with sulfuric acid. This production is discussed later.

Byproduct ammonium sulfate produced by any of the above-mentioned methods is usually in the form of crystals that are 90 percent or less than 1 mm in size, and thus are much smaller than the size preferred for present-day finished fertilizers. This small size is not undesirable if the material is to be used as feed to a fertilizer granulation plant, but it is undesirable for bulk blending (dry mixing) or direct field application. It is possible to produce suitably large crystals, but only at the expense of greatly reducing crystallizer capacity. Both compaction and granulation processes have been employed with some success on a limited scale to convert the small-crystal material to a larger-size product.[7]

Ammonia in Multinutrient Fertilizers. All the ammonia-based fertilizers discussed thus far contain only one of the three major plant nutrients, namely nitrogen. Referring again to Fig. 24.8, one may see that ammonia is the source of fertilizer nitrogen also, either directly or via nitrogen solids or solutions, in multinutrient fertilizers. These are fertilizers that contain two or three of the major plant nutrients—nitrogen, phosphorus, and potassium. Ammonium phosphates, both mono- and di-, are phosphate fertilizer products that also carry nitrogen. (These are discussed later as major suppliers of phosphate.) As suppliers of nitrogen, the ammonium phosphates and other multinutrient solid and fluid fertilizers collectively furnish about 20 percent of global fertilizer nitrogen. (Production of these fertilizers is also described later.) The source of their nitrogen is, in all cases, ammonia and/or ammonia-based solids or solutions. Nitric phosphates are suppliers of nitrogen through their content of nitric acid and ammonia. They are not presently produced or used to any significant extent in the United States but are produced in Europe and some other locations. (Their production too is discussed briefly later.)

Miscellaneous Low-Volume Nitrogen Fertilizers

Mineral Nitrogen. The only nitrogen-containing mineral that is mined commercially for fertilizer use is saltpeter (sodium nitrate, $NaNO_3$). An impure form of sodium nitrate known as "coliche" is found in large, rocklike deposits in a relatively dry desert area of Chile, and these deposits have long been mined to provide natural sodium nitrate for the fertilizer market. The ore is blasted from open mines, sized, and leached with water in vats. Evaporation of the resultant solution yields the commercial crystalline fertilizer product known widely as "Chilean nitrate," "nitrate of soda," or among some farmers simply "sody." Its nitrogen content is 16 percent. This product first was imported and marketed in the United States in 1830, so it is one of the oldest fertilizers on the American market. Sodium nitrate now, however, is a relatively insignificant component of the world's nitrogen fertilizer market, having been supplanted by synthetic nitrogen compounds.

Byproduct Ammonia. Coke, an essential ingredient in the smelting of iron ore and in some other metallurgical processes, is produced by the heating of coal in an essentially oxygen-free atmosphere. This heating volatilizes numerous hydrocarbon components of the coal and results in decomposition of some of these compounds. The nitrogen content of coals normally is about 1 percent, and approximately half of this is volatilized as ammonia gas in the coking process. Recovery of this ammonia has long been effected by passing the coke-oven effluent gas through scrubber–crystallizers containing sulfuric acid. The resultant crystalline by-product, ammonium sulfate, is an excellent fertilizer source of both nitrogen and the secondary plant nutrient sulfur. The nominal nitrogen content of the product is 20 percent, and the sulfur content is 24 percent. Prior to the introduction of synthetic ammonia production processes (1913–25), coke-oven ammonia was a major source of fertilizer nitrogen; however, its production was very small when compared with today's demand for fertilizer nitrogen. Today, ammonia production from coke ovens, although still carried out, is insignificant in volume compared with that from ammonia synthesis processes.

PHOSPHATE FERTILIZERS

Phosphorus intake is essential to the metabolism of both plants and animals. In the case of plants, the entire uptake is from the soil solution via root absorption. Absorption occurs only when the phosphorus is present in the soil solution in the form of $H_2PO_4^-$, HPO_4^{2-}, or PO_4^{3-} ions.[8] Furthermore, a large proportion of the soil phosphorus is present in chemical forms that are not "available" (assimilable), or are only very slowly available, to crops. Cropping of native soils without phosphate fertilization soon depletes the supply of phosphorus and renders the soil barren. In times before fertilizers became readily available, it was not uncommon to "wear out" a farm by repeated cropping. Crop rotation, which was mentioned earlier as a useful method of converting atmospheric nitrogen to available soil nitrogen, is ineffective as a means of phosphorus fertilization. In fact, the nitrogen-converting legumes generally are voracious consumers of phosphate.

Modern, high-yield agriculture is dependent on regular fertilization with phosphorus compounds that are either immediately soluble in the soil solution or become soluble at a rate sufficient to supply the crop. A factor to contend with in phosphate fertilization is soil "fixation" of phosphorus; that is, the characteristic of many soils to convert at least a portion of applied phosphate to chemical forms that are unavailable to plants. The fixation tendency varies with soil type, and generally is highest in soils of high clay content. The overall result of fixation is that considerably more phosphate must be applied as fertilizer than is removed with crops.

Natural Organic Phosphate Fertilizers

In animal metabolism, phosphorus concentrates in the bones and, in the case of Crustacea, in the shells. Manures and human wastes, previously mentioned as effective but low-volume sources of fertilizer nitrogen, are much less efficient sources of phosphorus than of nitrogen. The phosphorus content of such products is normally only 1.3–3.0 percent, which is only 25–50 percent as great as their nitrogen content. Bird droppings, including chicken manure and guano deposits, are somewhat higher in phosphorus content (7% P), but are available in only relatively insignificant amounts overall.

Raw animal bones normally contain 8–10 percent phosphorus (20–25% P_2O_5); thus they are a relatively rich source. The commercial grinding of bones for fertilizer use began in Europe in the early nineteenth century.[9] The practice persists today in the production of bone meal, but only in very low volume, chiefly to furnish slowly available nutrients for greenhouse and house plants. In about 1830, it was found that pretreatment of bone meal with dilute sulfuric acid greatly enhanced the "availability" of the phosphorus to plants, and the practice became common. The initiation of this practice now is regarded to have had considerable historic significance as the apparent beginning of the chemical fertilizer industry. The supply of bones being very limited, it soon was found (about 1840) that a similar acid treatment of mined phosphate ore rendered the phosphorus "available" as a fertilizer. Thus was born the still important "superphosphate" industry, and the supplanting of the very limited organic phosphorus sources by widely available mineral sources was begun. Today, organic sources of fertilizer phosphorus account for less than 1 percent of total worldwide consumption.

Fertilizers from Mineral Phosphates

Essentially all fertilizer phosphorus now is derived from mined ores. (The occurrence, mineral characteristics, mining, and beneficiation of major phosphate ores were described in some detail in Chapter 23.) Worldwide, about 85 percent of the mined phosphate eventually finds its way into fertilizer.[3] As mentioned earlier, the most conservative estimates indicate a sufficiency for hundreds of years at expected consumption levels. Supply problems of the immediate future will relate chiefly to exhaustion of the better ores, with the result that ores of lower grades and higher impurity contents will have to be processed.

Major routes of mineral phosphate (phosphate rock) into finished fertilizers are outlined in Fig. 24.9 and are discussed below. It is obvious from the figure that although phosphate rock is used directly in several major fertilizer production processes (single superphosphate, nitric phosphates), most important processes require that the rock phosphate first be converted to phosphoric acid (H_3PO_4). Phosphoric acid production, then, is a very significant component of the phosphate fertilizer industry. The processes used for the production of fertilizer-grade phosphoric acid are known collectively as "wet" processes, and involve, initially, dissolution of the rock in sulfuric acid. (The highly specialized technology of wet-process acid production was discussed in Chapter 23.)

Single Superphosphate (SSP). In 1842, Lawes in England followed up on the pioneering work of Liebig and received a patent on the use of sulfuric acid in reaction with raw phosphate material to produce "superphosphate" fertilizer. The industry grew slowly, and in 1862 about 150,000 tons of what later would be referred to as "ordinary" (OSP) or "normal" (NSP) or "single" (SSP) superphosphate (16–18% P_2O_5) was produced in England. By 1870, there were 70 single superphosphate plants in the United Kingdom and 7 in the Charleston, South Carolina, area of the United States.[10] In 1888, commercial shipment of phosphate rock from Florida was initiated, and a major mining industry followed in that state, which continues today. As late as 1955, SSP supplied over 60 percent of the world's phosphate fertilization and was the major phosphate fertilizer in the United States. Rock from Florida or South Carolina was shipped throughout the country to local SSP production facilities. These facilities usually included the capability of blending the SSP with nitrogen and potash materials and bagging the resultant mixtures.

In recent years the production of SSP, to a large extent, has given way to the production of the higher-analysis "triple superphosphate" and ammonium phosphates. SSP retains greater importance in some countries. For example, SSP remains popular in Australia, at least in part because its sulfur content is particularly needed there.

SSP is the simplest, as well as the oldest, of manufactured phosphate fertilizers. Its manufacture consists of reacting pulverized phosphate rock with sulfuric acid in comparatively simple equipment, followed by sufficient aging (curing) to complete the reaction and improve the physical condition. The acid– rock reaction converts the water-insoluble apatite structure of the rock to soluble monocalcium phosphate. When produced from high-grade rock of 30–32 percent P_2O_5 content, SSP contains about 20 percent available P_2O_5; the product made in earlier years from lower-grade rocks contained only 14–18 percent P_2O_5. SSP can be used for direct application, for bulk blending, or in the production of granular NPK fertilizers. If the product is to be used for direct application or bulk blending, it usually is granulated to improve handling properties.

The main equipment for manufacturing SSP consists of a mixer to bring together sulfuric acid and phosphate rock, followed by a den, and if granulation is used, some suitable type of equipment for granulation with steam or water. Early plants used batch-type mixers for acid–rock mixing, but these mixers mostly have been replaced by continuous types. Several types of continuous mixers have been employed; of these, the lowest-cost, simplest, and apparently most satisfactory one is the TVA cone mixer, which has no moving parts. Mixing is

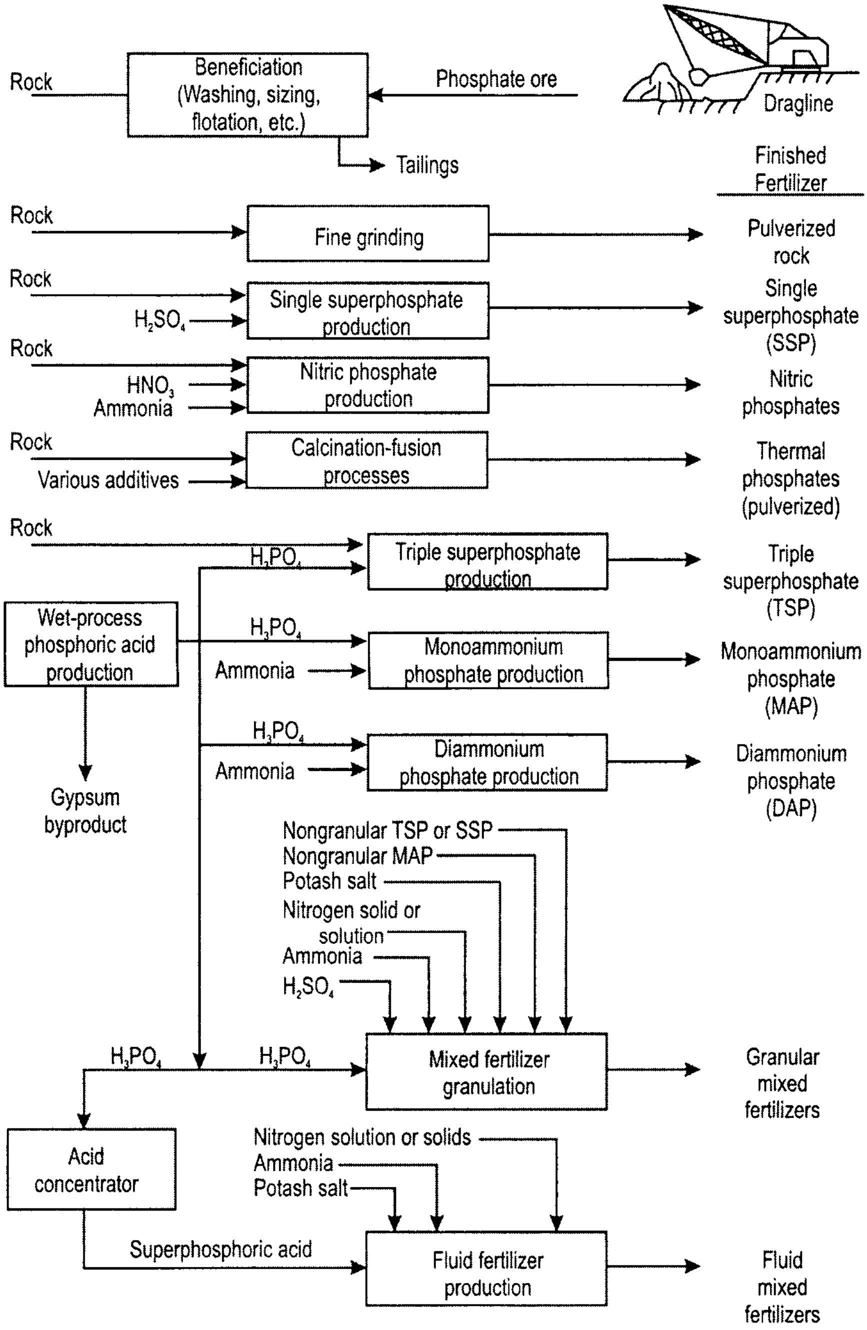


Fig. 24.9. Major routes of mineral phosphate into finished fertilizers. *(Courtesy TVA.)*

accomplished by the swirling action of the acid. Short, single-shaft or double-shaft pug mills also are used for continuous mixing. The mixers discharge into a den, the purpose of which is to allow time for the acid–rock reaction to progress and the physical condition to reach a dry, friable state. The dens can be of either the batch or the continuous type. A slat-conveyor continuous den, commonly referred to as a Broadfield den, is used in many continuous systems.[11] A diagram of a typical SSP plant employing a cone mixer and a continuous den (slat-conveyor) is shown in Fig. 24.10. The reaction of phosphate rock with sulfuric acid to produce SSP can be approximated in chemical stoichiometric terms. However, in general practice the proportioning

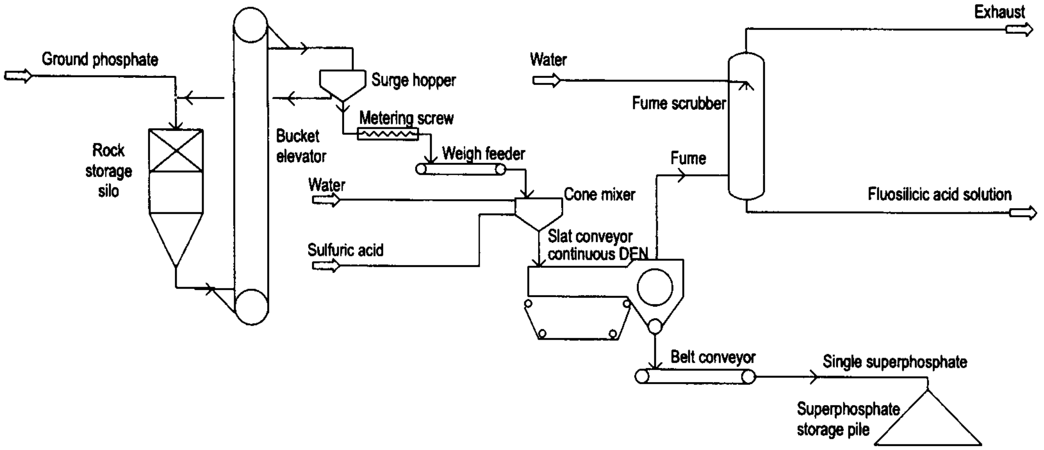


Fig. 24.10. Continuous process for manufacture of single superphosphate. *(Source: Fertilizer Manual.)*

usually is based on a simpler relationship of about 0.6 kg of sulfuric acid (100% H_2SO_4 basis) per kilogram of phosphate rock (30–32% P_2O_5). The phosphate rock usually is pulverized to about 90 percent smaller than 0.15 mm and 70 percent smaller than 0.075 mm.

