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## **Introduction**

Use of commercial fertilizers has only a short history compared to the length of time that man is known to have grown crops. It is believed that crop production began some 6,000 to 10,000 years ago.

For example, there are records of cropping dating back over 7,000 years in China and nearly that long in Norway. It was not until the 1840s that limited quantities of a few types of natural commercial fertilizer such as Peruvian guano and Chilean sodium nitrate were first used in the Western world.

## Ancient Practices Up To The Fall Of Rome

Many of the sound agricultural practices of today, including manuring, liming, and crop rotations with legumes were also important in ancient times. Also, the value of silt deposits from flooding rivers in maintaining soil productivity was recognized over 5,000 years ago by the early Egyptians living along the Nile River and by the Mesopotamian civilization occupying the region between the Tigris and Euphrates Rivers, now present day Iraq.



**Figure 1.1** Egyptian Agriculture

Organic manures have been used in Chinese agriculture for over 3,000 years. Descriptions of using human and animal wastes, plant ashes and grasses and how these materials benefited crop production and improved soil fertility were recorded in that country over 2,000 years ago.

The age of the Greeks, probably between 800 to 200 B.C., was a "Golden Age" and during this early period several historians and writers referred to the manuring of crops and adjusting the amounts for thin and rich soils. Use of city sewage on vegetable crops and olive groves and a canal system for delivering the sewage to fields was described in these ancient writings. Manures were also classified according to their value for crop production.

These same early Greek writers recognized the value of green manure crops, particularly legumes. Many of these ancients rated lupine as the best general-purpose green-manure crop because it grew well under a wide range of soil conditions, furnished food for man and beast, was easy to seed and quick to grow.

The value of marl and plant ashes for enriching the soil was recognized in both the Greek and the following Roman civilizations. Applications of ashes or lime were recommended to correct acidity in lowland soils.

Mineral fertilizers were not entirely unknown in past civilizations since mixing of different earths for "remedying defects and adding heart to the soil" was recommended by one of the early Greek writers. Fertilization of plants with saltpeter or potassium nitrate was mentioned in both early Greek and Roman teachings and in the book of Luke in the Bible. The Greeks reported the use of salt brines with applications being made around the roots of palm trees.

Several of the Roman intellectuals including Cato, Columella, Pliny, Varro and Virgil, in the period 234 to 19 B.C., wrote on the practical aspects of farming. They recommended that pits be dug near farm buildings for systematic collection of various wastes including animal, fowl and human excreta along with leaves, vegetables and other wastes. In addition, they described what can be considered as simple tests for evaluating the chemical and physical suitability of soils for crop production.

## After The Fall Of Rome To The Middle Ages

Following the decline of Rome, Western Europe entered into the six centuries of the "Dark Ages" when there was little interest in the sciences and scholarship. Fortunately, the reverse situation existed in the Arab countries with a strong focus on scholarship, education, literature and the sciences. Much of the Greek knowledge was preserved through the collection and translation of manuscripts from that civilization.

The one Islamic agricultural publication known to have survived, summarized farm practices of the period which had changed little from those of the Greeks and Romans. There appeared to be little new information on soil improvement in this book.

The ancients observed the effect that dead bodies and the blood of animals had on promoting crop growth. Omar Khayyam, the astronomer-poet of Persia around the latter part of the 11th century wrote:

*I sometime think that never blows so red  
The Rose as where some buried Caesar bled;  
That every Hyacinth the Garden wears  
Dropt in her Lap from some once lovely Head.*

## The Middle Ages: 12<sup>th</sup> to 16<sup>th</sup> Centuries

Publication of the agricultural book *Opus Ruralium Commodorum* by Pietro di Crescenzi of Italy was a notable development in this period of restoration of political and economic order and revival in classical learning of the past. However, its contents were based mainly on early Roman writings, personal observations and teachings from the Dominican monastery at Bologna. As a consequence, soil fertility and soil amendment practices remained much the same as in the days of the Greeks and Romans, relying principally upon animal manures; composts; sewage and other waste products; seas and, seaweed and fish in coastal areas; bones; and liming materials, usually marl.

## Chemical Discoveries In The 17<sup>th</sup> And 18<sup>th</sup> Centuries

Gold, silver, copper, tin, iron, lead and some of the simpler alloys and metallic salts were known at the time of the Greek and Roman civilizations. Crude potassium carbonate or potash had also been known for a long time. It was used primarily in glassmaking and soaps and it was obtained by leaching wood ashes in wooden tubs and evaporating to dryness.

Ammonium sulfate was discovered in the 1600s. Potassium nitrate or saltpeter was known but not its composition, and phosphorus was identified in 1669. Nitrogen, oxygen, hydrogen, manganese and molybdenum were all discovered between the early 1770s and 1782. Sulfur was classified as an element in 1777.

Ammonia was made for the first time in 1774 and by 1785 its exact composition was determined. Nitric acid, known earlier, was synthesized for the first time and by 1771 it was being produced commercially.

Urea was identified in 1773 and in 1775 the presence of large amounts of calcium phosphate in bones was confirmed. In 1784, the chemical nature of water was discovered.

## Early Understandings Of Plant Growth

The first true experiments with living plants appear to have been conducted by Jan Baptiste van Helmont (1577-1644), a Flemish physician and chemist, who studied the growth of a willow plant. The directness, simplicity and taking of quantitative measurements in his experiment played an important role in developing the experimental approach of the future.

Johann Glauber (1604-1670), a German chemist, concluded that saltpeter (potassium nitrate) collected from beneath cattle pens, came from the animal wastes and that it must have originated from the plants consumed by the animals. He observed large increases in growth of plants treated with saltpeter.

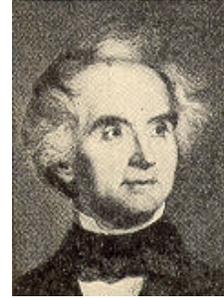
The investigations of John Woodward (1665-1728) in England revealed that most of the water taken up by a plant was transpired and that the plant grew in proportion to the amount of "matter" present in the water.

Several chemists studied the effect of plants on air but failed to recognize the reciprocal influence of air upon plants. A Dutch physician, Jan Ingen-housz (1730-1799) made an important discovery noting that plants could not take up carbon dioxide or release oxygen in the absence of sunlight and that oxygen was released by plants only when they were supplied with carbon dioxide. He concluded that atmospheric air was essential for plant growth.

