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Fluid Fertilizers

Fluid Fertilizers

J. M. Potts, Editor

Tennessee Valley Authority
National Fertilizer Development Center

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Chapter 1

History, Growth, and Status

By Ronald D. Young and Norman L. Hargett

Liquid (fluid) fertilizer production and use is generally regarded as a relatively new (mid-20th century) practice, which is true if we are thinking of commercial significance. But like many other developments popularly regarded as new departures, the beginnings of liquid fertilizer go far back in history.

Early History

Possibly the earliest recorded use of a fertilizer material in liquid form, if we broaden the definition of fertilizer to include the manures, was the practice in ancient Athens of fertilizing truck gardens and orange groves by city sewage carried in canals. Various other mentions of liquid manure, and of other liquids used to promote plant growth, are found in ancient histories.

Much later, but still quite early in the history of fertilizer technology, Sir James Murray in 1843 referred to the "new" practice in England of supplying fertilizers in solid form. The new type, he said, was "exempt from loss by leakage, more safe, portable, etc.," as compared with the previous liquid products, normally sold in 30-gallon casks. In the same year, Bishop in Scotland reported that aqua ammonia gave improved yields of grass. Subsequently, gas house liquors and other wastes were sold in liquid form.

One of the first references to use of a fertilizer in liquid form in the United States was by Joseph H. Webster, a "resident of Cumberland, in the County of Webster and State of Mississippi," who in 1899 patented a solution "consisting of water, saltpeter, sal-soda, blue-stone, nitrate ammonia, and potash." He did not use this solution directly as a fertilizer but sprinkled it over a mass of manure, "ashes, salt, lime, phosphate, kainit, and cotton-seed meats." However, his proposal deserves some note because the solution specified bears some resemblance to the liquid mixes made today (1).

Early Commercial Production

Possibly the first U.S. plant for producing a liquid fertilizer was the G&M Liquid Fertilizer Company, built in Oakland, California, in 1923. This was followed by the work of the Prizer Brothers who in 1928-30 developed the "Prizer Applicator," a machine for dissolving a solid fertilizer and metering the resulting solution into irrigation water through either a gravity-flow or pressure system (2).

Ammonia production began in this period in the United States. Plants were built in Syracuse, New York, in 1921 by a subsidiary of Allied Chemical Corporation; at Belle, West Virginia, in 1926 by E. I. du Pont de Nemours and Company; and at Hopewell, Virginia, in 1928 by Allied. With a domestic supply of ammonia available, the liquid fertilizer industry was in position to move forward at a faster rate. In 1932, Shell Chemical Company began research on introduction of ammonia into irrigation water and followed this by injection into the soil in 1942 (2). In about the same period, ammoniating solutions were developed for use in making solid fertilizers. For example, in 1932 du Pont first introduced urea-ammonia-water solution, composed of urea, ammonia, ammonium carbamate, and water. Such solutions, containing ammonia with urea or ammonium nitrate, were likely candidates for direct application, and the first application of a nitrogen solution took place on a cane field in Louisiana in 1942.

There were problems in handling and application of solutions that were under pressure and subject to emission of ammonia fumes. This led to research aimed at the development of nitrogen solutions without any vapor pressure of ammonia. In 1942, Allied Chemical Corporation

began testing a solution of urea and ammonium nitrate, materials that have such a mutual solubility effect as to allow nitrogen concentrations as high as 32%. This work was interrupted by the war and was resumed in 1950, when the first farm application took place. Prior to this, ammonium nitrate solutions were used in California as early as 1944.

Liquid mixed fertilizers, after the start in 1923, grew very slowly. The practice was of necessity based on dissolution of solid materials because little or no phosphoric acid was available. As late as 1943 less than 1,000 short tons of liquid mixed fertilizer was reported sold in California. The high cost of the raw materials restircted liquids mainly to special uses, such as foliar spraying, flower and garden fertilization, and correction of unusual soil deficiencies.

In 1937, Shell Chemical Company demonstrated the feasibility of adding phosphoric acid directly to irrigation water, and in 1940 the first commercial use of the method took place. Other pioneers in use of phosphoric acid were the John Pryor Company (Salinas, California) and the Hayward and Wood Company (Oxnard, California) (1).

In the 1940s, phosphoric acid—mainly the furnace type—became more available in California and production of liquid mixed fertilizers began to increase. The Leslie-Agriform Company, later to become a major producer of liquid mixes, started operation about 1946 in Newark, California. This company originally handled all its product in 15- and 30-gallon wooden barrels, and distributed solution as far as Phoenix, Arizona. The barrels were replaced a few years later with tanks of 1,000- to 2,000-gallon capacity. Corrosion was a severe problem and raw material costs were high. However, production by Agriform and others increased, to the point that by 1953 more than 22,000 tons of liquid mix was produced in California; this represented about 9% of all mixed fertilizer made in California.