Gases that are released while the superphosphate is solidifying (setting) cause the mass in the den to become porous and friable so that it can be "cut" (disintegrated) and handled readily. SSP made from typical rock will "set" in 40–50 min in a continuous den, whereas the set time in a batch den is 1.5–2 hr. The superphosphate usually is held in storage piles (cured) for 4–6 weeks in order to obtain better handling properties and to allow the chemical reactions to continue. The usual grade of SSP made from Florida rock is 20 percent available P_2O_5. A typical analysis is shown below:

Analysis, % by Weight

P_2O_5								
Total	Available	H_2O Soluble	CaO	Free Acid	SO_4	F	R_2O_3	MgO
20.2	19.8	18.0	28.1	3.7	29.7	1.6	1.6	0.15

Because of the low phosphate analysis of SSP (20% P_2O_5), economics favor shipping the rock (32% P_2O_5) to local plants and producing the superphosphate there. A majority of the producers use the locally produced SSP in formulations for granular NPK fertilizers made in an ammoniation–granulation process. The maximum amount of SSP possible is used in the NPK formulations because usually it is the lowest-cost form of P_2O_5; however, because of the relatively low P_2O_5 content of SSP, not much can be used in high-analysis NPK formulations. SSP will readily absorb about 6 kg of ammonia per 20 kg of P_2O_5 during the ammoniation–granulation process. Production of granular SSP can be carried out by starting with either cured or ex-den SSP. The SSP is fed to a rotary drum or pan granulator along with a water spray and/or steam. The granulator is followed by a dryer and screening (sizing) system. Fines and crushed oversize material are fed back to the granulator.

Triple Superphosphate. Triple superphosphate (TSP) is made by acidulation of phosphate rock with phosphoric acid, using equipment and processes similar to those for SSP. As in SSP production, the acid–rock reaction converts the water-insoluble apatite structure of the rock to water-soluble monocalcium phosphate. TSP, with its relatively high P_2O_5 content of 45–46 percent, did not appear on the scene in any appreciable quantity until wet-process phosphoric acid (see

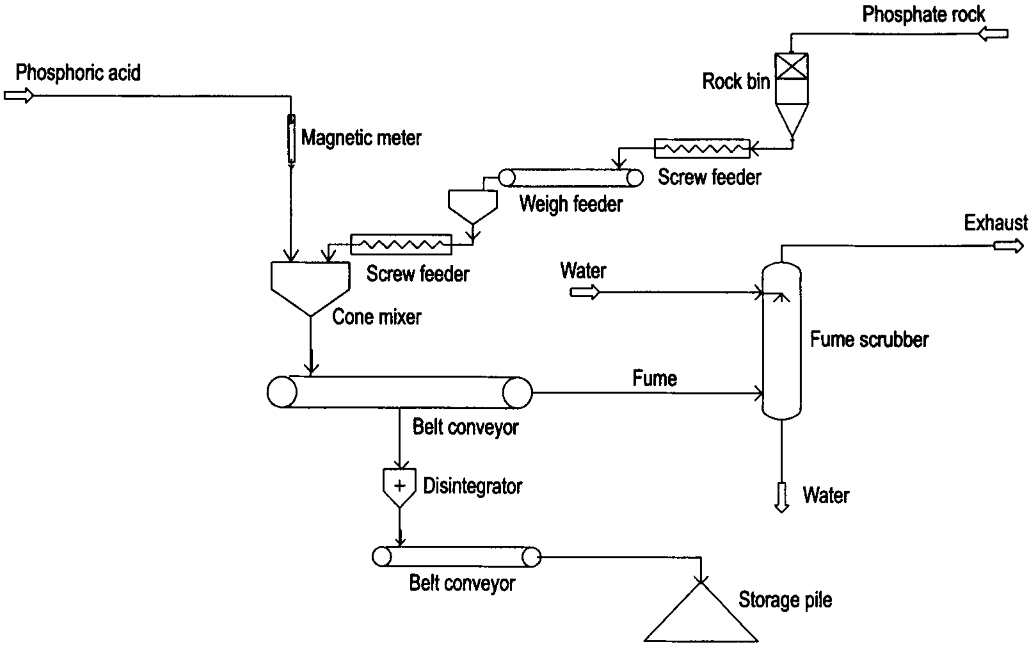


Fig. 24.11. Continuous system for manufacture of nongranular triple superphosphate. *(Source: Fertilizer Manual.)*

Chapter 23) was produced commercially. TVA carried out demonstration-scale production of triple superphosphate in the late 1930s by using electric-furnace phosphoric acid. Extensive agronomic testing and market development, through the use of large tonnages of this TSP by farmers and fertilizer manufacturers in TVA demonstration programs, led to the rapid acceptance of TSP. Producers of phosphate rock in the United States and other countries moved into production of wet-process acid and TSP. Logistics favored production of the higher-analysis TSP (46% P_2O_5 vs. 32% P_2O_5 in phosphate rock) near the source of the phosphate rock, and shipment of the TSP to distribution facilities or blending plants near the markets. Today, most producers of TSP are located adjacent to phosphate mining operations in Florida, Morocco, and Tunisia. Since its introduc-tion, TSP has steadily displaced SSP in the marketplace.

The cone mixer has been used almost universally in the production of nongranular TSP. Because the "set time" for TSP is only 14–20 min, as compared with 40–50 min for SSP, a simple, cupped conveyor belt usually is used to hold the acidulate until the TSP solidifies; this is instead of the slat-type den used for SSP. With a belt about 1.5 m wide and 30 m long, the production rate usually is 40–50 tons/hr. A flow diagram for TSP production by the cone mixer- "wet-belt" system is shown in Fig. 24.11.

Proportioning for TSP typically is 2.4–2.5 kg of P_2O_5 from acid for each kg of P_2O_5 from rock. Nongranular TSP usually is cured 4–6 weeks prior to shipment or used at the site. Typical chemical analysis of TSP made with Florida rock is shown below:

Analysis, % by Weight

P_2O_5								
Total	Available	H_2O Soluble	Free Acid	CaO	R_2O_3	MgO	F	H_2O
46.9	46.3	42.0	3.4	19.3	3.1	0.5	2.7	4.5

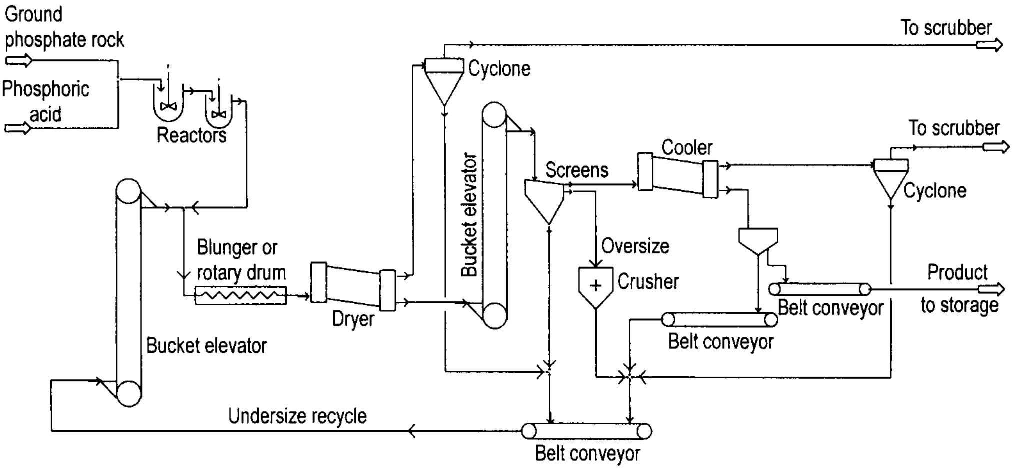


Fig. 24.12. Slurry process for the manufacture of granular triple superphosphate. *(Source: Fertilizer Manual.)*

The use of TSP in granular NPK fertilizer formulations, together with or in place of SSP, has allowed the production of higher-analysis grades of granular NPK fertilizers, such as 13–13–13 instead of 10–10–10. The TSP can readily be ammoniated using 3.5 kg of ammonia per 20 kg of P_2O_5 during the granulation process.

TSP is produced in large quantities in granular form for use in direct application and for use in bulk blends. In some processes cured or ex-den TSP, like SSP, is granulated in a rotary drum or pan granulator using steam and water to promote granulation.[3] A slurry-type granulation process, as outlined in Fig. 24.12, is now the process of choice of major producers of TSP. Pulverized phosphate rock is treated with wet-process phosphoric acid in a two-stage reaction system, and the slurry is sprayed into a pug mill or rotary drum where it is layered on recycled undersize and crushed oversize at a ratio of 1 kg per 5–12 kg of recycle. Product granules (45% P_2O_5) are quite spherical and dense. The lower grade of the granular product, as compared with that of cured nongranular TSP, results from the need to decrease the acidulation ratio from the usual 2.45 kg of acid P_2O_5 per kilogram of rock P_2O_5 to about 2.25 in order to control the free-acid content and to minimize stickiness. For production rates higher than about 25 tons/hr, a rotary drum usually is used instead of a pug mill.

Nitric Phosphate. Fertilizers that are referred to as nitric phosphate or nitrophosphate are produced by acidulation of phosphate rock with nitric acid or with mixtures of nitric and sulfuric or phosphoric acids. The primary advantage of nitric phosphate processes is that no sulfur or less sulfur is required as compared with superphosphates or ammonium phosphates; this is particularly important during a shortage of sulfur, or in locations where sulfur must be shipped long distances. A variety of processes and equipment have been used in Europe since the late 1930s.[3,12] Also there are a number of plants in Central and South America and in Asia. The production of nitric phosphates is complex. Simple substitution of nitric acid in a superphosphate-type acid–rock reaction is not feasible because (1) decomposition of the nitric acid would occur and cause noxious fumes and loss of nitrogen and (2) the product would be extremely hygroscopic and unstable.

One process modification that overcomes these difficulties uses only nitric acid for acidulation; the extraction slurry is cooled to crystallize calcium nitrate, which then is removed by centrifugation. This process is referred to as the Odda process. The calcium nitrate byproduct is either sold as a fertilizer or converted to co-product ammonium nitrate. The extraction slurry, with its lowered calcium content, then is ammoniated and granulated.

Various process modifications utilize a rotary drum, pug mill, or spray drum (Spherodizer) for granulation of the slurry. NPK nitric phosphate grades also have been produced by a prilling process in a few European plants. In earlier years, a main disadvantage of nitric phosphate processes was the low water solubility of phosphate in the products, as the main phosphatic constituent was dicalcium phosphate. The use of supplemental phosphoric acid, or "deep cooling" by refrigeration to remove a higher proportion of calcium nitrate in the Odda-type processes, now allows water solubility of 60 percent or higher. The remaining 40 percent of the phosphate, although water-insoluble, is almost completely citrate-soluble, and this is "available" as plant nutrient. Popular grades of nitric phosphates include 14–14–14, 22–11–11, 20–20–0, and 16–13–0.

Diammonium Phosphate (DAP). Ammonium phosphates did not come on the fertilizer scene in significant quantities until the early 1960s; however, they have rapidly become the leading form of phosphate fertilizer in the world. Almost all new phosphate fertilizer complexes built in recent years, and those planned, are for the production of ammonium phosphate as the major product. In 1960, world production of ammonium phosphates was equivalent to only 0.5 million mt of P_2O_5. By 1990 it was up to 15.4 million mt and by 1999 it has reached 16.7 million mt. Ammonium phosphates now provide two-thirds of total world phosphate fertilization.

Prior to the late 1940s, diammonium phosphate $(NH_4)_2HPO_4$ was considered to be too unstable for use as a fertilizer. However, at about that time, exploratory work by TVA indicated otherwise. The first demonstration-scale diammonium phosphate made by TVA for fertilizer use was a monocrystal product made by ammoniation of pure electric-furnace acid in a vacuum crystallizer.[13] Demonstration programs showed this material to be stable and to be an excellent high-analysis fertilizer. Small amounts of similar product were produced by others using electric-furnace acid and by-product ammonia. However, general acceptance of diammonium phosphate by the fertilizer industry was not possible until procedures could be developed to produce it from wet-process phosphoric acid instead of the relatively expensive electric-furnace acid. This occurred in 1960–61 with the development and patenting of the "TVA process" for production of granular 18–46–0 grade DAP from wet-process acid.[14,15] This relatively simple process was rapidly adopted by the industry, and remains the basic process for production of this major phosphate fertilizer. Many granular DAP plants have production capacities of about 50 tons/hr, with some going as high as 70–100 tons/hr.

The flow diagram of a typical granular DAP production unit of the TVA type that has become standard in the industries is shown in Fig. 24.13. Wet-process phosphoric acid of about 40 percent P_2O_5 content (often a mixture of 54% P_2O_5 acid and acid from the scrubbing circuit of 28–30% P_2O_5 content) is fed to a preneutralizer vessel. Anhydrous ammonia is sparged into this preneutralizer through open-end pipes that project through the walls. A key feature of the process is that this neutralization of the acid is carried to a closely controlled $NH_3{:}H_3PO_4$ mole ratio of about 1.4. Ammoniation to this degree provides maximum solubility of ammonium phosphate, as is shown by the solubility curve of Fig. 24.14. The heat of the ammoniation reaction evaporates considerable water, with the result that the water content of the slurry is reduced to only 16–20 percent. The slurry still is fluid and pumpable because of the high solubility at a 1.4 mole ratio.

The preneutralizer slurry is pumped at a controlled rate to a rotary-drum, ammoniator–granulator; there it is distributed onto a rolling bed of recycled solids. The most commonly used metering system for the preneutralized slurry is a variable-speed centrifugal pump with automatic control from a magnetic flowmeter. Some plants have had success with a magnetic flowmeter and automatic control valve of a special ball type.