A significant enlightenment in the understanding of plant nutrition was made by Theodore de Saussure (1767-1845) when he demonstrated that hydrogen and oxygen from water and carbon dioxide from the air contributed to the dry matter content of plants and that these sources were more important than humus. This Swiss scientist also showed that for normal nutrition, plants must take up, in dilute concentration, nitrates and other mineral matter from the soil. He recognized that salts present in plants were subject to selective absorption and some plants absorbed salts that were of no benefit to them or were actually harmful.

Sir Humphrey Davy, who discovered the elements potassium, sodium, calcium, chlorine and boron in rapid succession between 1807 and 1810, published in 1813 a series of lectures in a book entitled Elements of Agricultural Chemistry. It became a standard text for 50 years and it coordinated and summarized a considerable body of knowledge on growth and nourishment of plants. He believed that most of the carbon in plants was taken up by the roots and even recommended fertilization with oil as a carbon source.

The German chemist Justus von Liebig (1803-1873) is considered by many to be the father of agricultural chemistry and the fertilizer industry. Among his many outstanding contributions are (a) several important conclusions regarding the source and role of plant nutrients, e.g. carbon in plants being derived from atmospheric carbon dioxide and the necessity of phosphorus for seed formation, (b) the concept of developing fertilizer recommendations based on the chemical analysis of plants and interpretation of the analyses, (c) the principle that plant growth is proportional to the amount of mineral substances available in the fertilizer and (d) outlining the Law of the Minimum which essentially states that if one nutritive element is deficient, plant growth will be limited even though supplies of all other vital nutrient elements are adequate. Also, plant growth will be improved by increasing the amount of the deficient nutrient up to the point that it is no longer deficient.



**Figure 1.2** Justus von Liebig

Liebig strongly believed that soil fertility could be maintained by the addition of mineral elements present in plant ashes and that nitrogenous manures were unnecessary because of the ammonia occurring in the atmosphere and supplied in rainfall. Benefits of manure were attributed to the release of ammonia to the air in contact with plants.

Although von Liebig showed that treatment of bones with a strong acid, such as sulfuric acid, would increase the availability of phosphorus, he developed a fertilizer in which the phosphate and potash salts were fused with lime and as a result it was a failure.

Following closely on von Liebig's notable activities was the work of Lawes and Gilbert at England's Rothamsted Experiment Station founded in 1843. Twelve years after starting this research unit they settled a number of important issues including (a) crops require both phosphorus and potassium and the amount of these elements in plant ash is not a measure of plant requirements, (b) nonlegume crops require a supply of nitrogen and the amount of ammonia provided by the atmosphere is insufficient for crop needs, (c) soil fertility could be maintained for many years by using chemical fertilizers and (d) the beneficial effect of fallowing is the increase in availability of soil nitrogen.



**Figure 1.3** Sir Joseph Henry Gilbert

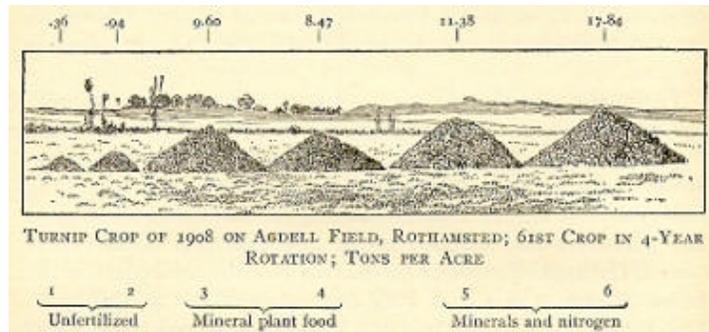
## Early Field Experiments With Chemical Fertilizers

Several famous French chemists conducted quantitative experiments and demonstrations to determine the benefits of chemical fertilization. Lavoisier began his studies in 1778 and found large yield increases on unproductive soils in his area of France. Boussingault established a farm at Alsace and from 1834 to 1871 conducted quantitative field plot experiments with manures, fertilizers and other materials. His inputs and the harvested crops were weighed and analyzed. Also, the numerous sound

field experiments carried out between 1848 and 1863 by Georges Ville of Vincennes greatly advanced the practical understanding and use of chemical fertilizers.

The Highland and Agricultural Society of Scotland initiated farmer trials with salt in about 1818. Its programs were extended in 1823 to include farmyard manures, bone and a fish compost. Sodium nitrate was introduced into the comparisons in 1831. The treatments were increased further in 1841 with the inclusion of ammonium sulfate, ammonium chloride, aqua ammonia, guano, urine, gypsum and other substances.

The renowned long-term field experiments at Rothamsted, England, deserve special mention. The first classical experiments involved wheat and turnips treated with farmyard manure, no manure and ammonium salts of sulfate or chloride. In 1852, the experiments were established in their final form on continuously cropped wheat, barley, roots, clover and shortly afterwards grass hay. Treatments of nitrogen only; minerals only, including superphosphate and potassium, sodium and magnesium sulfates; nitrogen plus these same minerals; farmyard manure and no manure were compared on all of the crops. These experiments have been conducted for many years and some are still continuing. Careful records have been maintained of weather, soil and crop conditions and crop and soil samples analyzed.



**Figure 1.4** Results of field experiment: Turnip Crop of 1908 on Agdell Field, Rothamsted; 61st Crop in 4-Year Rotation; Numbers at top are in Tons per Acre.

## Nitrogen (N)

### Sodium Nitrate

The world's first commercial nitrogen fertilizer was sodium nitrate mined from natural deposits in Chile. It was imported into Europe and North America from about 1830 onwards. During the 1920s sodium nitrate imports from Chile were still a very important source of nitrogen in the United States with consumption amounting to about 600,000 tons annually.



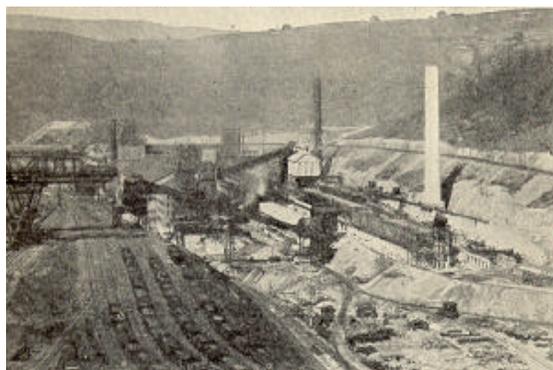
**Figure 1.5** Old sodium nitrate production facilities in Chile. (Chilean Nitrate Corporation)

Synthetic production of this material in the US began in 1928 and by 1935 it reached 500,000 tons annually. Consumption of the domestic, synthetic and natural Chilean

product totaled 730,000 tons in 1950 and has since declined steadily to just 84,000 tons in 1980 and 34,700 tons in 1994.

## Ammonium Sulfate

Ammonium sulfate was the next commercial source of fertilizer nitrogen. It was originally a by-product of the manufacture of coal gas for use in illumination and later from the coke industry serving the steel industry in Europe and America in the late 1800s. The initial product in England in 1815 was of poor quality but by the 1830s substantial amounts were being used by farmers in that country.



**Figure 1.6** By-product coke plant in Hamilton, Ohio.

Little of this fertilizer was used in the United States until the late 1800s. For example, total consumption from all sources was estimated to be only 500 tons in 1860 and 2,000 tons in 1870. By 1900, its use had increased modestly to 5,000 tons. It did, however, become a major nitrogen source following the establishment of numerous coke ovens associated mainly with the steel industry of this country.

By-product ammonium sulfate from coke oven gases became the most important nitrogen fertilizer from the 1920s until 1944 when it was overtaken by ammonium nitrate. After attaining a maximum of 981,000 tons in 1955, production from this steel industry related source declined thereafter.

Synthetically manufactured ammonium sulfate began to appear in the 1920s and production rose from 89,000 tons in 1945 to over 1,000,000 tons in 1950. It gained even greater prominence in subsequent years and in 1980 production was 2.1 million tons compared to 398,000 tons of by-product ammonium sulfate. Total usage of ammonium sulfate in 1994 was 950,000 tons.

## Calcium Cyanamide

Nitric acid and calcium nitrate were being manufactured in Norway by 1905. Shortly before this time, German chemists discovered how to synthesize calcium cyanamide and its agronomic value was confirmed around 1901. The first commercial plant for its manufacture was built in Italy in 1905. By 1918, there were 35 plants operating globally in such countries as Germany, Dalmatia, France, Switzerland,



**Figure 1.7** Air nitrogen plants for taking this element from the air and combining it with other elements for form fertilizer compounds. American Cyanamid Company plant, Niagara Falls.

Norway, Japan and Canada.

It is noteworthy that calcium cyanamide was the first fixed nitrogen fertilizer to be produced on an ongoing basis in North America. Manufacturing of this material started in 1910 at Niagara Falls, Ontario and moderate consumption at levels of about 100,000 tons annually occurred in the 1920s and 1930s. Following maximum usage of 131,000 tons in 1946, it has virtually disappeared from the market place with only 71 tons consumed in 1980.

## Anhydrous Ammonia

After Haber and Bosch's 10 or more years of intensive research and development on the synthesis of ammonia from its elements, the first commercial plant for production of ammonia opened in Germany in 1911. Manufacturing of synthetic ammonia in the United States began in 1921 with water gas as the source of hydrogen. A second U.S. plant, utilizing by-product hydrogen from the electrolytic formation of chlorine came on stream in 1922. By 1932, nine companies were operating 11 ammonia plants in the U.S. with most of them having small capacities of 25 short tons or less per day. However, two of these plants had much larger capacities of 120 and 27 short tons/day and they represented 87 percent of the nation's capacity.

With the onset of World War II, 10 new ammonia synthesis plants were constructed, the first of which commenced production in 1941. At the end of 1950, 19 plants with an annual capacity of 2.7 million tons of ammonia were operating and at this time 70 percent of the country's domestic nitrogen consumption was from ammonia synthesis.

As a result of another round of expansions in ammonia capacity ending in 1960, the number of plants increased to 56 with an annual capacity of 5.2 million tons. Now synthetic ammonia represented 95 percent or more of the nitrogen in U.S. fertilizers. Use of natural gas as an ammonia feedstock became dominant in the 1950s. Of the 53 ammonia plants operating in 1957, 72 percent were using natural gas.



**Figure 1.8** The world's first 1,000-ton-per-day ammonia plant was designed and built for Coastal Chemical Company at Yazoo City, Mississippi.

In 1960, about one-half of the ammonia synthesis plants also produced nitrogen fertilizers, either at the plant site or nearby. Eighteen of the 56 plants operating at that time also produced solid ammonium nitrate and 700,000 tons of dry urea fertilizer were made at 13 of these plants. At five of the plants both ammonium nitrate and urea were manufactured. Various nitrogen solutions were also being made at some of the ammonia plants.

A major advance in the technology of ammonia production occurred in the early 1960s when the M.W. Kellogg Company introduced the jumbo-size, single train, centrifugal compressor ammonia plants. Ammonia could be produced in these large efficient plants at one-half

the cost of smaller plants equipped with the conventional reciprocal compressors. The number of new plants based on this advanced technology grew rapidly from one in 1963 to 10 in 1967, 28 in 1969, 38 in 1971, 39 in 1976, and 43 by 1980. Ammonia production capacity of the new plants in 1980 totaled 14.7 million tons/year or 71 percent of total U.S. ammonia capacity.

As more of the large 1,000 - and 1,500 ton/day plants came into operation, many of the older, smaller obsolete plants were shut down. Although the new plants were more reliable and economical, their operating rates could not be lowered to less than about 70 percent of capacity. Thus, it became much more difficult to maintain an economical supply-demand balance.

Accompanying the rapid acceptance of the new generation of ammonia plant, were major changes and modernization in storage and transportation of the enormous amounts of ammonia being produced. For example, there was a marked shift to refrigerated storage tanks capable of holding liquid ammonia at atmospheric pressure; jumbo rail tank cars of 70 to 80 ton capacities; fully dedicated, refrigerated barges with capacities of 2,000 to 3,000 tons; ocean-going vessels with refrigerated tanks or holds for transporting liquid ammonia, and long-distance pipelines.

The first use of anhydrous ammonia on cropland took place in 1932 in California where it was applied in irrigation water. It was first directly injected into soil in 1942, also in California. By the mid-1940s, ammonia became available from large U.S. government plants in the Midwest which facilitated the spread of its use east of the Rocky Mountains.

Due to the adaptability of ammonia to a wide variety of conditions and its price competitiveness, growth in consumption in the U.S. has been rapid, from just a few thousand pounds in 1934, to over 1.1 million tons in 1964 and 5.5 million tons in 1994. Anhydrous ammonia, excluding aqua ammonia, now accounts for 35.9 percent of the nitrogen applied to U.S. cropland.

## **Ammonium Nitrate**

This nitrogen compound was first employed as a fertilizer in Europe following World War I when large stocks not utilized for explosives were released for agricultural use. Because of explosions in Germany in 1920 and 1921, it was usually dry-mixed with limestone, gypsum, chalk or ammonium sulfate to avoid such danger and to also serve as conditioning agents.