Ammonia is sparged beneath the bed in the rotary drum to ammoniate the slurry further to near the theoretical DAP ratio of 2.0; the

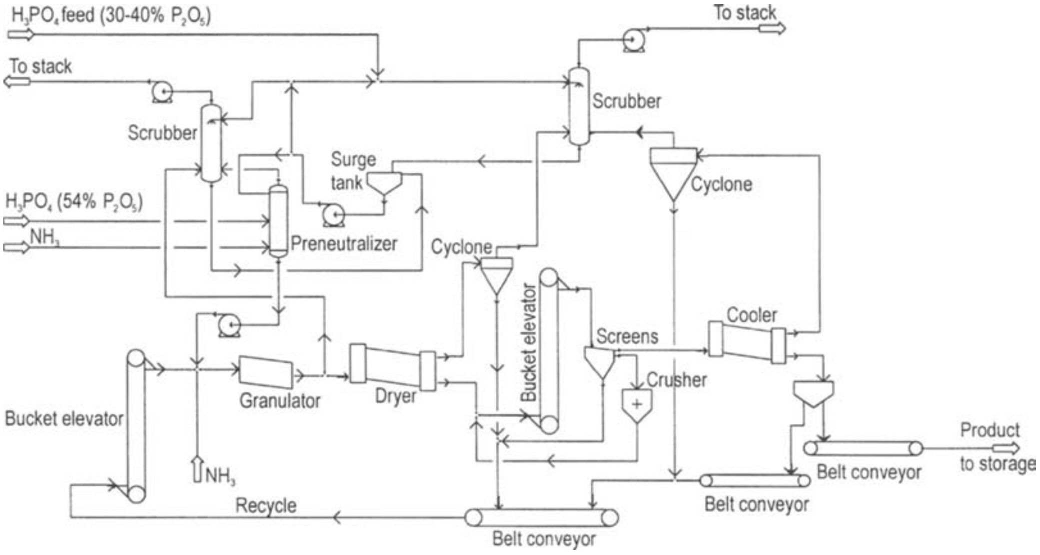


Fig. 24.13. TVA process for production of granular diammonium phosphate. *(Source: Fertilizer Manual.)*

usual finishing $NH_3 : H_3PO_4$ mole ratio is 1.85–1.94. Metallic phosphate impurities such as iron, aluminum, and calcium phosphates account for most of the deviation from theoretical. This ammoniation in the granulator drastically decreases ammonium phosphate solubility (Fig. 24.14), and thus promotes solidification and granulation. Ammonia absorption is not 100 percent complete in either the preneutralizer or the granulator. However, the unabsorbed ammonia is recovered in a scrubbing circuit containing phosphoric acid of about 30 percent P_2O_5 content. Solid recycle to the granulator drum consists of undersize from screening of dried product plus some crushed, dry product and oversize. These combined materials are recycled at a rate of 5–7 kg per kilogram of product, and variation of this recycle rate is the primary method of controlling granulation efficiency. Product discharged from the granulator is dried with moderate heat to a 180–190°F product temperature. Higher drying temperatures must be avoided because of a relatively low melting point for DAP. Most plants screen hot and cool only the product fraction because the material is not too sticky for recycle without cooling. Rotary coolers or fluidized-bed-type coolers are used. The product, with a moisture content of 1.5–2 percent, does not require a conditioner. It has excellent storage and handling properties in bags or in bulk. It has been shown that the iron and aluminum phosphate impurities in the product are present in a gel-like structure that favorably hardens the granules and increases their resistance to moisture.[16] The critical relative humidity of diammonium phosphate made from wet-process acid

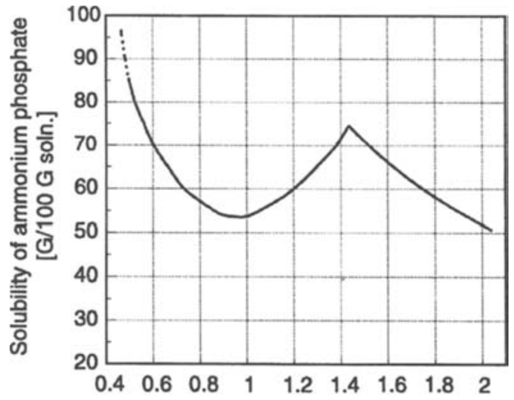


Fig. 24.14. Effect of $NH_3 : H_3PO_4$ mole ratio on solubility of ammonium phosphate at 75°C. *(Source: Fertilizer Manual.)*

is about 70 percent; thus it is relatively nonhygroscopic.

Construction materials other than mild steel are required only for the acid lines, the preneutralizer, the slurry handling system, and the scrubbing circuits. Type 316L stainless steel or rubber- and brick-lined mild steel is used for the preneutralizer. Type 316L stainless is used also for the slurry pumps and piping. Fiberglass-reinforced polyester plastic and high-density polyvinyl chloride are sometimes used for wet-process acid pipes and for scrubbers. Scrubbers also may be constructed of rubber-lined mild steel.

Monoammonium Phosphate (MAP). "Diammonium Phosphate," "DAP," and the grade designation "18–46–0" have become extremely familiar terms in the world fertilizer industry. However, substantial interest has developed also in fertilizer use of monoammonium phosphate, $NH_4H_2PO_4$. Agronomically, MAP is favored where soils are mainly alkaline, for example in Canada, Egypt, and Pakistan. From an economic standpoint, the relatively high P_2O_5 contents of typical MAP grades (11–52–0 to 10–54–0) make them attractive where the primary interest is in producing and shipping phosphate; the MAPs provide a higher P_2O_5 payload than does DAP.

TVA developed two comparatively minor modifications of the granular DAP process to allow production of granular MAP.[17] In one method, the acid is ammoniated to an NH_3:H_3PO_4, mole ratio of only about 0.6 in the preneutralizer and then to about 1.0 in the granulator drum. The 0.6 ratio is, like the 1.4 used in DAP production, a high-solubility point in the ammonium phosphate system (Fig. 24.14); the subsequent ammoniation to 1.0 in the granulator decreases solubility and thus promotes granulation. In the other procedure, which has been preferred by the industry, acid in the preneutralizer is ammoniated to the high-solubility $NH_3 : H_3PO_4$ ratio of about 1.4, as in DAP production; then additional wet-process acid is distributed onto the bed in the granulator to adjust back to the low-solubility MAP mole ratio of about 1.0. With either modification, the remainder of the process is the same as for DAP, except that, because of the higher temperature stability of MAP, a higher drying temperature can be used to increase the production rate for MAP.

Starting in about 1968, simple processes were developed for the production of nongranular (sometimes called powdered) MAP. Chief developers were Fisons and Scottish Agricultural Industries (SAI) in the United Kingdom, Swift in the United States, and Nissan in Japan. These processes involve variations in the simple reaction of wet-process acid with ammonia followed by spray-type drying with air. On the basis of this work, a number of comparatively low-cost units for production of nongranular MAP have been built commercially, including plants in the United Kingdom, the Netherlands, Japan, Australia, Spain, the United States, Brazil, and Iran. This intermediate usually is shipped to other plants, where it then is used in the production of NPK solid or fluid fertilizers. Thus far, however, the nongranular MAP has not attained the popularity that was predicted for it in the mid-1970s.

Miscellaneous Low-Volume Phosphate Fertilizers

Phosphate Rock for Direct Application. Application of finely pulverized raw phosphate rock directly to the soil has been utilized almost from the beginning of fertilization practice. Although such direct use eliminates the need for most processing, there are major drawbacks. The ores are of low phosphorus content in comparison with most manufactured fertilizers, which increases shipping cost. Also, the very fine grinds that are required to encourage solubility are difficult to handle and to apply. The major drawback, however, is agronomic. The agronomic effectiveness of raw rock depends upon the origin and the chemical and mineralogical nature of the particular rock, the pH and other characteristics of the soil, and the crop produced. Researchers at TVA and IFDC have characterized phosphate rocks from a large number of sources as to their reactivity.[3,18] In general, phosphate rock of sedimentary origin is more reactive than igneous source. Phosphate rock from North Carolina (U.S.), Sechura (Peru), and Gafsa (Tunisia) are at the top, and are about equal in reactivity and suitability for direct application. Other phosphate rocks that are reasonably reactive and are marketed for this purpose include some types from Morocco, Israel, Algeria, and a few other locations. In 2002, less than 1.0 million mt of phosphate rock was used for direct application.

Defluorinated Phosphate Rock. There is substantial production of defluorinated phosphate rock for fertilizer use in Japan (about 100,000 mt/year). Ground, high-grade rock is mixed with small proportions of sodium carbonate or sulfate and wet-process acid. The mixture is calcined at a temperature of 1350°C in an oil-fired rotary kiln 45.0 m in length and 2.7 m in diameter. The product contains 38–42 percent P_2O_5 of which more than 90 percent is soluble in neutral ammonium nitrate solution and is an effective fertilizer on acid soils. During the production of defluorinated phosphate rock, substantially all fluorine is driven off. Sodium bifluoride ($NaHF_2$) is recovered as a byproduct. A similar product is made in the United States, but it is mainly used for animal feed supplement.

Calcined Aluminum Phosphate. Ores consisting mainly of hydrated aluminum phosphate minerals are useful for direct application after thermal treatment (calcination) at a controlled temperature. Calcination removes the combined water and destroys the crystallinity of the phosphate minerals, thereby improving the reactivity of the phosphate.[3]

At present, only two aluminum phosphate ores are known to be used for direct application after thermal treatment. One such ore is found near Thies, in Senegal. The "as-mined" ore contains about 29 percent P_2O_5 on a dry basis; after calcination it contains over 34 percent P_2O_5. The calcined product is ground to about 95 percent smaller than 0.15 mm and marketed for direct application under the trade name "Phosphal." About 75 percent of the P_2O_5 is soluble in alkaline ammonium citrate, and the product is effective as superphosphate in calcareous, neutral, and acid soils. The product is used in France, Senegal, and some nearby countries.

A similar ore occurs in the upper stratum ("C-grade") of the phosphate deposit on Christmas Island. The C-grade ore contains about 25 percent P_2O_5 dry basis. Calcination is carried out in a fluidized bed, operated in the range of 400–600°C. The maximum solubility in alkaline ammonium citrate solution is about 70 percent.

Partially Acidulated Phosphate Rock. Not all phosphate rock is suitable for direct application and may require the addition of a more soluble form of phosphate. An alternative is partial acidulation to render its P_2O_5 more available. The partially acidulated phosphate rock (PAPR) process depends on treating ground phosphate rock with only a portion of the stoichiometric value of acid, for example 50 percent PAPR.[19] The amount of water-soluble phosphate in PAPR varies according to the degree of acidulation. The crop response to the product is often quite similar to fully acidulated products such as SSP or TSP.

Sulfuric and phosphoric acids are the most common acids used for partial acidulation. Possibilities exist for using three processes: a conventional run-of-pile process followed by granulation, IFDC-developed singlestep acidulation and granulation, and a slurry granulation triple superphosphate-type process.

Enriched Superphosphate. This product, which is also referred to as "double" superphosphate, is essentially a mixture of SSP and TSP, usually made by acidulation of phosphate rock with a mixture of sulfuric and phosphoric acids. The desired concentration of mixed acid can be obtained by mixing concentrated sulfuric acid (93 or 98% H_2SO_4) with dilute phosphoric acid (30%) thus avoiding the need for concentrating the latter. Production processes and equipment are about the same as for SSP.[20]

Theoretically, any grade between SSP and TSP can be produced, but the usual range is 25–35 percent P_2O_5. The product is useful in sulfur-deficient areas where SSP would supply more sulfur than necessary. Only a small amount of enriched superphosphate is produced and used in Australia.

Basic Slag. This is also known as Thomas slag and is a byproduct of the steel industry. Iron made from high-phosphorus ore is converted to steel in a Thomas converter by oxidation in contact with a basic (high CaO) slag. Sometimes phosphate rock is deliberately added to the blast furnace charge to increase the phosphorus content of the iron thereby increasing the P_2O_5 content of the slag. A typical range of composition of high-grade basic slag is:

Composition, % by Weight

P_2O_5	SiO_2	CaO	MnO	AL_2O_3	MgO	F
15–20	4–6	42–50	3–6	0.5–2.5	2–4	9–13

While the present market for basic slag is quite small, it is primarily produced and used in Western Europe where high-phosphorus iron ore occurs.

Fused Calcium Magnesium Phosphate. In a process developed by TVA, a mixture of phosphate rock and olivine or serpentine (magnesium silicate) is fused in an electric furnace.[21] The molten product is quenched with water and used in a finely divided state as a fertilizer. The product, a calcium magnesium phosphate (CMP) glass, contains about 20 percent P_2O_5 and 15 percent MgO. Over 90 percent of the product is soluble in citric acid.

The theoretical compositions of some magnesium-containing minerals that can be used to produce CMP are:

Olivine	$(Mg,Fe)_2SiO_4$
Serpentine	$Mg_3H_4Si_2O_9$
Garnierite	$(Mg,Ni)H_2SiO_4$
Magnesite	$MgCO_3$

Although small compared with soluble phosphates, CMP is used in Japan, China, Korea, Taiwan, and South Africa. The reason for the decline in production and use is the relatively high (850 kWhr/ton of product) energy requirements.

The CMP is found to be more effective than superphosphate when used on acid soils. The product has a liming value equivalent to 0.5–0.7 ton of calcium carbonate per ton of material. The magnesium oxide and soil-soluble silica is available to growing plants.

Rhenania Phosphate. Rhenania phosphate is another thermally produced phosphate fertilizer. It is made by calcining a mixture of phosphate rock, sodium carbonate, and silica in a rotary kiln at 1250°C.[3] Enough sodium carbonate is used to form the compound $CaNaPO_4$ and enough silica to form Ca_2SiO_4 with excess calcium. Typical charge proportions are one part sodium carbonate to three parts of phosphate rock and enough silica to raise the SiO_2 content of the product to about 10 percent. The overall reaction in producing Rhenania phosphate is assumed to be:

$$Ca_{10}F_2(PO_4)_6 + 4Na_2CO_3 + 2SiO_2$$
$$\rightarrow 6CaNaPO_4 + 2Ca_2SiO_4 + 2NaF + 4CO_2$$

Any grade of phosphate rock can be used, but since the grade of the product is determined by the grade of the rock, a high grade is preferred.

A typical product contains 28–30 percent P_2O_5, nearly all soluble in neutral or alkaline ammonium citrate solution. The product is applied in a powdered form or granulated with potash salts. Some grades are produced containing magnesium or boron, which are added during granulation as kieserite or borax, respectively.

POTASSIUM SALTS

The element potassium has been recognized to be beneficial to plant growth since J.R.

TABLE 24.2 Common K Minerals

Mineral	*Formula*	*K Content (g/kg)*	*K_2O Content (g/kg)*
Sylvite	KCl	524.4	631.7
Carnalite	$KCl \cdot MgCl_2 \cdot 6H_2O$	140.7	169.5
Kainite	$KCl \cdot MgSO_4 \cdot 3H_2O$	157.1	189.2
Langbeinite	$K_2SO_4 \cdot 2MgSO_4$	188.5	227.0
Leonite	$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$	213.3	256.9
Schoenite	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$	194.2	233.9
Polyhalite	$K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$	129.7	156.2

Source: Stewart, J. A., in *Potassium in Agriculture*, R. D. Munson (Ed.), p. 83, ASA-CSSA-SSSA, 1985.

Glauber in the Netherlands first proposed, in the middle of the seventeenth century, that saltpeter (KNO_3) was the "principle" of vegetation. This salt, derived from the leaching of coral soils, was thus the first chemical compound intentionally applied to crops to satisfy their nutrient needs. Justus von Leibig had established the essentiality of the element for plant growth in his pioneering work published in 1840. The potassium or potash chemical industry dates from the year 1861, following the discovery by German chemists of a process for recovery of KCl (muriate of potash) from rubbish salts, the residues remaining from the extraction of sodium chloride (NaCl).

The term "potash" generally refers to potassium chloride, but it is also used to designate other potassium compounds that may be qualified by the words muriate of potash, sulfate of potash, etc.

The functions of potassium in the plant are manifold. This element serves to activate or catalyze a host of enzyme actions, to facilitate the transport of nutrients and assimilates in the xylem and phloem, to maintain the structural integrity of the plant cell, to regulate turgor pressure, to mediate the fixation of nitrogen in leguminous plant species, and to protect plants to some degree from certain plant diseases.

Potassium is a relatively abundant element in the earth's crust, ranking seventh in concentration. It is widely distributed geographically and is commonly found in association with sodium compounds. The feldspars, muscovite (white mica), granite, and gneiss are rich sources; but because they are siliceous and refractory, they are difficult and costly to convert to forms suitable for use as fertilizers. The common potassium minerals are listed in Table 24.2.

The name potash derives from an early production method in which potassium carbonate, leached from wood ashes, was crystallized by evaporating the leachate in large iron pots. The salt potassium chloride (muriate of potash or KCl) is now the major source of the element (95%); other important salts are potassium sulfate (sulfate of potash, K_2SO_4), potassium magnesium sulfates of varying K/Mg ratios, and potassium nitrate (KNO_3).

The potash industry is based on very large deposits of water-soluble potassium minerals resulting from the evaporation of shallow seas or natural brine lakes over a geological time span. These evaporates normally are located at depth in the earth's mantle. Ironically, the best deposits are found in areas quite remote from the more productive agricultural regions, which thus are the areas most in need of this element. Typically, the deposits are to be found in horizontal tabular bodies or beds and may occur at depths up to 2100 m or more. The beds may be only a few centimeters to a few meters thick, but commercial production is limited to strata that are at least 1 m thick. As with hard-rock mining, the potash-bearing ores are extracted or harvested with continuous mining machines and brought to the surface through vertical shafts. Where the ores occur below a depth of about 1100 m, or where the beds exhibit geological anomalies (e.g., folding), the potash is dissolved in a brine solution and pumped to the surface for recovery using solution-mining techniques.

Potassium Minerals

The ore zone or stratum typically contains potassium or potassium–magnesium minerals along with halite (sodium chloride). Muriate of potash is refined from sylvinite ore, a mechanical mixture of potassium chloride (KCl) and sodium chloride (NaCl). Because the latter salt is injurious to most crop plants, the KCl (sylvite) must be separated from the NaCl (halite).

For coarse-grained ores, physical methods employing froth flotation and/or heavy-media methods are employed to achieve separation. The heavy medium may consist of, for example, pulverized magnetite in a brine solution. The specific gravity of the medium is adjusted so that it falls between that of KCl (1.99 g/cm^3) and that of NaCl (2.17 g/cm^3).

When the crushed ore is placed in this medium, the potassium values are floated off, and the contaminating sodium values sink and are drawn off and rejected from the bottom of the flotation vessel. Entrapped magnetite from both the product and waste streams is easily recovered magnetically and returned to the flotation vessel.

In froth flotation the crushed ore, which has been scrubbed to remove contaminating clay particles, first is treated with an aliphatic amine acetate and a froth-promoting alcohol. The water-repellant amine acetate is attracted preferentially to the sylvite particles. In a subsequent step, the ore or pulp is maintained in suspension, and the coated sylvite particles are attracted to and entrained on the rising air bubbles generated by the flotation agitator. They rise to the surface and are collected by hydraulic and mechanical means. The potassium-depleted pulp is then discarded. The sylvite or muriate is collected, centrifuged to remove the hydraulic medium, dried, screened, into various particle size ranges, and sent to storage.

Potassium–Magnesium Minerals

Other important sources of potassium for fertilizer use are the double salts kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) and langbeinite ($K_2SO \cdot 2MgSO_4$). The former is recovered from potash mines in Germany and Sicily; the latter is recovered and processed from mines in New Mexico (U.S.). These minerals supply important quantities of both magnesium and sulfur as well as potassium, and all are essential nutrients for plant growth. Kainite has a theoretical composition of 15.99 percent K (19.26% K_2O), 9.94 percent Mg, and 13.11 percent S, and langbeinite contains 18.85 percent K (22.7% K_2O), 11.71 percent Mg, and 23.18 percent S.

In the processing of langbeinite, the contaminating chlorides (NaCl, KCl) are removed by extracting the crushed ore with water. Centrifugation, drying, and screening follow to prepare the product in various size grades for the market. Where the mixed ore contains recoverable quantities as KCl as well as langbeinite, froth flotation and heavy-media methods may be employed to recover both potassium-containing salts.

Potassium Sulfate

Sulfate of potash (K_2SO_4), unlike the earlier-discussed potash salts, does not occur as natural deposits. It can be recovered by fractional crystallization from such natural brines as those of the Great Salt Lake in Utah and Searles Lake in California. Here separation and recovery are achieved by solar evaporation in shallow ponds. These processes can be utilized only where a suitable brine source is available, and where solar evaporation rates are high.

A much more important source of K_2SO_4 is the product resulting from either a controlled decomposition reaction of a complex sulfate salt, reaction of the salt with KCl, or both. Thus, kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) may be reacted with water in a two-step reaction, first to form schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$), with the schoenite then reacted with KCl to form K_2SO_4.

Langbeinite likewise is reacted with KCl to form sulfate of potash, according to the following reaction:

$$\underset{\text{langbeinite}}{K_2SO_4 \cdot MgSO_4} + \underset{\substack{\text{potassium}\\ \text{chloride}}}{4KCl} \longrightarrow \underset{\substack{\text{potassium}\\ \text{sulfate}}}{3K_2SO_4} + \underset{\substack{\text{magnesium}\\ \text{chloride}}}{2MgCl_2\,(\text{solution})}$$

Approximately 50 percent of world K_2SO_4 production is derived from the reaction of KCl with either kainite or langbeinite.

For those producers who do not have access to such suitable sulfate salts to serve as the sulfate donor, the so-called Mannheim process, in which sulfuric acid is reacted with KCl, may be utilized. The following reaction unfortunately generates the corrosive substance hydrochloric acid as a co-product:

$$\underset{\substack{\text{potassium}\\ \text{chloride}}}{2KCl} + \underset{\substack{\text{sulfuric}\\ \text{acid}}}{H_2SO_4} \longrightarrow \underset{\substack{\text{potassium}\\ \text{sulfate}}}{K_2SO_4} + \underset{\substack{\text{hydrochloric}\\ \text{acid}}}{2HCl}$$

Potassium sulfate, though relatively costly to produce, is a preferred source of potassium for some vegetable and fruit crops and tobacco—crops that are sensitive to the chloride forms.

Potassium Nitrate

The third most widely used potassium salt in agriculture is potassium nitrate (KNO_3). An ore containing sodium nitrate, potassium nitrate, some chlorides, and sulfates is mined in Chile. The ore is leached and part of the sodium nitrate is crystallized and removed.

The salt is produced in small amounts commercially in the United States, Israel, and Norway by the reaction of KCl with nitric acid. Though the salt is an attractive fertilizer material containing the two essential nutrients, nitrogen and potassium, in plant-available form, it is expensive to produce and thus enjoys only a limited market.

Potassium Phosphates

Potassium phosphates are excellent fertilizers, and their very high analysis is an advantage that has stimulated much research in an effort to find an economical production process. However, no process has been developed that is economical enough to result in widespread production; therefore, present use is limited to special purposes for which the high cost can be justified.

At present, most of the potassium phosphates used in fertilizers are produced from potassium hydroxide or carbonate and phosphoric acid and are used in liquids for foliar application or other specialty uses.

Some of the potassium phosphates are:

		Approximate grade
Monopotassium phosphate	KH_2PO_4	0–52–35
Dipotassium phosphate	K_2HPO_4	0–40–54
Tetrapotassium pyrophosphate	$K_4P_2O_7$	0–43–57
Potassium metaphosphate	KPO_3	0–60–40

In addition, a potassium polyphosphate solution of 0–26–27 grade has been produced from superphosphoric acid and potassium hydroxide; it contains a mixture of ortho, pyro, and higher polyphosphates.

Another process that received attention involves the use of concentrated sulfuric acid to treat potassium chloride to produce potassium bisulfate:[22,23]

$$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl$$

The hydrogen chloride is recovered as a dry gas and can be used for certain oxychlorination reactions or other industrial purposes for which elemental chlorine is now used. The potassium bisulfate is used, with more sulfuric acid, to make monopotassium phosphate and phosphoric acid. A simplified equation, representing phosphate rock as tricalcium phosphate, is:

$$KHSO_4 + 2H_2SO_4 + Ca_3(PO_4)_2 + 6H_2O \longrightarrow 3CaSO_4 \cdot 2H_2O + KH_2PO_4 + H_3PO_4$$

After removal of the gypsum by filtration, the mixture of phosphoric acid and monopotassium phosphate can be ammoniated to produce a chloride-free NPK fertilizer such as 8–48–16, or monopotassium phosphate can be separated from the phosphoric acid by precipitation in methanol solution and marketed separately. If desired, the monopotassium phosphate can be converted to a pyro-orpolyphosphate by pyrolysis.

The obvious advantage of the process is the recovery of HCl in a useful form. Another advantage is that a standard wet-process phosphoric acid plant can be adapted with a minor change. Numerous other processes for making potassium phosphate from KCl have been proposed, patented, or developed on a commercial scale, but none is known to be in commercial use for fertilizer purposes.

COMPOUND FERTILIZERS

The preceding sections of this chapter have described the production of nitrogen fertilizers, phosphate fertilizers, and potash fertilizers from basic raw materials. These fertilizers, without further processing, are referred to as "straight materials." Worldwide, in 1999/2000 (Fig. 24.15), straight materials accounted for about 195 million mt—about 55 percent of the total production. The remaining 45 percent was in the form of "mixed" fertilizers, that is, fertilizers that contain more than one of the major plant nutrients nitrogen, phosphorus, and potassium. Application of nitrogen fertilizer as straight material is much more

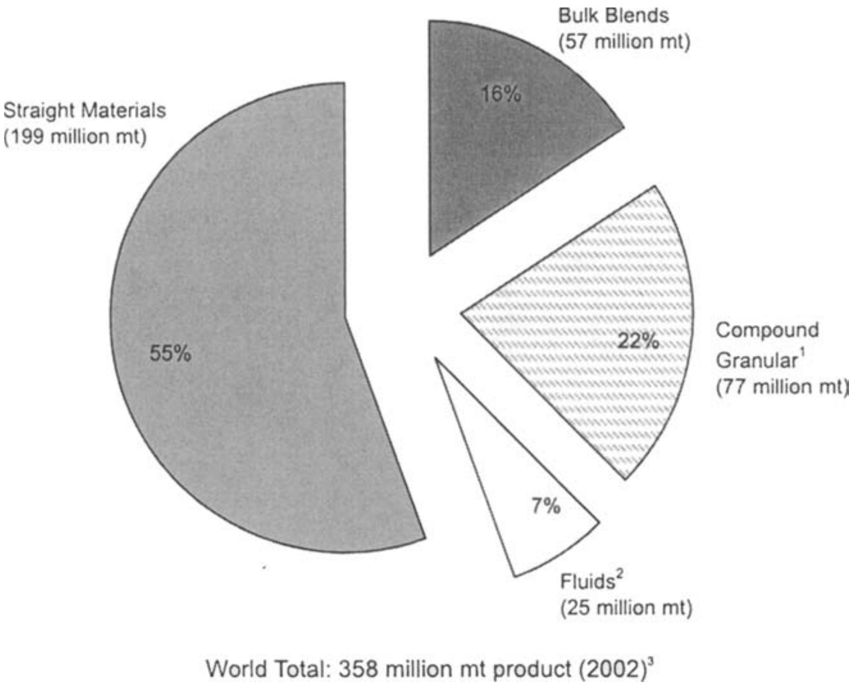


Fig. 24.15. Estimated world production of fertilizers by product type. 1. Steam/water, chemical (including ammonium phosphate), and compacted granular products. 2. Single- and multiple-nutrient fluids, including anhydrous ammonia. 3. As reported by IFA, nutrient production (2002/03 reporting year) amounted to 152.2 million mt (N + P_2O_5 + K_2O). Product mt were calculated by multiplying 2.35 times the nutrient mt.

prevalent than phosphate fertilizer. The reasons for these patterns are both agronomic and economic. Agronomically, large applications of nitrogen alone—for example, in the rice production and "side dressing" of corn—often are of considerable importance. For phosphate, there usually is no similar agronomic need for single-nutrient application; so application in mixtures, with the resultant elimination of multiple handling, is preferred. In the United States and Europe, with highly mechanized farming practices, the present trend is toward "precision" agriculture, which involves variable rates of application of nutrients at different locations in the same field based on the nutrient status. This method of application requires straight fertilizers rather than compounds.[24]

Mixed fertilizers can be divided, by physical characteristics and production methods, into the following categories, all of which will be discussed in some detail:

- nongranular mixtures
- compound granulars
- bulk blends
- fluid mixtures

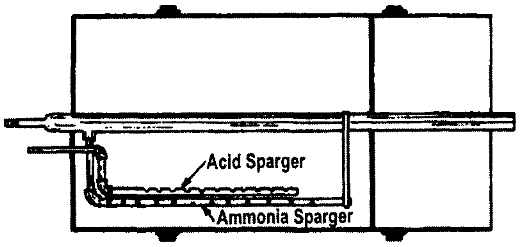
Nongranular Mixtures

Until about 1950, essentially all the mixed fertilizers available to farmers were of the nongranular type. Production was by simple batch weighing and blending of available nitrogen, phosphorus, and potassium ingredients, usually in locations that were convenient with respect to rail or water receipt of raw materials and out-shipment of bagged mixtures to dealers in farm areas. The source of phosphate almost invariably was nongranular SSP produced at the mixing location from in-shipped phosphate rock and locally produced sulfuric acid. In-shipment of elemental sulfur was required to produce the acid, usually by the now obsolescent "chamber" process. The major nitrogen ingredient used in the mixtures was fine-crystal by-product ammonium sulfate, and the potash source was nongranular potassium chloride. In some plants the superphosphate was "ammoniated" by reaction with ammonia solution, either in a separate operation before mixing with the other ingredients or during the mixing operation. Such ammoniation was beneficial in reducing the corrosiveness (acidity) of the superphosphate and in improving its physical condition. The ammonia also provided nitrogen at relatively low cost, but the amount that could be absorbed by the superphosphate was limited. Organic materials often were included in the mixtures as nutrient sources, bulking agents, or physical conditioners. Materials used included fish meal, packinghouse wastes, dried blood, tobacco stems, cottonseed hulls, and others. Mineral materials such as kaolin clay, diatomaceous earth, and vermiculite sometimes were included as conditioners. Batch-type drum mixers of 1- to 3-ton capacity were used with the ammonia solution piped directly into the mixer. Mixture grades were low by present-day standards, and storage and handling properties of these nongranular mixtures were generally poor. Caking problems, in particular, were considerable. Production of this type of fertilizer now persists in only a very few locations.