The first use of ammonium nitrate in the United States occurred in 1926 with product imported from Germany. It was not until 1943 that significant amounts of this nitrogen source were available to American farmers when supplies exceeded the needs for munitions. Additional surplus quantities of this material were released for fertilizer use in 1944 and 1945.

In the 1970's ammonium nitrate was produced at 29 locations separate from ammonia plant sites. Production of solid and solution ammonium nitrate fertilizer increased continuously from 383,000 tons in 1943 to 7.3 million tons in 1980. Manufacture of solid product was greater than the solution form until 1978, after which it accounted for less than half of the total produced.

Ammonium nitrate accounted for about one-third of all the nitrogen applied directly to U.S. cropland in 1955. By 1980, this use had declined to 10 percent. The tonnage of directly applied nitrogen as ammonium nitrate was exceeded by anhydrous ammonia in 1960, by nitrogen solutions in 1970 and by urea in 1978. Ammonium nitrate supplied 5.3 percent of the total 12.6 million tons of nitrogen consumed nationally in 1994.

## **Urea**

The present commercial method of synthesizing urea through the reaction of ammonia and carbon dioxide was first introduced in Germany in 1920. In the U.S., commercial synthesis of urea was first achieved in 1932.

Use of urea, including calcium nitrate-urea as a fertilizer in this country, started in the early 1920s with imported material mainly from Germany. Production of urea in the U.S. for fertilizer purposes increased dramatically from 47,000 tons in 1948 to 549,000 tons in 1960. Expansion in urea capacity slowed between 1960 and 1975, eventually reaching 3 million tons at the end of this period. By 1980, production of fertilizer urea was 7.2 million tons, 60 percent of it in solid form. In 1960, 75 percent of the total primary urea solutions produced at anhydrous ammonia plants was utilized as fertilizer and by 1982 this usage had increased to 92 percent.

Urea consumption in 1994 accounted for 14.7 percent of the 12.6 million tons of nitrogen applied to U.S. croplands.

## **Natural Organics**

Poudrette or human excrement, cottonseed meal, fish scrap and slaughterhouse wastes were major sources of fertilizer nitrogen in the United States from about 1850 to 1900. In 1910, 90 percent of the fertilizer nitrogen consumed in the U.S. was in the form of natural organic materials including cottonseed meal, dried blood, fish scrap and animal tankage. The significance of these materials subsequently declined rapidly and by 1920 and 1950 they provided only 34 and 3.4 percent, respectively, of fertilizer nitrogen usage. Much of this decrease after 1920 was the result of increasing competition from synthetic nitrogen fertilizers derived from ammonia plus diversion of the higher quality organics to more profitable livestock feed supplements. Two new natural organics, activated sewage sludge and digested sewage sludge were introduced in the 1950s.

## Phosphorus (Phosphate, P<sub>2</sub>O<sub>5</sub>)

### Phosphate Rock

Phosphate rock is the only economical source of phosphorus for production of phosphate fertilizers and phosphate chemicals. Most of the world phosphate rock reserves are widely distributed marine phosphorite deposits.

Phosphate ores were first mined in relatively small amounts in the mid-1840s in England, France and Spain and in the 1860s in Norway and Germany. Between 1863 and 1895, phosphate rock was shipped from deposits in Ontario and Quebec to England for processing.

Mining of phosphate in the United States began in 1867 in South Carolina where the ore was first discovered in 1837. Utilization of the vast phosphate rock deposits of Florida found in the 1880s started in 1889. In the Rocky Mountain States, mining of phosphate began in 1906 in Idaho, in Wyoming and Utah in 1907 and in Montana in 1921. The North Carolina deposits were the latest to be exploited and mining started there in the mid-1960s .

Ore in Algeria and Tunisia was discovered in 1873 and mining initiated in 1889. Production from the large Moroccan deposits, first identified in 1914, began in 1921. The guano phosphate deposits in the Pacific Islands were found in the 1890s and mining commenced in 1900 on Ocean Island, in 1906 on Nauru Island and in 1908 on Makatea Island.

The extensive deposits of igneous apatite of the Kola Peninsula in the Former Soviet Union (FSU) were recognized in about 1930. Many other deposits were found in the period 1960 to 1980 in Mexico; Brazil, Peru and Colombia in South America; Israel, Turkey, Jordan, Iraq and Saudi Arabia in the Near East; Angola, South Africa and Western Sahara in Africa; India and Australia. A large number of these recent finds are now in commercial production.

Currently the leading countries in the mining of phosphate rock are the U.S.A., FSU, Morocco and Algeria, People's Republic of China, Tunisia, Jordan, Republic of South Africa, Brazil, Togo, Israel, Nauru, Senegal and Syria. Morocco has the greatest reserves, followed by South Africa, U.S.A. and the FSU. China's reserves are believed to be much more extensive than reported and may rank as high as fourth in the world.



**Figure 1.9** Artist's rendition of phosphate operations of Charleston Mining and Manufacturing Company. The oldest U.S. phosphate mining company, it began operations in 1866 and was acquired by Virginia-Carolina Chemical Company in 1900. (*Mobile Mining and Minerals Company*)



**Figure 1.10** U.S. phosphate rock reserves.

Phosphate rock reserves in the U.S. occur mainly in Florida; North Carolina; the Western states of Idaho, Utah, Wyoming and Montana; and Tennessee. Although the greatest reserves exist in the Western states, Florida leads in mining of phosphate ore. Factors such as the generally high grade of ore, vastness of the resource, ease of recovery and closeness to both requisite sulfur used in processing the phosphate rock and ocean shipping have all contributed to the economic success of the Florida phosphate operations.

## Phosphoric Acid

Phosphate in the naturally occurring phosphorite ores exists in several variations of the very stable apatite compound. In the manufacture of the common phosphate fertilizers, the strong bonding in the apatites is broken by chemical or thermal processes to render the phosphate more soluble. Treatment with sulfuric acid to produce phosphoric acid is the most widely used method of accomplishing this breakdown.

The first phosphoric acid plant was built in Germany in about 1870. In the U.S., phosphoric acid was first manufactured in 1890.

## Phosphatic Fertilizers

Animal and human bones were not always effective in improving or sustaining crop yields and the superphosphate industry came into being as a result of attempts to increase the effectiveness of bones and also to find a more plentiful and secure source of phosphate. The brisk demand for bones in England in the early 1800s led to the importation of bones from the Continent starting in 1815 and reaching a high of 30,000 tons annually. Justus von Liebig criticized the English for collecting bones from old battlefields and burial sites such as the catacombs of Sicily.

As early as 2,000 years ago, Chinese farmers applied calcined or lime-treated bones to their fields. Several individuals, including von Liebig, in Europe during the early 1800s to 1842 acidulated bones, usually with sulfuric acid, to improve the solubility of phosphorus.

In 1842, Lawes of Rothamsted fame was granted a patent for the production of superphosphate and he began manufacturing and selling this fertilizer the same year. His patent was amended in 1848 restricting the sulfuric acid treatment to only apatite and phosphorite. By 1853, there were 14 superphosphate manufacturing plants in England.

Superphosphate production was adopted in the late 1840s and the 1850s by the United States and a number of other countries using bones as the primary source of phosphate. U.S. superphosphate manufacturing began in South Carolina in 1849 and a thriving



**Figure 1.11** Sir John Bennet Lawes

industry involving up to 16 companies subsequently evolved with an output of about 140,000 short tons by the mid-1880s.

For more than 100 years superphosphate was the world's leading phosphate fertilizer. It predominated in the U.S. from 1870 to 1964 and peaked in 1952. Triple or concentrated superphosphate replaced it as the principal phosphate source for a short interval between 1964 and 1967. In 1994, consumption of ordinary or normal superphosphate was a mere 10,500 tons.

Triple (concentrated) superphosphate was initially produced in Germany in 1872. Its manufacture in the U.S. started on a limited scale in 1890 with sustained production not commencing until 1907. This higher analysis phosphate source assumed greater importance after World War II up to about 1970 when its popularity began to decline. By 1994, it represented only approximately 4.8 percent of the 4.5 million tons of plant nutrient phosphorus used in this country.

Ammonium phosphates, which are now the dominant phosphate sources worldwide, were first produced commercially in the U.S. in 1916. The very popular and dependable TVA process for granular diammonium phosphate (DAP) was introduced in 1961 and by 1967 it became the principal phosphate fertilizer in the U.S. Nineteen plants utilizing this technology with a combined capacity of 2 to 3 million tons of product annually were installed in 1962. Two years later there were 31 such plants.

By 1974, DAP became the most widely used phosphate fertilizer worldwide. Mono- and diammonium phosphate accounted for about 60 percent of global fertilizer phosphate production in 1981. Di- and monoammonium phosphates supplied 38.8 and 14.3 percent, respectively of U.S. phosphate usage in 1994.

## Potassium (Potash, $K_2O$ )

Virtually all of the economic sources of potassium occur in sedimentary salt beds remaining after the evaporation of ancient seas and lakes. World reserves of such potassium-bearing deposits are immense and they total about 250 billion tons of  $K_2O$ , of which 9.4 billion tons are considered commercially exploitable. With current global consumption of about 25 million tons of  $K_2O$  annually both economical reserves and total resources are sufficient to satisfy world demand for centuries.

## Location Of Potash Deposits

The potassium fertilizer industry originated in Western Europe where significant ores exist in several countries including Germany, France, Italy, Spain and the United Kingdom. Depletion of reserves is expected in the medium term in Spain, France and Germany.



**Figure 1.12** When completed in the mid-1960's, this IMC facility at Esterhazy, Saskatchewan was the world's largest potash complex, able to supply one-tenth of the world demand.

North America, with the world's greatest known reserves of potassium, is now the largest producing and exporting region in the world. The reserves are located in the Canadian province of Saskatchewan with smaller deposits in New Brunswick and Manitoba and also in the U.S.A. in the states of New Mexico, Utah, California and Michigan.

The former Soviet Union (FSU) has extensive proven reserves of potassium ore and prior to its division it was the world's largest producer of potassium fertilizers.

In the Near East, potassium fertilizer salts are extracted from the Dead Sea in Israel and Jordan.

Small amounts of potassium fertilizer are obtained from brines in Qinghai Province of China and a substantial expansion in utilization of this is currently underway. Elsewhere in Asia, development work has started in the ore deposits of northeastern Thailand and the feasibility of utilizing another substantial source of potash in that country is being evaluated.

Reserves of potassium salts are limited in South America. Limited quantities of potassium fertilizer are produced in Brazil's Sergipe Basin. The feasibility of producing potassium fertilizer in Argentina and from potash brine in Chile is currently under study. Chile's production of specialty potash products is based on its nitrate deposits.

Capacity for production of potassium fertilizer salts is currently much in excess of world demand. For example in 1992, Canadian mines operated at close to 60 percent of capacity while those of the FSU functioned at 58 percent and other major world producers operated at levels of 80 to 95 percent.

## Mining Of Potash Deposits And Production Of Fertilizers

At least 95 percent of world production of potassium fertilizers is in the form of potassium chloride. Potassium sulfate is the next most important source followed by much smaller quantities of specialty materials such as potassium magnesium sulfate, potassium nitrate, potassium thiosulfate, potassium polysulfide, potassium carbonate and potassium bicarbonate.

The potassium fertilizer industry originated in Western Europe with the world's first potash factory being installed in Germany in 1857. The existence of potassium-rich deposits in that country had been known several years earlier but manufacturing was delayed until processes were developed for separating potassium chloride from unwanted carnallite in the ore. Germany held a monopoly on potash production up to World War I and in the period immediately after this conflict. It continued to have a dominant role in potash even up to World War II.



**Figure 1.13** IMC Continuous Mining Machine

At the end of these later hostilities and the political division of the nation, all aspects of the potash industry including production and marketing were separated. This split resulted in the German Democratic Republic (East Germany) becoming a slightly larger producer than the Federal Republic of Germany (West Germany). Upon reunification of the two Germanys in the early 1990s, a significant portion of the less efficient capacity in the former East Germany was closed. However, Germany still remains the largest producer of potassium fertilizers in Western Europe.

France began production of potash in about 1910 and its capacity decreased in the early 1990s. Italy and Spain continue to be minor producers. The United Kingdom started production of potassium fertilizer from its difficult ore body in 1974.

Extensive reserves of high-grade potassium ores were discovered in the FSU in 1925. Prior to the separation of the FSU's potash fertilizer industry into the Russian and Byelorussian sectors at the end of the 1980s, it had the world's largest potash production capabilities.

Recovery of potassium salts from the Dead Sea in the Near East region was undertaken in 1931 and then discontinued in 1947. Israel first began to extract potassium fertilizer salts from the Dead Sea in 1952 while Jordan initiated its operations to exploit the same source in 1983.

1979 was the first time that production of small amounts of potassium fertilizer was recorded in China. Production continued at modest levels through the 1980s with a significant increase in capacity planned for 1997 or 1998.

Africa and Asia (excluding China) are now without potash fertilizer production capability. Limited production in northeastern Thailand is anticipated after 1998.