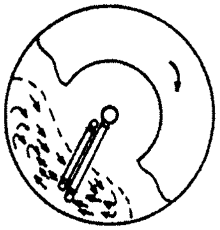
Compound Granulars

Continuous Ammoniator–Granulator Process. Following the close of World War II in 1945, farmer demands developed for much increased quantities of fertilizer and for products with better handling properties. Granulation, which provides an increase in particle size and the elimination of fines, was a promising avenue for the physical improvement that was pursued by researchers in both the United States and Europe. A milestone in this movement to granulation was the development, patenting, and demonstration by TVA, in 1954, of a continuous rotary-drum granulation process for mixed fertilizers.[25,26]

The rotary drum granulator in this process is essentially the same as was pictured for the diammonium phosphate granulation process. In early versions of the process, feed to the drum of SSP consisted of (1) crushed oversize product and fines, (2) nongranular SSP, (3) nongranular potassium chloride, (4) ammonium sulfate crystals, (5) sulfuric acid, and (6) anhydrous ammonia or an ammonia-containing nitrogen solution.



Side View



Feed End View

Fig. 24.16. Sparger location under rolling bed in TVA-type ammoniator-granulator. *(Courtesy TVA.)*

The acid and the ammonia or ammoniating solution were sparged under the rolling bed of solids in the drum with a sparger arrangement, as shown in Fig. 24.16. With the proper balance of liquid and solid feeds, granulation occurs as a result of the rolling action in the action in the drum, and it is completed, with hardening, in a rotary-drum dryer.

This process was rapidly and widely adopted by mixed-fertilizer producers throughout the United States and later adopted by producers in Europe, Latin America, and Asia.

The process was particularly attractive because: (1) the raw materials were essentially the same as materials that were already available at most batch-type nongranular plants, (2) higher proportions of relatively cheap anhydrous ammonia or nitrogen solution could be used, (3) continuous-type processing allowed higher production rates, and (4) product physical properties were much improved as a result of granulation. Today, the same basic process, but with numerous modifications, is used in most mixed-fertilizer granulation plants. However, the number of plants has dwindled in favor of bulk-blending and fluid fertilizers. One early modification to the process was the addition of phosphoric acid as a feed material, either along with or in place of sulfuric acid. Other feed materials used in some variations include TSP, monoammonium phosphate, ammonium nitrate, and urea. The use of urea has become more attractive in compound fertilizer production in Asia because higher grades can be achieved. The molten urea or concentrated urea solution is sprayed onto the bed of materials in the granulator and the wet product requires gentle drying. Most urea-based compound fertilizers are more hygroscopic, requiring dehumidified bulk storage facilities before the product is bagged.[27]

Use of Preneutralizer (Slurry Granulation). A major improvement to the basic TVA granulation process was the incorporation in most plants of a preneutralizer vessel for prereaction of phosphoric acid with ammonia. The procedure, as applied to the production of DAP, was described earlier and was pictured in Fig. 24.13. As in the DAP process, the preneutralizer used in the production of mixed fertilizers is operated at an NH_3:H_3PO_4 mole ratio of about 1.4 to give maximum ammonium phosphate solubility and thus maximum fluidity of the slurry pumped to the granulator. Subsequent further addition of ammonia in the granulator sharply decreases solubility and thus promotes solidification and hardening of granules. As in ammonium phosphate production, the iron and aluminum impurities normally present in wet-process phosphoric acid contribute significantly to the hardening of granules during ammoniation.[17] Sulfuric acid, when used, is fed directly to the granulation drum, not to the preneutralizer. The use of the preneutralizer allows the inclusion of higher proportions of acid in formulations. Also, better use is made of the heat of the ammonia–acid reaction for the evaporation of water, with resultant savings in dryer fuel.

Use of a Pipe Reactor (Melt Granulation). A more recent development that has been adopted in most U.S. granulation plants involves the substitution of a pipe reactor or a pipe-cross reactor for the preneutralizer vessel as the locale for the ammonia–acid reaction.[28–32] A simple pipe reactor differs from the pipe-cross reactor in that only one acid inlet port, usually for phosphoric acid, is provided.

The salient feature of the pipe reactor and pipe-cross reactor systems is that the heat of the ammonia-acid reaction is confined to the pipe and is efficiently utilized there to vaporize essentially all the moisture in the feed acid. The resultant steam exits the pipe discharge end in the granulator and is swept away in an air stream. The ammonium phosphate melt, which is of very low moisture content, also exits the pipe and is discharged onto the rolling bed of dry solids in the granulator. This melt serves as the binder for granule formation. The reaction temperature in the pipe reactor usually is held below 150°C to avoid a buildup of troublesome scale in the pipe. In view of this temperature limitation, there is little or no conversion of the phosphorus to polyphosphate forms. By allowing the pipe temperature to rise to about 200°C or higher, polyphosphate can be formed without scaling, but this mode of operation seldom is used in mixed-fertilizer granulation. TVA has used such high pipe temperatures to produce 11–57–0 and 28–28–0 grade ammonium polyphosphate granules in which 15–25 percent of the P_2O_5 is in polyphosphate form.[28] The physical properties of these products are exceptionally good, and the polyphosphate content makes them particularly suitable for dissolution to form fluid fertilizers. Because of the very low moisture content of the pipe reactor melts, even at the lower operating temperatures, the normally expensive drying of finished granular product usually is not needed: passage of the product through a cooler with an air sweep is sufficient for final drying. This results in a major fuel saving, which is a very significant economic advantage.

Steam Granulation. A simple method for granulating dry mixtures of fertilizer materials was developed in Europe in the early 1950s and still is employed there to some extent. In this procedure, which is pictured in Fig. 24.17, the feed materials are finely ground to ensure their incorporation in the granules. A dry mixture is made and then is moistened in a rotary drum or pan-type granulator with either water spray or steam, or both. This added moisture forms a salt solution by partial dissolution of the mixture ingredients. The granules form because of the plasticity and rolling action in the granulator. Initially, these granules are very soft; but, with further rolling and drying in a subsequent drying operation, salt bridging imparts the required granule hardness. In

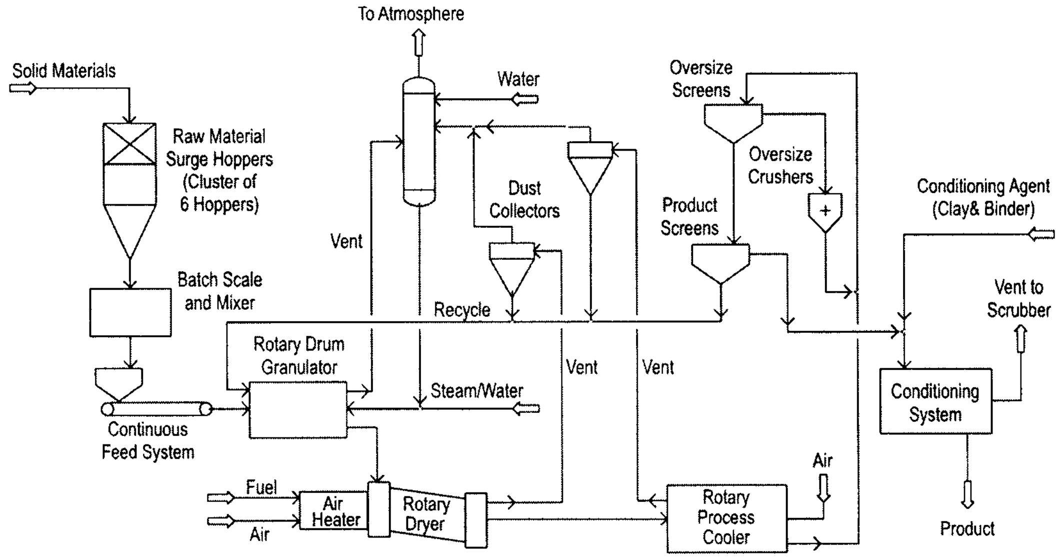


Fig. 24.17. Typical NPK fertilizer granulation plant using steam and/or water. *(Source: Fertilizer Manual.)*

contrast to the TVA ammoniation–granulation process, the steam granulation process usually causes no significant reaction between mixture ingredients. In Europe, this feature is of considerable significance when superphosphate is used as a feed material. Ammoniation of superphosphate, which occurs in the TVA ammoniation–granulation process, converts part of the water-soluble P_2O_5 content of the superphosphate to water-insoluble but citrate-soluble forms that are beginning to be accepted as marketable phosphate fertilizer in some European countries. The citrate-soluble forms are accepted as effective, marketable phosphate forms in the United States.

Compaction Granulation. This process involves the use of mechanical force to form granules (dense particles) from finely divided solid materials.[7] In this process (Fig. 24.18) the fine materials are weighed and, depending on the desired grade, thoroughly mixed. The mixture is then continuously fed to a pressure-roll compaction machine that forms the powdered mixture into a dense, hard sheet of material usually about 2–3 cm thick and 60–100 cm wide. The compaction machine consists of two horizontally opposed rollers that turn inward toward each other. The shaft of one roller is fixed while the other is movable. The pressure from a hydraulic system is applied to the movable shaft. The pressure is dependent on the fertilizer materials. The compacted sheet of material is crushed in a controlled manner to form smaller particles. The crusher discharge is screened to obtain the desired product-size fraction. The oversize material is crushed and recycled to the screens and the undersize material is returned to the compaction machine after thorough mixing with fresh feed. This is a dry process and does not involve chemical reaction. Some typical pressing force for fertilizer materials is shown in Table 24.3.

Compacted fertilizers have a more irregular shape as compared with the more smooth and round granules produced by other granulation processes. This irregular shape may cause some resistance among users who are accustomed to the more traditional spherical fertilizer granules. However, compacted fertilizers are produced and used in Europe.

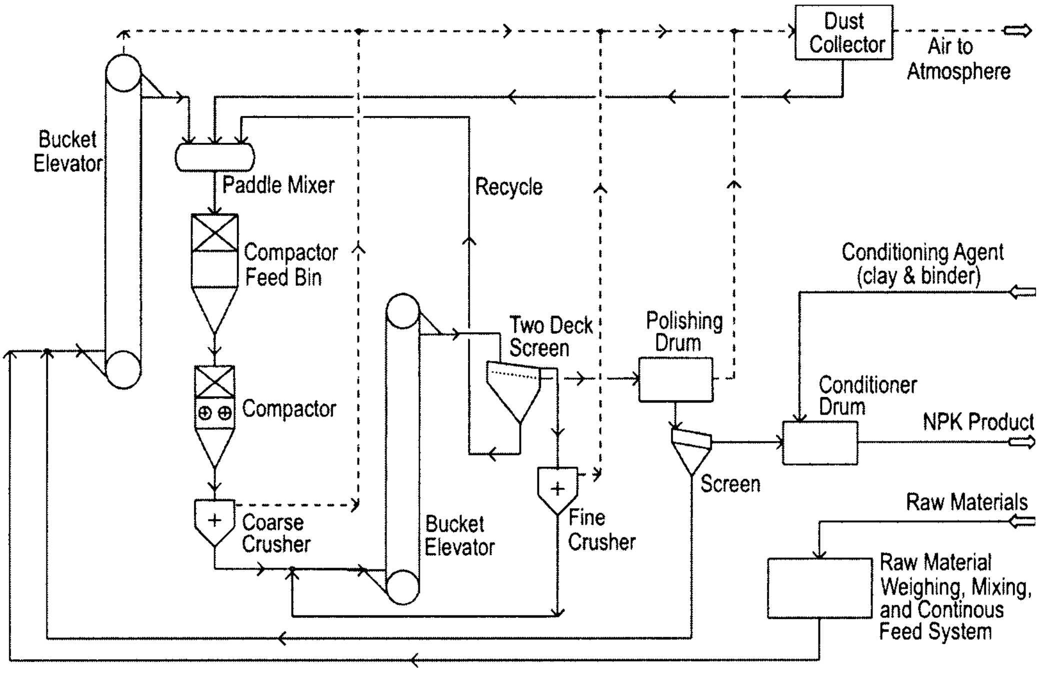


Fig. 24.18. Typical NPK fertilizer compaction granulation plant. *(Source: Fertilizer Manual.)*

TABLE 24.3 Typical Pressing Forces for Fertilizer Compaction[a]

Feed Material	*Pressing Force*[a] *(kN/cm)*[b]	*Water Content (%)*	*Feed Particle Size (mm)*
Ammonium sulfate	100–120	0.5–1.0	<1.0
Potassium chloride			
Feed temperature >120°C	45–50	nil	<1.0, with max.
Feed temperature 20°C	70	nil	of 3% <0.06[c]
Potassium sulfate			
Feed temperature >70°C	70	1.0	<0.5
Potassium nitrate	100	0.5–1.0	<1.0
Calcium nitrate	60	nil	<1.0
Urea	30–40	nil	1–3
Compound fertilizer containing			
• No raw phosphate rock	30–80	<1.0	<1.0
• Raw phosphate rock	>80	<1.0	<1.0
• Urea	30–40	<1.0	<1.0

Source: Fertilizer Manual, United Nations Industrial Development Organization and International Fertilizer Development Center, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1998.

[a] Indicated pressing force is for machine having 1.0-m diameter rollers.

[b] 1 kN/cm = approximately 0.1 tonne/cm.

[c] Size criteria apply to material feed temperature as indicated.

Bulk Blends

History and Growth. In the "compound" (mixed) fertilizer granulation processes just described, the starting materials are nitrogen, phosphorus, and potassium in the form of (1) nongranular solids, (2) liquids, or (3) gas (ammonia). When nitrogen, phosphorus, and potassium materials are all available from basic producers in granular form, as they now are, granular mixed fertilizers of almost any nutrient proportion (grade) can be made by simple proportioning and dry blending of granular nitrogen, phosphorus, and potassium materials; further granulation or other processing is not required. This is the basis of the presently popular "bulk-blending" system of mixed fertilizer preparation and distribution.

In 2002/03 about 57 million mt of bulk-blended fertilizers was produced. This corresponded to about 16 percent of the global fertilizer production.

The simplicity of the bulk-blending procedure is illustrated in Fig. 24.19. The operations consist of (1) in-shipment of granular fertilizer materials, (2) temporary storage, (3) proportioning, (4) blending, and (5) movement of the finished blend to the field for spreading.

Key factors in the rapid growth of bulk blending have been: (1) convenience in providing the farmer with a wide choice of plant-food ratios or grades on a "prescription" basis in relatively simple, small mixing plants located in the immediate farm area; (2) economy due to handling in bulk rather than bags; and (3) provision of spreading and other farmers services by the local blender.

Typical blending plants produce and market only 2000–6000 tons of blend per year. However, the present trend is for larger capacity plants covering a 30-mile radius of farming area designed to serve relatively large areas. The capital investment in blending plants is comparatively low. Blending plants operate on a quite seasonal basis, and often the operators have supplemental business enterprises.

Intermediates Used in Bulk Blending. The bulk-blending system came into being only after suitable nitrogen, phosphorus, and potassium intermediates became available in granular form. In particular, the introduction of granular DAP of 18–46–0 grade in about 1960, as described in a previous section, was a major catalyst to bulk blending. Characteristics of that product that make it an ideal material for shipping and subsequent blending

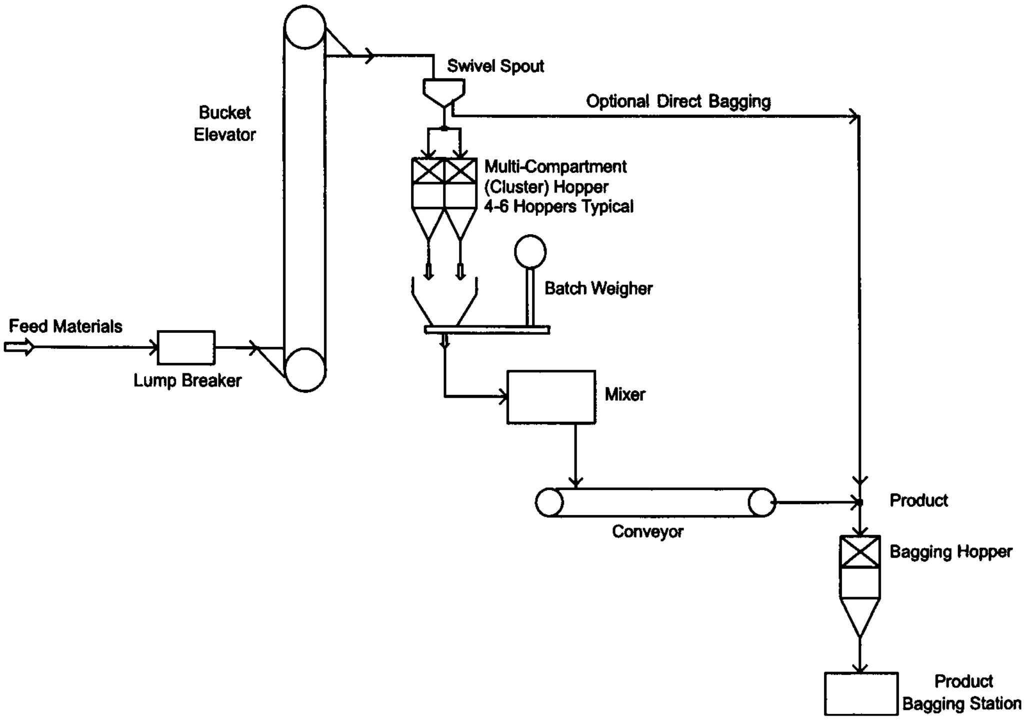


Fig. 24.19. Typical batch-type NPK fertilizer bulk-blending plant. *(Source: Fertilizer Manual.)*

are: (1) a high plant food content of 64 percent, (2) a high phosphorus content of 46 percent, (3) excellent storage and handling properties, (4) compatibility with essentially all other fertilizer materials, and (5) economy of production near phosphate deposits. Most NPK bulk blends are prepared with DAP as the phosphate source. Granular TSP is used for no-nitrogen (PK) grades, but for NPK blends TSP has the disadvantage of being incompatible (reactive) with urea.

In the preparation of bulk blends, it is of great importance to ensure that all ingredients of the blend are reasonably matched in particle size.[33] The use of unmatched materials results in poor mixing, segregation during handling, and uneven distribution on the field. Nitrogen materials used with the greatest success in bulk blends are (1) granular urea, (2) granular ammonium nitrate, and (3) large-crystal or granulated ammonium sulfate. Prilled ammonium nitrate can also be made of large-enough particle size for good blending, but prilled urea normally is of smaller size than desirable. The chief potash material used in blends is granular-grade potassium chloride, which is sized specially by potash producers for use in blends. Although granular-size potash usually consists of irregular crusher fragments rather than well-rounded granules, studies have shown that this particle shape difference does not promote segregation or otherwise impair blend quality.[34] A somewhat smaller-size, coarse-grade potassium chloride sometimes is used in blends because it is cheaper, but segregation problems are invited. Potassium sulfate and potassium magnesium sulfate are made in granular form for the blending of specialized formulations.

The addition of micronutrients to bulk blends poses special problems because of the small quantities usually added. Although many micronutrients are available in granular form, intergranule spacing on the field can be excessive when the granular micronutrient constitutes only a very small proportion of the blend. Procedures have been devised and used for adding finely powdered micronutrients to blends together with a small amount of liquid binder.[35] The result is that each blend granule is coated with micronutrient, and thus the field distribution is better.

Operating experience and TVA studies have identified several combinations of materials that are incompatible in blends and should be avoided: (1) unammoniated superphosphates react with urea, and the result is wetting and caking and (2) urea in contact with ammonium nitrate forms an extremely soluble hygroscopic mixture that liquefies in the presence of only minute amounts of moisture. Therefore, these two materials can never be used together in the same blend. Essentially all other combinations of available fertilizer materials are compatible in blends.

Equipment and Operating Technique. There are different arrangements of equipment in the blending plants throughout the world. The operations in such plants generally consist of: (1) receipt of the intermediate granular components in bulk by truck or railroad car, (2) storage of the intermediates separately in bins, (3) removal of the granular blend components from storage and weighing in desired proportions, (4) mixing to obtain uniformity, and (5) discharge of the mixed batch directly into a spreader truck or into a holding bin. The most popular type of mixer is the batch-type rotary drum.

Such mixing plants can be highly automated so that the output with a mixer of only 1-ton capacity can be as much as 15–20 tons/hr. Mixers of several types are available with capacities ranging between 5 to 8 tons per batch; in some cases batch mixer capacities can be 10 tons per batch.[36]

Problems in Bulk Blending. Bulk blending is a simple practice that can provide uniform mixtures in almost any desired proportions. However, unless proper materials are used and certain handling precautions are taken, segregation can occur, and nonuniform blends will result. The factors involved and the precautions that are necessary have been described in several publications.[3] The main requirements are the use of granular materials with a well-matched range of particle size and the handling of the mixture after blending in ways that will minimize segregation. The mixing step is seldom a problem; it is quite easy to obtain a uniform blend by the use of proper materials and a few minutes of mixing. However, maintaining this uniformity during handling on the way to the farm and onto the soil requires precautions. Handling procedures that may cause segregation include coning (as occurs if the blend is allowed to drop from a discharge pipe onto a pile), vibration in hauling vehicles, and ballistic action imparted by some types of spreaders.

The problem of adding small quantities of micronutrient materials to bulk blends was mentioned earlier. This problem is being met by either using micronutrients in granular form or coating the blend particles with finely ground micronutrients and a liquid binder.[35]

Fluid Mixtures

Mention was made earlier of the significant quantity of nitrogen applied to farmlands in the form of urea–ammonium nitrate solution and aqua ammonia. Since the late 1950s, there has also been a growing practice of applying mixed fertilizers (NP and NPK) in fluid form. In fact, the growth of the fluids market paralleled bulk-blended products. In 2002/03 about 25 million mt of fluids was produced and corresponded to 7 percent of the world production. North America, and Europe are major markets for fluids. Fluids are also used in high-value crops in some countries of the Middle East and Latin America.

Numerous advantages have been cited to explain the growth of fluid mixed fertilizers.[3] Of these, the most significant probably is the ease and the precision with which fluids can be applied to the soil. When placement of the fertilizer is important, as in row fertilization, fluids often have an advantage. Also important is the adaptability of fluids to the homogeneous incorporation of micronutrients, herbicides, and insecticides. Another factor that encouraged the adoption of fluid mixtures was the prior existence of equipment and facilities for handling and applying nitrogen fluids; it was only logical for this practice to be expanded to include the preparation and application of mixtures. There are some claims of agronomic superiority for fluid fertilizers over similarly applied solids, but such claims are debatable and are not widely accepted.

Solution Fertilizers. Fluid fertilizers in use today can be divided into two major categories: (1) solutions, in which the plant food content is entirely in solution, and (2) suspensions, in which the plant food content exceeds its solubility, and the excess is held in suspension, usually by the addition of a suspending agent. The solution-type mixtures were the first to achieve commercial importance. Beginning about 1950, the practice of making solution mixtures was begun with pure electric-furnace orthophosphoric acid (54% P_2O_5) as the source of phosphorus. Ammoniation of this acid yielded an 8–24–0 grade ammonium orthophosphate solution that could be shipped to mixing plants in farm areas and used as a base for blending with other fertilizer materials. Blending usually was with urea–ammonium nitrate solutions (28–32% N) and a pure grade (solution grade) potassium chloride.

With the system that employed these raw materials, numerous advantages of fluid mixtures were established, but a need to improve the economics of the procedure was obvious. Pure electric-furnace acid is much more expensive than wet-process acid, so ways were sought to use the cheaper but impure wet-process acids. Direct ammoniation of wet-process acid causes precipitation of numerous impurities as an intolerable, gelatinous sludge. Also, plant-food solubilities are undesirably limited in the orthophosphate system, so the concentration (grade) of the product made with electric-furnace orthophosphoric acid was limited to 8–24–0. A series of developments by TVA led the way to solving both of these problems.

The problem of limited plant-food solubility was much alleviated by TVA's introduction of superphosphoric acid in 1957.[37] Superphosphoric acids are acids of high P_2O_5 content (up to 80% P_2O_5) that contain significant proportions of polyphosphates (nonortho, polymerized phosphates). The superphosphoric acid first produced by TVA was a pure electric-furnace product of 76 percent P_2O_5 content, of which about 50 percent was in polyphosphate form. With ammoniation of this acid, it was possible to produce an 11–37–0 grade base solution instead of the 8–24–0 grade maximum made from ortho acid. Demonstration use of 11–37–0 base in a number of mixing plants showed that solution mixtures of relatively high concentration could be made. Also, it was found that the polyphosphate content enhanced the solubility of micronutrient additives by a sequestering action.

The unfavorable economics of the electric-furnace acid process, however, discouraged the commercial production of electric-furnace superphosphoric acid; so attention was directed toward concentration of the cheaper wet-process phosphoric acid to give wet-process superphosphoric acid. Satisfactory concentration methods were developed,[38] but the effects of acid impurities on the handling properties of the concentrated acids limited the final P_2O_5 concentration and hence the polyphosphate content. The best handling properties were obtained with acids made from calcined rocks and with P_2O_5 concentration limited to 68–70 percent P_2O_5. In acid of this concentration, from 20 to 35 percent of the P_2O_5 is in the polyphosphate form, and the acid is referred to as low-conversion superphosphoric acid. Such acid today is the chief source of P_2O_5 for solution-type fertilizers.

The most popular scheme by which solution-type fertilizers are made from low-conversion, wet-process superphosphoric acid is outlined in Fig. 24.20. The first step is ammoniation of the acid to produce ammonium polyphosphate base solution. By carrying out this ammoniation in a pipe reactor, a temperature of over 200°C is developed, which promotes an increase in polyphosphate content to 65–70 percent of total P_2O_5 in the ammoniated acid.[39,40] The grade of the resultant base is usually 10–34–0; an 11–37–0 grade can be made, but its storage properties are not as

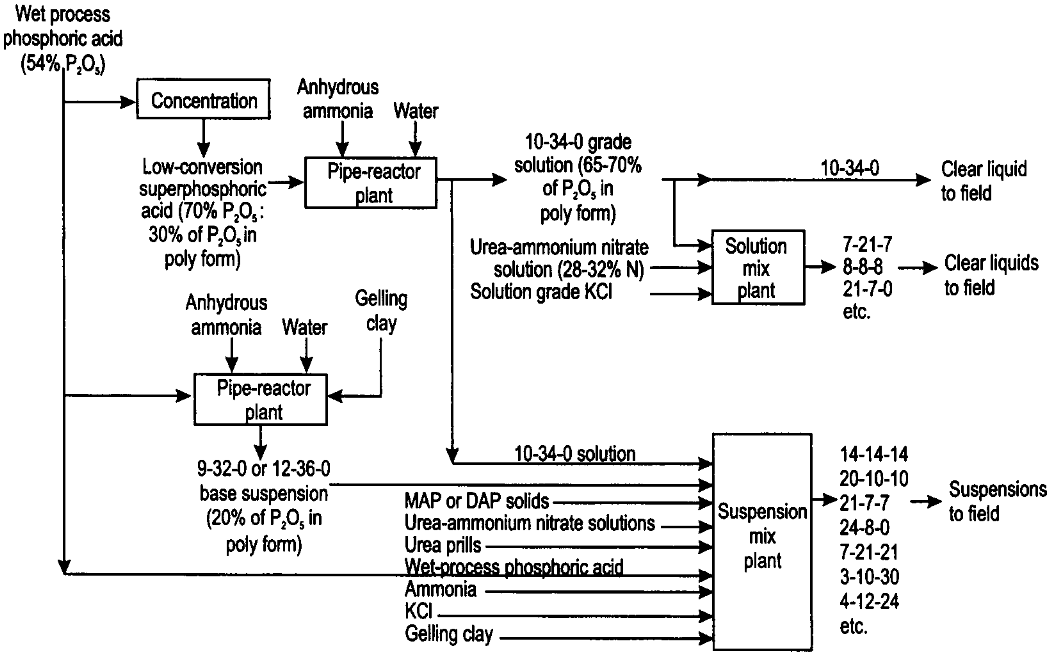


Fig. 24.20. Production methods for solution-type and suspension-type mixed fertilizers.

good, especially in cold weather. A sketch of a typical pipe-reactor system for the production of high-polyphosphate base solution from low-conversion, wet-process superphosphoric acid is shown in Fig. 24.21.

More than 100 U.S. plants use this pipe-reactor process to produce an estimated 2 million metric tons of 10–35–0 or 11–37–0 grade product per year. Other countries such as Belgium and France also use this process to produce ammonium polyphosphate solution. A considerable amount of the solution is used for direct application in the U.S. wheat belt and other areas in which potassium is not deficient. The rest is used in small mix plants to produce mixtures. The ammonium polyphosphate base solution is mixed with nitrogen solutions containing 28–32 percent N (urea–ammonium nitrate solutions) and sometimes also with potash to produce such clear liquid grades as 21–7–0, 7–21–7, and 8–8–8. As with bulk blending, the solution-mixing operation usually is carried out in small mixing plants located in farm areas (Fig. 24.22).

Suspension Fertilizers. Suspension fertilizers were developed chiefly as a means of breaking the grade barriers imposed on solution fertilizers by solubility limitations. The low solubility of potassium chloride was particularly troublesome, in that high-potash solution grades were not possible.