Reserves of potassium salts are modest in South America where production of small amounts of potassium fertilizer began about 1986 in Brazil's Sergipe Basin. There is a strong possibility that potassium fertilizer manufacturing will be started in Argentina

shortly before the year 2000. The feasibility of producing potash fertilizer from brine in Chile is being evaluated. Chile's current production of specialty potassium fertilizers is based on its nitrate deposits.

## **Potash Production And Consumption In The United States**

Potash was an important component of U.S. fertilizers in the years 1870 to 1920. At the beginning of this period, the only obtainable sources, in limited amounts, were tobacco stems, wood ashes, cotton hulls and cotton boll ashes. The potash supply situation improved in about 1875 with importation of potash salts from Germany. By 1890, the German supplies dominated all other sources, and they continued to do so until 1914, at the beginning of World War I hostilities. These German imports ceased in 1917 when the U.S. entered the War.

During the World War I years of 1914 to 1918, a wide variety of potash sources were utilized including brines from Searles Lake, California; alunite (a potassium aluminum sulfate mineral) from Utah; brines from lakes in Western Nebraska; salty waters from Great Salt Lake; dust from cement kilns; wastes from distilleries and sugar refineries; kelp harvested off the shores of California and other materials of lesser importance. The brines represented 73 percent of the potash produced in these years.

An intense search for domestic supplies of potash began in 1910 in an attempt to become independent of the German potash monopoly. The German potash embargo in World War I heightened this search. These hunts led to the discovery of the New Mexico potash beds in 1925. Further exploration clearly identified the existence of a substantial deposit of potash salts and between 1932 and 1935 a thriving potash fertilizer industry founded on these deposits was established. Also it marked the beginning of an extended period of potash independence lasting from 1935 to 1966. Before 1935, domestic production of potassium fertilizer was restricted mainly to Searles Lake and a number of smaller operations based primarily on recovery of by-product potash and low-grade products from brines.

By 1966, seven potash mines in New Mexico and one in Utah were being operated. Potassium fertilizers were also being produced from the Searles Lake brines by two companies and by one other operation at the Salduro Marsh in Utah. Domestic production reached an all-time high in 1966 and it has declined steadily since that time. This reduction was due to two important factors including the quality and competitiveness of the New Mexico ores and the impact of the newly established Canadian potash industry.

Recovery of potassium salts from the natural brines of Great Salt Lake was initiated in 1970. A major expansion scheduled for completion in 1996 will approximately double potash fertilizer production capacity at this source.

In the mid-1990s, the centers of potash fertilizer production were located in New Mexico, Utah, California and Michigan. Approximately 80 percent of the total production capacity existed in New Mexico.

As early as 1937, potassium chloride accounted for 85 percent of the total U.S. potash consumption and since then its popularity has increased to the point that it now represents 94 to 95 percent of total potash usage in this country.

In the late 1970s, 84 percent of the total U.S. potash fertilizer production was in the form of potassium chloride with the remainder being principally potassium sulfate and potassium magnesium sulfate.

U.S. consumption of potash has grown significantly from 239,000 tons of  $K_2O$  in 1934, to 1.10 million tons of  $K_2O$  in 1950, to 2.15 million tons of  $K_2O$  in 1960 and reached a maximum of 6.32 million tons of  $K_2O$  in 1981. In the first four years of the 1990s, usage has ranged between 5.00 and 5.27 (in 1994) million tons of  $K_2O$ .

## **Potash Production In Canada**

The potash deposits discovered in Saskatchewan in 1943 are believed to be the greatest reserves of high-grade potassium reserves in the world. Mining of these ores commenced in 1962 and production capacities were expanded in the 1970s and 1980s. Substantial quantities of the potassium chloride produced from these immense deposits soon began to be exported to the U.S. and by 1966 these exports comprised 38 percent of total consumption and this figure was 79 percent in 1980.

Because global capacity for production of potassium fertilizer salts has for many years been in excess of world demand, the Saskatchewan mines have at times operated at much below capacity, as low as 45 percent or less. In 1992, the nine mines in Saskatchewan operated at close to 60 percent. By way of comparison, the U.S. potash industry ran at 84 percent in 1992 and 92 percent in 1993.

The potash ore in Saskatchewan is extracted by dry mining methods at seven of its nine mines while solution mining is used at the two remaining mines.

In addition to the extensive potash mining and fertilizer production in Saskatchewan, there are now two potash fertilizer production facilities in the Atlantic province of New Brunswick. The high-grade ores in that province were found in 1971. The first of the two mines came on-stream in 1983 followed by the second in 1984. Of the total Canadian potash fertilizer production capacity of 13.11 million tons of  $K_2O$ , New Brunswick accounts for about 1.43 million tons or 11 percent.

## **Granular, Homogeneous, Mixed Fertilizers**

The impetus for production of granular, homogeneous NPK fertilizers in the U.S. occurred in 1953 with the introduction of the Tennessee Valley Authority's (TVA) continuous ammoniator-granulator. This equipment was originally developed to replace the commonly used batch process of ammoniating superphosphate.

It was observed that the granulation often encountered during ammoniation could be controlled by adding water or steam and, if the heat of reaction was insufficient, by also

supplying sulfuric or phosphoric acid and more ammonia. These findings lead to the development of a process for producing high-analysis, granular compound fertilizers. The initial grades of 6-12-12 and 10-20-20 were later replaced by typical analyses such as 8-24-24, 10-20-30, 12-24-12, 13-13-13 and 15-15-15.

Although the homogeneous, granular NPK plants required relatively large capital investment, by 1962 there were 250 granulation plants of varying size operating in the



**Figure 1.14** Ammoniation-granulation plant of Missouri Farmers Association, Palmyra. (F. J. Myers, TVA)

United States. Approximately two-thirds of these plants used the TVA technology and typically produced about 70,000 tons annually. Production from the larger plants was destined primarily for the farm market and distributed through bulk handling outlets. About 40 percent of the granulated, compound fertilizers

were sold to bulk blenders for use in their prescription mixes or resale to farmers. The smaller manufacturers served mainly the non-farm and specialty markets with most of their production being bagged.

The number of ammoniation-granulation plants in the U.S. has declined from a high of 300 in 1964 to 108 in 1981, 72 in 1985, 37 in 1989 and 25 in 1995. Most of the survivors are large regional plants, producing in excess of 130,000 tons per year, and they may often manufacture base NPK fertilizers, containing significant amounts of secondary and micronutrients, for use in formulating bulk blends. Also, many of the remaining plants produce both granular, homogeneous NPKs and diammonium and monoammonium phosphates for sales to bulk blenders and retailers in their areas.