The feasibility of preparing and handling suspension-type fertilizers was demonstrated by TVA and others in 1959.[41,42] Two essential requirements for the preparation of a successful suspension were shown to be: (1) small particle size of the suspended solids and (2) the addition of a gelling-type clay as a suspending agent along with sufficient high-shear agitation to properly disperse the clay. The most satisfactory gelling-type clay is attapulgite.[43] Attapulgite is a hydrated magnesium aluminum silicate, which is composed of needle-shaped crystals so small that they can be seen only with the use of high magnification. In the dry state, these crystals bond together in bundles as larger particles. These bundles must be disrupted and the individual crystals freed before they can assume the structural arrangement that is characteristic of a gel. When this disruption of the crystal bundles is carried out in the presence of an electrolyte, such as any of the common fertilizer

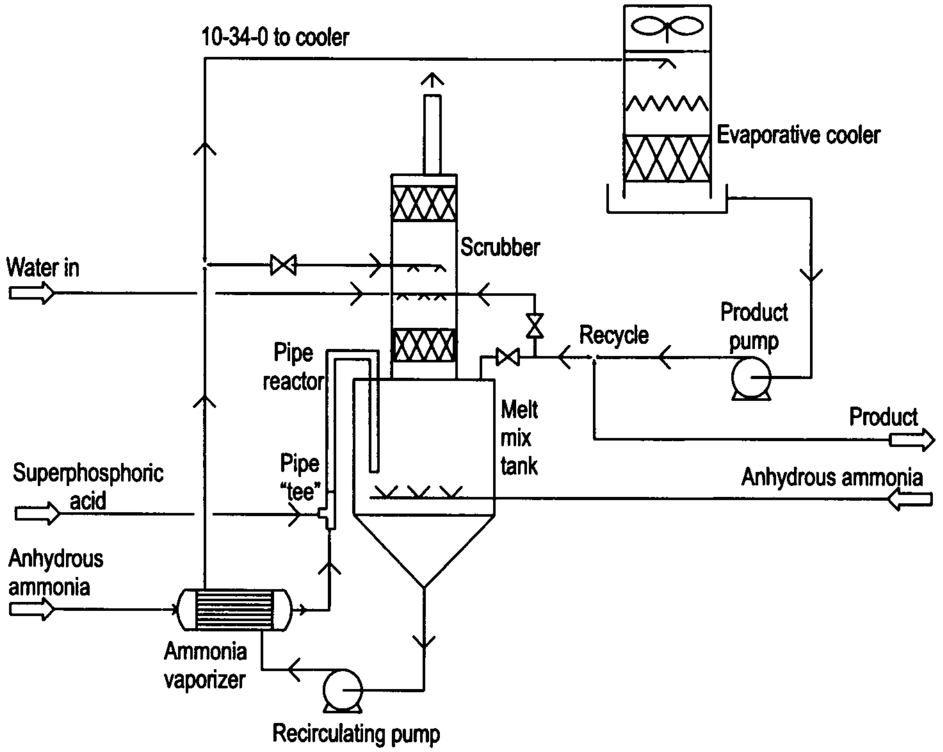


Fig. 24.21. Typical pipe-reactor plant for production of ammonium polyphosphate solution. *(Source: Fertilizer Manual.)*

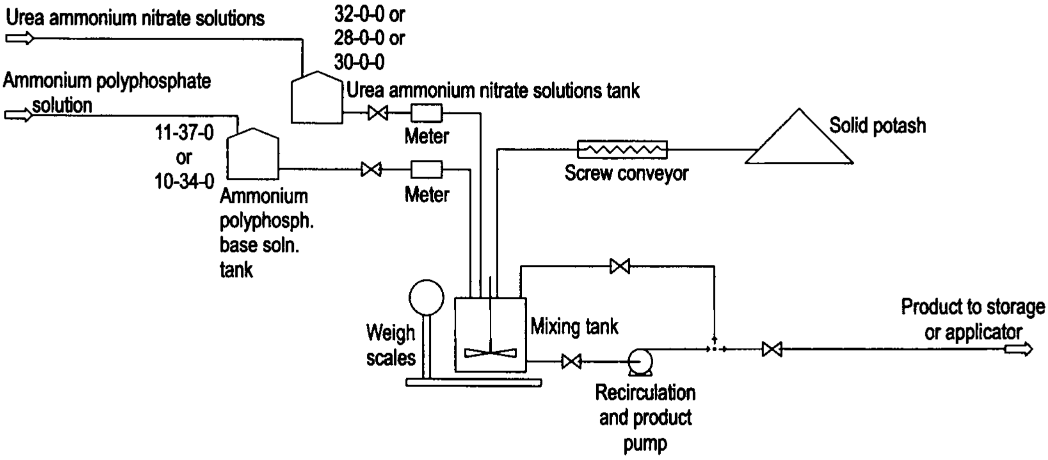


Fig. 24.22. Liquid fertilizer mix plant. *(Source: Fertilizer Manual.)*

salts present in fluid fertilizers, the individual crystals immediately assume the regular structural orientation of a weak gel, and thus provide the desired suspending action.

Wetting of the clay by the fluid fertilizer causes some of the required disruption of crystal bundles and freeing of individual crystals but not enough to provide good gelling without high-shear agitation. The addition of 2–3 percent of attapulgite is sufficient for most fertilizer suspensions. Instead of providing high-shear agitation for the entire batch of

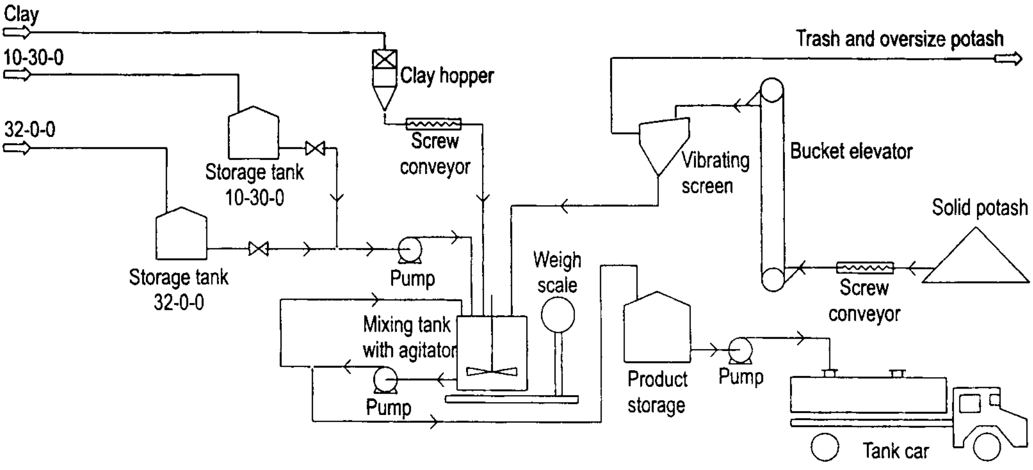


Fig. 24.23. Typical mix plant for production of suspension mixtures. *(Source: Fertilizer Manual.)*

suspension, some operators carry out a pre-gelling operation in which high-shear agitation is applied only to the clay plus a limited amount of water or fertilizer solution. The pre-gelled mixture then is added to the major body of fertilizer with only mild mixing. Pregelled clay is also marked as liquid clay and is transported in tank cars. The provision of a high-shear mixer is essential not only for gelling of the suspending clay but also for disintegration of any granular products such as DAP or MAP that might be used in the suspension. A high-shear recirculation pump is also an aid to gelling of the clay.

Figure 24.23 shows the layout of a typical suspension mix plant in which all the major suspension ingredients are received as solids. This is presently a popular mode of operation. Raw material costs for such a plant often are less than for bulk blending because nongranular materials can be used. Piping for the optional addition of phosphoric acid and ammonia is shown. Such addition develops heat, which hastens the disintegration of some solids.

The storage and handling properties of suspensions can be enhanced by the inclusion of some polyphosphate in the suspension. Low-temperature storage properties, in particular, are enhanced. One popular method of providing polyphosphate is to supply all or part of the P_2O_5 as 10–34–0 ammonium polyphosphate base solution, such as is used in solution fertilizers. A second method is the use of a pipe reactor to prepare 9–32–0 or 12–36–0 grade ammonium polyphosphate base suspension from relatively inexpensive wet-process orthophosphoric acid (54% P_2O_5), ammonia, and gelling clay.[44] About 20 percent of the P_2O_5 in the 9–32–0 form or 12–36–0 product is in polyphosphate form. The clay content is 2 percent. When these base solutions are used for mixing with other suspension ingredients, their clay content often is sufficient to provide all the clay required in the final suspension. Commercial acceptance of 9–32–0 or 12–36–0 base suspension preparation has not yet occurred. At present, apparently it is most economical to furnish polyphosphate as 10–34–0 ammonium polyphosphate solution.

Controlled-Release Fertilizers

The term "controlled-release fertilizer," as used in the following discussion, refers to fertilizers that release, either by design or naturally, their nutrient content over an extended period of time. Potential advantages claimed for controlled-release fertilizers are increased efficiency of uptake by plants; minimization of losses by leaching, fixation, or decomposition; a reduction in the release of nutrients and byproducts to air and water; and avoidance of burning of vegetation or damage to seedlings. In spite of this impressive list of potential advantages, the controlled-release fertilizer market remains small and primarily restricted to high-value crops and/or ornamental plants and golf courses.

Controlled-Release Phosphate Fertilizers. Several controlled-release phosphates have been produced commercially. Important among them are ground phosphate rock, basic slag, and fused calcium magnesium phosphate. These products have been discussed earlier.

Most of the insoluble or slightly soluble phosphate materials are used because they are less expensive than soluble phosphates or because they supply other elements. These products are rarely agronomically superior to soluble phosphates. However, some of them are valued for specialty uses because they may be safely placed in contact with seeds or roots in some situations. Slightly soluble phosphates are found to be useful in tropical agriculture where conditions are quite different from those in temperate zones.

Controlled-Release Nitrogen Fertilizers. Because of economics and environmental considerations, the slow-release nitrogen fertilizers are much more important than phosphate (or potash), particularly under certain soil and climatic conditions. In most cases unutilized phosphate and potash remain available for subsequent crops. In contrast, there is seldom much carryover of fertilizer nitrogen from one crop to the next. Nitrogen applied as fertilizer is lost from the soil through: (1) leaching or surface drainage, (2) volatilization as ammonia, and (3) decomposition. Because of these losses, nitrogen use efficiency by crops seldom exceeds 50 percent and may be as low as 20 percent under flooded rice conditions when grown under conditions of intermittent flooding or poor water control. Thus, improved utilization is particularly important because it would favorably impact the cost of production and simultaneously reduce the release of nitrogen compounds to air and water.[45]

Slightly Soluble Materials. One group of controlled-release nitrogen fertilizers comprises chemical compounds that are inherently only slightly soluble in water or soil solution. 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 a 2 : 1 mole ratio. When pure, it contains 32.18 percent N.[46] 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 percent nitrogen.

Urea–formaldehyde reaction products, usually called "ureaform," are produced by about six manufacturers in the United States and 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 percent nitrogen.

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

Ureaform is produced by reaction of urea with formaldehyde in aqueous solution in the presence of an acid that catalyzes the reaction. The degree of polymerization depends on the mole ratio of urea to formaldehyde and on the pH, time, and temperature of reaction. The reaction is stopped by neutralizing the acid. Production processes have been described by Clark et al.[47] and by Kolterman and Rennie.[48]

In Japan, ureaform is also produced as a component of compound fertilizers by the addition of formaldehyde solution to the urea solution fed to the granulator.[49] In one process a methylene urea reactor is used to react urea and formaldehyde solution to produce a slurry that feeds directly to a granulation plant with other materials to make compound fertilizers.[50] Some slow-release nitrogen is formed, and the physical properties of the products are improved.

In the United States, ammoniating solutions containing urea, formaldehyde, and ammonia are used to prepare compound fertilizer containing water-insoluble nitrogen. The composition of one such solution is: urea—35.3 percent, formaldehyde—8.0 percent, CO_2—8.4 percent, NH_3—25.0 percent, and H_2O—23.3 percent. Other solutions with high formaldehyde content (up to 60%) are available for use with additional urea.[51]

The addition of sulfuric or phosphoric acid (or superphosphate) neutralizes the ammonia and catalyzes the formation of methylene urea. Products containing about 20–30 percent of their nitrogen in a water-insoluble form are produced. Good control of conditions in the granulator and dryer is needed to produce a satisfactory quality of water-insoluble nitrogen. In some cases, a prereactor is used prior to the granulator.[50]

The consumption of ureaform in the United States is approximately 75,000 tons/year, not including that formed in compound fertilizers from solutions. Most of the production goes into compound 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 tests made by TVA and IFDC 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 an economical process, none of these materials has been manufactured commercially for fertilizer use.

Magnesium ammonium phosphate ($MgNH_4PO_4$) is a slowly soluble source of nitrogen although it contains more phosphate than nitrogen. The commercial product, called "Mag Amp," contains a variable amount of water of crystallization and some impurities; a typical grade is 8–40–0. A similar product containing potash is marketed under the trade name "En Mag" in the United Kingdom. The grade is 5–24–10. The rate of solution of these slightly soluble materials is controlled by the size and hardness of the granules.

Coated Soluble Materials. A wide range of materials and techniques has 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 first 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.[52] 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 16–4–8. The weight of the coating ranges from 10 to 15 percent of the gross weight. Osmocote products are recommended for turf, floriculture, nursery stock, and high-value row crops.

Sulfur-coated urea (SCU) is a controlled-release material developed by TVA during the 1960s and 1970s.[53] Sulfur was selected as the coating material on the basis of economy and efficiency after many 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. However, it was discovered that the addition of an oil wax sealant over the sulfur coating provided a successful coating. The process has been commercialized and the product is mainly used for turf and golf courses.

In this process granular urea is preheated in the first rotating drum to 77°C with electric radiant heaters to prevent the sulfur from freezing too rapidly on the granules. The molten sulfur is atomized and sprayed onto the rolling bed of granules in the second drum. Wax is applied in the third drum. The coated granules are then cooled in a fluidized bed cooler, and an absorbent powder is applied in a fourth drum to eliminate the tacky condition of the wax and to prevent the granules from floating when applied in water (as in a rice paddy).

The rate of dissolution of coated urea can be varied by varying the thickness of the sulfur coating and, to some extent, by varying the amount of sealant. 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 TSPs or SSPs, which are incompatible with uncoated urea. Also the sulfur coating is a slowly available source of sulfur, which would be an advantage in sulfur-deficient areas.

The sulfur-coating technique may be applied to fertilizers other than urea. Experimental work has included a coating of DAP, potassium chloride, potassium sulfate, and various compound fertilizers, including a pan-granulated urea-potassium chloride product of 32–0–16 grade.

Nitrification Inhibitors. Nitrogen fertilizers in the ammonium form are immobilized by sorption on clay particles and hence are resistant to leaching. However, the ammonium form is converted to the nitrate form under aerobic conditions by microbiological processes known as nitrification. The rate of conversion depends on the temperature; below 10°C it is very slow, but at 20°C and higher it is rapid. 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, prevention of denitrification losses, 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-(trichloromethyl) pyridine which is promoted under the name N-Serve. 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 ppm.

The N-serve literature 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, and soil in the pH range where nitrification readily occurs. Nitrate thus formed will leach down into anaerobic soil layers.

Potassium azide (2–6% 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 and Washington. PPG Industries, Inc., is exploring this and other agricultural uses (e.g. as a herbicide in rice culture) for the azide.

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. Other nitrification inhibitors that have been used in Japan in compound fertilizers are sulfathiazole, dicyandiamide, thiourea, N-2, 5-dichorphenyl succinamide, 4-amino-1, 2, 4-triazole hydrochloride, and guanylthiourea.[50]

In flooded or waterlogged soils, as for example, in a continuously flooded rice paddy, anaerobic (reducing) conditions exist in the soil below the surface, and hence nitrification of ammoniacal nitrogen does not occur in this layer. Therefore, when ammonia, ammonium salts, or urea (which hydrolyzes in the soil to

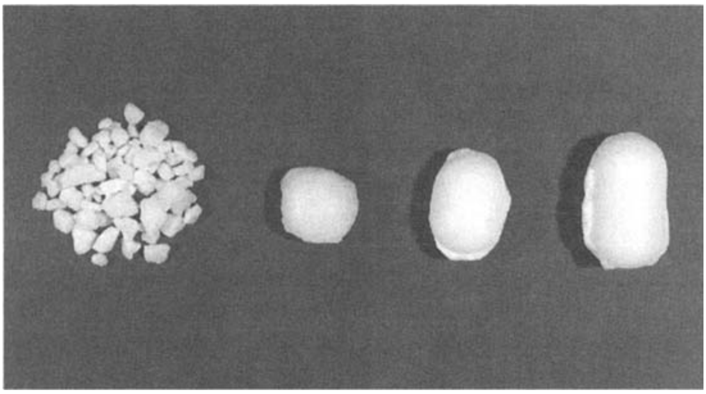


Fig. 24.24. Compacted urea product and briquetted urea particles of three particle sizes (from left).

ammonia and carbon dioxide) is placed in the reducing zone of the soil, it remains in the ammonium form and is more or less immobilized by sorption on the clay. Some of the advantages of controlled release may be attained by placement of ammoniacal nitrogen in the reducing zone of the rice paddy soil. However, this placement is difficult since applicators quickly become clogged with mud and wet fertilizer. To facilitate subsurface placement, large granules or briquettes of urea have been produced experimentally that can be pressed into the soil by hand (or foot) (Fig. 24.24). Experiments with this placement have shown substantially increased efficiency of nitrogen utilization by rice as compared with the usual broadcast placement.

IFDC has designed a village-level briquetting machine that can produce urea briquettes ranging in weight from 1 g to 2.7 g (Fig. 24.25). The capacity of these machines varies from 20 kg/hr to 1 ton/hr and can be operated intermittently. As of 2004 more than 1,000 of these machines are operating in Bangladesh, providing briquettes for nearly 500,000 ha of rice paddy. Using this technology the farmers are able to increase rice yields by about 20 percent while using 25 percent less urea. This technology is now being tested in Vietnam, Cambodia, and several countries in Africa.

Physical Quality of Fertilizers

Physical quality is an important determinant used by a farmer-consumer in selecting a particular fertilizer. The acceptability of a fertilizer in the marketplace depends not only on its nutrient content but also on its physical quality. Although the available nutrient content and its effect on crop response is the ultimate reason for the use of fertilizers, physical quality is often the reason for selecting one fertilizer over another. It is important that fertilizers remain free flowing (noncaking), relatively nondusty, and be able to withstand a reasonable amount of exposure to normal atmospheric humidity to withstand transportation, distribution, and application. Many production techniques, including various physical conditioning treatments, have been developed to provide favorable physical properties.[55]

The quality of a fertilizer product is basically judged by two criteria: chemical properties and physical properties. The chemical properties (nutrient content, form, and availability to the crop) and their effectiveness for crop growth are the main reasons for using a fertilizer. In contrast, physical properties of a fertilizer product are important with respect to processing, handling, storage, and field application.

The consumer, through simple observation, cannot ascertain whether a fertilizer actually meets the guaranteed nutrient content; however, federal or state laws normally regulate the nutrient content thereby giving some protection to the consumer. In contrast, physical condition usually is a matter only of agreement between purchaser and supplier. Normally fertilizer regulatory laws do not regulate fertilizer physical

Fig. 24.25. A village-level briquetting machine.

properties. However, the consumer can certainly see whether a fertilizer is caked or free-flowing, dusty or dust-free, wet and sticky or dry. The most frequently encountered problems resulting from deficiencies in physical properties are caking (agglomeration or lump formation), dustiness, poor flowability, excessive hygroscopicity (moisture-absorption characteristics), and segregation (nonuniformity of composition throughout a fertilizer lot).

The physical quality of a fertilizer can be evaluated by many different methods that can vary from simple observation to sophisticated techniques. Producers have adopted and/or developed methods to evaluate their particular products. International, national, and regional organizations have adopted, developed, and/or published procedures intended for general application to a variety of fertilizer products and raw materials.[3,56,57]

REFERENCES

1. Smil, V., *Cycles of Life*, Scientific American Library, New York, NY, 1997.
2. Food and Agriculture Organization of the United Nations (FAO), FAOSTAT database <http://faostat.fao.org>, Rome, Italy (2002).
3. United Nations Industrial Development Organization (UNIDO) and International Fertilizer Development Center (IFDC), *Fertilizer Manual*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1998.
4. Herring, J. R., and Fantel, J. R., "Phosphate Rock Demand into the Next Century: Impact on World Food Supply," *Nonrenewable Resources*, **2**(3), 226–241 (1993).
5. British Petroleum–Amoco, *Statistical Review of World Energy*, 1998.

6. Odell, P., Fossil *Fuel Resources in the 21st Century*, International Atomic Energy Agency, Vienna, Austria, 1999.
7. International Fertilizer Development Center (IFDC), *Compaction—Alternative Approach for Granular Fertilizers*, IFDC Technical Bulletin T-25, 1983.
8. McVicar, M. H., *Using Commercial Fertilizers*, 3rd ed., The Interstate Printers and Publishers, Inc., 1970.
9. Hignett, T. P., "History of World Fertilisers and Manufacturing Processes," *Ind. Chem. Manufacturer*, **9**(4), 13–17 (1971).
10. Young, R. D., and Achorn, F. P., "Trends in U.S. Fertilizer Technology," *TVA Bull. Y-133*, pp. 5–7, Tennessee Valley Authority, Muscle Shoals, AL (Aug. 1978).
11. *The Role of Phosphorus in Agriculture*, Am. Soc. Agron., Crop Science Soc. Am., and Soil Science Soc. Am., pp. 198–199, Madison, WI, 1980.
12. Hignett, T. P. "Nitrophosphate Process Advantages and Disadvantages," in *Proc. 15th Annual Meeting Fert. Ind. Round Table*, pp. 92–95, 1965.
13. Getsinger, J. G., Houston, E. C., and Achorn, F. P., "Production of Diammonium Phosphate by Continuous Vacuum Crystallization," *J. Agr. Food Chem.*, **5**, 433–436 (June 1957).
14. Young, R. D., Hicks, G. C., and Davis, C. H., "TVA Process for Production of Granular Diammonium Phosphate," *J. Agr. Food Chem.*, **10**, 442–447 (Nov. 1962).
15. U.S. Patent 3,153,574.
16. "New Developments in Fertilizer Technology," 8th Demonstration, *TVA Bull. Y-12*, Tennessee Valley Authority (1970).
17. Young, R. D., and Hicks, G. C., "Production of Monoammonium Phosphate in a TVA-Type Ammonium Phosphate Granulation System," *Comm. Fert.*, **114**(2), 26–27 (Feb. 1967).
18. Lehr, J. R., and McClellan, G. H., "Phosphate Rocks; Important Factors in Their Economic and Technical Evaluation," *CENTO Symposium on the Mining and Beneficiation of Fertilizer Minerals*, pp. 192–242, November 19–24, 1973.
19. Pelovski, Y., and Garrett, M. K., *Partially Acidulated Phosphate Rock Fertilisers—Agronomic, Environmental and Production Aspects*, Proceedings No. 364, The Fertiliser Society.
20. Yates, L. D., Nielsson, F. T., Fox, E. J., and Magness, R. M., "Enriched and Concentrated Superphosphate," *Industrial and Engineering Chemistry*, **45**(3), 681–690 (1953).
21. Walthall, J. H., and G. L. Bridger, "Fertilizer by Fusion of Rock Phosphate with Olivine," *Ind. Eng. Chem.*, **35**(7), 744–777 (1943).
22. Thompson, W. H., "New Route Cuts Costs for Potassium Orthophosphates," *Chem. Eng.*, **78**(8), 83–85 (1971).
23. Drechsel, E. K., "Potassium Phosphates: The New Generation of SUPER Phosphates," Paper presented to the American Chemical Society, Division of Fertilizer and Soil Chemistry, Chicago, Illinois, August 28, 1973.
24. Giese, A., "Environmental Responsibility on the Farm—The Impact on the Fertilizer and Agriculture Industry," in *Environmental Challenges of Fertilizer Production—An Examination of Progress and Pitfalls*, Proceedings of an International Workshop, J. J. Schultz and E. N. Roth (Eds.), IFDC, Muscle Shoals, AL, September 17–19, 1998.
25. Yates, L. D., Nielson, F. T., and Hicks, G. C., "TVA Continuous Ammoniator for Superphosphates and Fertilizer Mixtures," Part I and Part II of *Farm Chemicals* (August 1954).
26. U.S. Patent 2,741,545.
27. *Environmental Challenges of Fertilizer Production—An Examination of Progress and Pitfalls*, Proceedings of an International Workshop, J. J. Schultz and E. N. Roth (Eds.), Muscle Shoals, AL, September 17–19, 1998.
28. "New Developments in Fertilizer Technology," 9th Demonstration, *TVA Bull. Y-50*, Tennessee Valley Authority (1972).
29. "New Developments in Fertilizer Technology," 11th Demonstration, *TVA Bull. Y-107*, Tennessee Valley Authority (1976).
30. Medbery, J., "Experience with Pipe-Cross Reactor," *Proc. Fert. Ind. Round Table*, pp. 52–55, 1971.
31. Baggett, K. J., and Brunner, D. J., "MFA's Experience with TVA Cross-Pipe Reactor," *Proc. Fert. Ind. Round Table*, pp. 64–70, 1977.
32. Fittell, R. S., Hollingworth, L. A., and Forney, J. G., "Manufacture of Granular Ammonium Phosphates Using a Pipe Reactor Process," *Proc. Fert. Ind. Round Table*, pp. 70–81, 1977.
33. Hoffmeister, G., Watkins, S. C., and Silverberg, J., "Bulk Blending of Fertilizer Material: Effect of Size, Shape, and Density on Segregation," *J. Agr. Food Chem.*, **12**, 64–69 (Jan./Feb. 1964).
34. Hoffmeister, G., "Compatibility of Raw Materials in Blended Fertilizers—Segregation of Raw Materials," *Proc. 12th Annual Meeting Fert. Ind. Round Table*, pp. 83–88, 1962.
35. Young, R. D., "Providing Micronutrients in Bulk-Blended, Granular, Liquid and Suspension Fertilizer," *Comm. Fert.*, **118**(1), 21–24 (Jan. 1969).
36. Young, R. D., "Production of Compound Fertilizers from Intermediates in Local Plants," *TVA Bull. Z-30*, pp. 12–20, Tennessee Valley Authority (1971).

37. McKnight, D., and Striplin, M. M., "Phosphoric Acid of High Concentration," *J. Agr. Chem.*, **13**, 33–34 (Aug. 1958).
38. Phillips, A. B., "Concentration Wet-Processes Acid to Superphosphoric Acid," *Farm Chem.*, **126**, 36, 38, 62 (June 1963).
39. Meline, R. S., Lee, R. G., and Scott, W. C., "Use of Pipe Reactor in Production of Liquid Fertilizers with Very High Polyphosphate Content," *Fert. Soln.*, **16**(2), 32–45 (Mar./Apr. 1972).
40. U.S. Patent 3,775,534.
41. Walters, H. K., Jr., "Salt Suspension Fertilizers," *Comm. Fert.*, 25–26 (Sept. 1959).
42. Newsom, W. S., Jr., "Suspension Fertilizers," *Solutions*, 30–35 (Jan.–Feb. 1960).
43. Sawyer, E. W., Polon, J. A., and Smith, H. A., "The Stabilization of Suspension Fertilizers with Colloidal Attapulgite," *Solutions*, 36–43 (Jan.–Feb. 1960).
44. Mann, C., II, McGill, K. E., and Jones, T. M., *I&EC Product Research and Development*, pp. 488–495 (Sept. 1982).
45. Trenkel, M. E., *Improving Fertilizer Use Efficiency: Controlled-Release and Stabilized Fertilizers in Agriculture*, International Fertilizer Industry Association, Paris, France, 1997.
46. Hamamoto, M., "Isobutylidine Diurea as a Slow-Acting Nitrogen Fertilizer and Studies in this Field in Japan," *Proceedings No. 90*, The Fertiliser Society, London, 1966.
47. Clark, K. G., Yee, J. Y., and Love, K. S., "New Synthetic Nitrogen Fertilizers, Preparation and Properties of Urea-Form," *Ind. Eng. Chem.*, **40**(7), 1178–1183 (1948).
48. Kolterman, D. W., and Rennie, W. W., "Ureaform Fertilizers," in *The Chemistry and Technology of Fertilizers*, pp. 48–54, V. Sauchelli (Ed.), Rheinhold Publishing Co., New York, NY, 1960.
49. Ando, J., "Developments in Granulation of Mixed Fertilizers in Japan," *Proceedings of the 20th Annual Meeting Fertilizer Industry Round Table*, pp. 85–93, Memphis, TN, 1970.
50. Kuwabara, M., Hayamizu, S., and Hatakeyama, A., "Trends in Urea-Based Compound Fertilizer Technology," in *Granular Fertilizers and Their Production*, pp. 125–147, British Sulphur Corporation, London, England, 1977.
51. Nielsson, F. T., "IMC Experience in Specialty Fertilizer Manufacture," *Proceedings of the 23rd Annual Meeting of the Fertilizer Industry Round Table*, pp. 33–42, Washington, DC, 1973.
52. Powell, R., *Controlled Release Fertilizers*, Noyes Development Corporation, Park Ridge, NJ, 1968.
53. Young, R. D., "TVA'S Development of Sulfur-Coated Urea," *TVA Bull. Y-79*, Tennessee Valley Authority, Muscle Shoals, AL (1974).
54. United Nations, Department of Economic and Social Affairs, Population Division, *World Population to 2300* (2004).
55. Rutland, D. W., "Fertilizer Caking: Mechanisms, Influential Factors, and Methods of Prevention," *Fertilizer Research*, **30**, 99–114 (1991).
56. Hofstee, J. S., *Physical Properties of Fertilizer in Relation to Handling and Spreading*, Wageningen Agricultural University, Wageningen, The Netherlands (1993).
57. International Organization for Standardization, Central Secretariat, 1, rue de Varembe, Case Postale 5b, ch-1211, Geneva 20, Switzerland.