TVA's invention of the pipe-cross reactor in 1974 was an important advance in granulated, homogeneous mixed fertilizer technology making possible greater production capacity and lower energy requirements.

In the early 1960s, the ammoniation-granulation plants accounted for almost 80 percent of the mixed fertilizer market. By the early 1980s this proportion had decreased to 27 percent of the mixed fertilizers consumed nationally.

## Bulk Blending

Acceptance and expansion in the bulk blending system of marketing dry fertilizer materials in the U.S. and neighboring Canada has been phenomenal. This fertilizer distribution system features the production of high-quality granular products at large strategically located manufacturing plants and the transport of these materials to relatively small, local bulk blending plants for the mechanical formulation of specific fertilizer mixtures containing nitrogen, phosphorus, potassium, sulfur, magnesium and micronutrients. These mixtures, comprised of two or more dry granular fertilizer

materials, are applied in bulk to farm fields. Custom spreading of bulk blends is often one of the services provided at bulk blend plants.



Figure 1.15 In a bulk blending plant, ingredients typically are mixed in rotating equipment and discharged to a delivery vehicle. (F. J. Myers, TVA)

This mode of fertilizer marketing had its roots in Illinois in the late 1940s. It is a refinement of the early practice of adding potassium chloride, plus in later years ammonium sulfate, to pulverized phosphate rock. The materials most commonly used today include mono- and diammonium phosphate, triple superphosphate, potassium chloride, ammonium nitrate, urea and ammonium sulfate. These and any other products used in blending must be well granulated, the particles closely sized and sufficiently dry and strong.

In 1947, there were only four bulk blending operations in the U.S., all located in Illinois. By 1953, there were 14 such plants operating in Illinois and the numbers increased rapidly to 92 in 1957. This approach to serving farmers spread quickly throughout the Corn Belt and elsewhere in the country and by 1959 there were 186 plants operating. By 1966, the numbers had increased to more than 3,100 and in the early 1980s there were between 5,000 and 5,300 bulk blending plants. It has been reported that the numbers reached approximately 7,500 in 1995.

By 1967, 35 percent of all fertilizers consumed in the U.S. were in the form of bulk blends. This proportion increased to 40 percent in 1976 and since 1979 it has remained at about 52 percent of the total fertilizer marketed nationally.

## Fluid Mixed Fertilizers

As was noted earlier, fluid fertilizers (clear liquids and suspensions) have been used for centuries. The Greeks transported sewage from Athens through a system of canals to adjacent vegetable gardens and olive groves. It was, and continues to be, common practice in Asian countries such as China, Japan, Korea and Vietnam to collect slurries of human and animal wastes and following transfer to fields by means of buckets and small barrels on carts, etc. they are ladled onto cropland.

In 1808, the Englishman, Sir Humphrey Davy tested an inorganic liquid fertilizer which he had developed. An Irish physician, James Murray, began in 1841 to produce and sell liquid fertilizers made by pouring sulfuric acid over crushed bones. The use of liquid barnyard and sewage wastes on agricultural lands was reported in numerous farm publications in the 1800s.

### Liquid Mixed Fertilizers In The United States

After a modest beginning in California between 1923 and 1928, the U.S. liquid mixed fertilizer sector grew slowly until the decade of the 1950s when it expanded rapidly in

the Midwest and Pacific Northwest. The early mixed fertilizers prepared from phosphoric acid and dissolved ammonium nitrate and potassium chloride were acidic and very corrosive. Successful methods were developed to produce solutions that were near neutral in reaction.

Cold mixes, formulated by dissolving solid ammonium nitrate or urea, ammonium phosphates and potassium chloride were prevalent in the 1950s. Later hot mixing, utilizing the heat generated from the neutralization of phosphoric acid with ammonia to aid in the dissolution of potassium chloride, became popular.

Three major advances were made between the mid-1950s and 1972 in the technology of producing high quality, clear liquid fertilizers. First, there was the discovery of the importance of superphosphoric acid in sequestering aluminum, calcium, magnesium and the metallic micronutrients copper, iron, manganese and zinc when ammonium polyphosphate solution was made by ammoniating superphosphoric acid. This development was followed with the finding in 1961 that wet process superphosphoric acid could be made by simply concentrating regular wet process acid.

The third significant breakthrough occurred in 1972 when TVA developed and introduced a simple pipe reactor for the production of ammonium polyphosphate (11-37-0 and 10-34-0) solutions. This process proved to be an economical method of producing clear liquid mixes of higher nutrient content than was previously possible.

In response to the need to increase the nutrient content of liquid fertilizers, especially with respect to potassium, TVA introduced suspensions in 1963. They are composed of finely divided solids or crystals of fertilizer salts kept in suspension, by means of a gelling clay such as attapulgite or sodium bentonite, in saturated fertilizer solutions.

Plant nutrient consumption as fluid fertilizers increased at the rate of seven percent annually during the 1970s and early 1980s which greatly exceeded the four percent annual gain in total plant nutrient consumption experienced during the same period in the U.S. In 1980, 17 percent of all fertilizer consumed nation-wide was in the form of fluid products. Their share of the total domestic fertilizer market increased in 1991 and 1994 to 20.3 percent of 44.3 million tons and 20.5 percent of 52.3 million tons, respectively.

Mixed fluid fertilizers, those containing nitrogen and phosphorus; nitrogen and sulfur; potassium and sulfur; nitrogen, phosphorus and potassium or nitrogen, phosphorus, potassium and sulfur have gained wide acceptance and by the years 1990 and 1991 they represented about 22 percent of the total mixed fertilizer market. Their use in 1993 and 1994 has remained steady at between 20.3 and 20.9 percent of this fertilizer industry sector.



**Figure 1.16** Elevated view of small Kansas fluid fertilizer plant showing simple mixing equipment. (F. J. Myers, TVA)

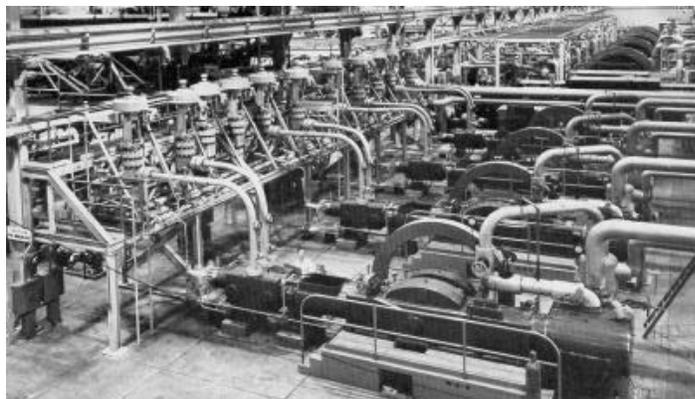
Use of suspensions increased rapidly in the 1980s in the U.S. and at one time they probably accounted for up to 40 percent of the fluid mixtures consumed in this country. Their popularity has diminished in recent years and they may now account for only 25 to 30 percent of fluid mixture usage.

## Summary

Commercial fertilizers have a short history compared to the 6,000 to 10,000 years man is known to have grown crops. It was not until the 1830s that limited amounts of a few types of naturally occurring commercial fertilizers such as Peruvian guano and Chilean sodium nitrate were first used in the United States and elsewhere in the Western world. However, many of the ancient civilizations and cultures attempted to maintain and improve crop production through the use of a variety of mineral and organic substances of uncertain nutrient content, such as marl, plant and wood ashes, ground animal and human bones, saltpeter, gypsum, animal and human wastes, crop residues and green manures.

The German chemist, Justus von Liebig, is considered by many to be the father of agricultural chemistry and the fertilizer industry beginning in about 1840. In 1842, the first commercial fertilizer patent was granted to Lawes of Rothamsted fame for the manufacture of superphosphate. Production of commercial fertilizer in the U.S. began in 1849 in South Carolina at the nation's first superphosphate plant.

Many changes have occurred in the United States fertilizer industry since its early beginnings in the 1830s of importing low analysis nutrient sources such as guano and sodium nitrate. From about 1850 to 1900, poudrette or human excrement, cottonseed meal, fish scraps and slaughterhouse wastes were the principal sources of fertilizer N. By-product ammonium sulfate from coke oven gases became the most important N fertilizer from the 1920s until 1944 when it was overtaken by ammonium nitrate. Synthetically manufactured ammonium sulfate which began to appear in the 1920s had by the 1980s become much more important than by-product ammonium sulfate. For a short time in the 1920s and 1930s, there was moderate consumption of calcium cyanamide imported from Canada.



**Figure 1.17** Some of the equipment at a small ammonia plant built at Muscle Shoals in the early 1940's. Worthington circulators are in foreground and Cooper-Bessemer compressors in right background. (G. L. Bracey, TVA)

Rapid expansions of the ammonia industry starting in the early 1940s resulted in the availability, after 1943, of significant amounts of ammonium nitrate for fertilizer purposes. Consumption of ammonium nitrate increased rapidly up to 1955 when it represented about one-third of the N applied directly to U.S. cropland. However, by 1994 ammonium nitrate usage had declined to only 5.3 percent of the total fertilizer N used nationally.

The same developments in ammonia production, particularly

between 1960 and 1980, greatly increased the production and importance of urea as a N fertilizer. In 1994, it accounted for 14.7 percent of the N applied to the nation's cropland.

Urea-ammonium nitrate, nonpressure fertilizer solutions are readily made from the concentrated urea and ammonium nitrate solutions available at ammonia plants. Beginning about 1960, consumption of these solutions grew rapidly and in 1994 they provided 21.5 percent of total N fertilizer use in the U.S.

Due to the adaptability of ammonia and its price competitiveness, it too has undergone very large and rapid increases in usage during the past 40 years. About 36 percent of the N currently used in the U.S. is in the form of anhydrous ammonia.

The United States is rich in phosphate rock resources found mainly in Florida; North Carolina; the Western states of Idaho, Utah, Wyoming and Montana; and Tennessee. Although the greatest reserves exist in the Western states, Florida leads in the mining of phosphate ore.

Superphosphate was the dominant processed fertilizer P material in the U.S. from 1870 to 1964. Triple or concentrated superphosphate replaced it as the principal P source in 1964. Diammonium phosphate became the principal P fertilizer in 1967. Di- and monoammonium phosphate provided 39 and 14 percent, respectively, of U.S. phosphate usage in 1994.

Potash became an important component of U.S. fertilizers in 1870 with it being obtained in limited quantities from the low analysis materials tobacco stems, wood ashes, cotton hulls and cotton boll ashes. From 1875 to 1914, imports of potash salts from Germany satisfied most of U.S. requirements. A wide variety of domestic potash sources such as lake brines, alunite, cement kiln dust, distillery and sugar refinery wastes and kelp were utilized when German imports were interrupted during the World War I years of 1914 to 1918.

The potash deposits of New Mexico were discovered in 1925 and mining commenced in 1932. This potash resource adequately served the nation's needs up to 1966 after which its importance declined steadily due to the competitiveness of high quality potash from the Canadian mines in Saskatchewan and New Brunswick. Significant recovery of potash salts from the natural brines of Great Salt Lake began in 1970 and is now being expanded.

Granular, homogeneous, high analysis NPK fertilizers became widely available in the U.S. after 1953 through adoption and subsequent modifications to the granulation process which took place during the ammoniation of superphosphate.

The number of ammoniation-granulation plants has declined from a high of 300 in 1964 to 25 in 1995. Many of the surviving plants manufacture base NPK fertilizers, containing significant amounts of secondary and micronutrients, for use in formulating bulk blends.

The first commercial production of bulk blends in the United States occurred in Illinois in the late 1940s. This approach to supplying farmers with prescription mixtures of NPK and other essential nutrients formulated for specific areas of their cropland gained rapid acceptance. The number of blenders increased from just six in 1950 to 1,536 in 1964 and about 7,500 in 1995. Noteworthy reasons for this phenomenal acceptance include the flexibility in producing a virtually endless range in NPK plus other nutrient mixtures to satisfy specific local soil and cropping conditions; lower cost of nutrients compared to the granular, homogeneous NPKs; improved quality of the high analysis N, P and K materials used in blending and the various attractive services offered to farmer customers.

After a modest beginning in California between 1923 and 1928, the liquid mixed fertilizer sector experienced little growth until the 1950s when it expanded rapidly in the Midwest and Pacific Northwest. The major advances made during the mid-1950s to 1972 involving recognition of the importance of ammonium polyphosphate in producing high quality, clear liquid fertilizers and processes for its production contributed greatly to the growth in use of mixed liquid fertilizers. They now account for approximately 20 to 21 percent of the nation's total mixed fertilizer market.

All fluid fertilizers, including N only materials and the various NP, NS, KS, NPK, and NPKS, etc. mixes, represented 20.5 percent of the total nationwide fertilizer market of 52.3 million tons in 1994.

### **Links to other sections of the Efficient Fertilizer Use Manual**

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