In other areas of the country, Cominco Products, Inc., began making an 8-24-0 solution at Trail, B.C., in 1955. This was a new departure, because Cominco made the 8-24-0 from lower cost wet-process phosphoric acid (in conjunction with ammonium phosphate production), whereas the production in California was based on furnace-type acid. Much of the Cominco product was sold in Washington and Oregon.

In the middle and eastern parts of the United States, the only known production of liquid mixes prior to 1953 was in the form of specialty liquids made from soluble salts and usually packaged rather than sold in bulk. Startup of the Liquilizer Corporation plant at Vincennes, Indiana, in 1953 marked the beginning of the new practice—neutralization of phosphoric acid with ammonia and dissolution of potash in the resulting hot solution. The first grade made was a 4-10-10 but the next year ammoniating solution and solid urea were used to give such products as 9-9-9, 12-6-6, and 12-8-4 (1).

Two Dramatic Decades

The preceding discussion brings us to 1955, at which time both nitrogen liquids and liquid mixed (NPK) fertilizers were struggling industries. They were striving to break into an established, conservative, industry with a drastically different product form. The need for a different marketing system and for providing additional services, including custom application, were already apparent. The early pioneers had both technical and economic problems, and some of the companies did not survive. In a few years, however, the liquid products began to gain acceptance and use increased rapidly. The rate of growth from 1955 to about 1975 was greater than for any fertilizer in any similar period in fertilizer history.

Probably the first review of liquid mixed fertilizer production and use was published in 1955 (4). About 147 companies reportedly were operating in the field, but only 72 appeared to be making bulk fertilizer for farm use. Only 25 were reported east of the Rockies and most of these had gone into production in 1954-55. U.S. production in the year ended June 30, 1954, was only 27,500 tons. The dramatic growth in fluid mixed fertilizers during the period of 1954-75, both in number of producing units and in production of material, is shown in figure 1.

The approximately 1 million tons of liquid mixed fertilizers consumed in 1965 represented about 7% of the total mixed fertilizers consumed in the United States. Production for the approximately 1,200 fluid plants averaged less than

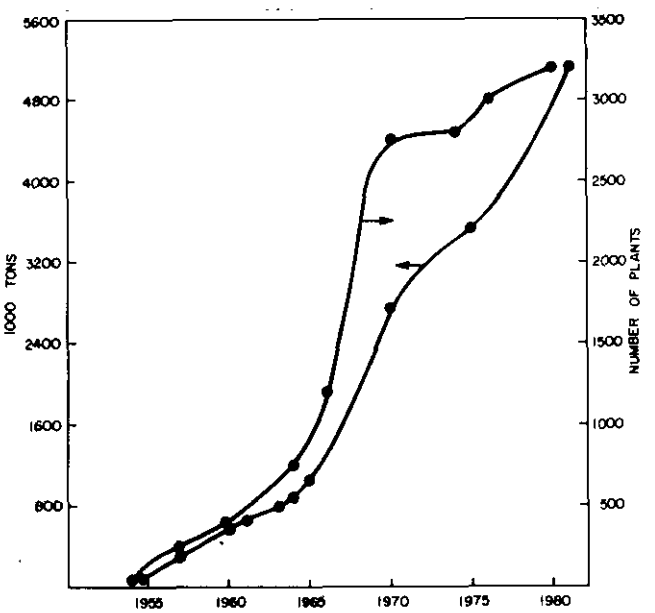

Figure 1. Growth in production of fluid mixed fertilizers, U.S.

1,000 tons per year. The next decade (1965-75) saw even more rapid growth in production and use of fluid mixed fertilizers. Suspension fertilizers, fluids in which some particles are suspended rather than dissolved, came into the picture after 1963 when TVA shipped the first tank car of 12-40-0 base suspension, offering considerably higher analysis than liquid (solution) fertilizers. Production of suspensions became substantial by the late 1960s and their production and use have grown steadily since. Suspensions contributed substantially to fluid production by 1970.

The number of mixed fluid plants in the United States grew from 1,200 in 1965 to about 2,800 in 1974. Total nutrient consumption as mixed fluids was only 143,000 tons ($N + P_2O_5 + K_2O$) in 1960. This increased sharply to 823,000 tons in 1970 and to about 1.3 million tons in 1975. Total nutrient content of mixed fluids ($N + P_2O_5 + K_2O$) was estimated to be about 28% in 1960. Growth of the higher analysis suspensions resulted in an increase to about 34% in 1974, and to about 35.2% total plant food content in 1981 (5).

Growth in number of plants slowed, but the total reached about 3,000 in 1976 and 3,200 in 1980. The total tonnage of mixed (NPK) fluids increased to about 1.8 million tons of nutrients ($N + P_2O_5 + K_2O$) in 1981. This represented about 5 million tons of fluid fertilizer materials. The 1.8 million tons of nutrients as mixed fluid fertilizers in 1981 accounted for about 7.5% of total nutrients applied in the United States, or 17% of total nutrients in mixed fertilizers.

T. P. Hignett in his Sixth Francis New Memorial Lecture in 1969 (6) gave a good assessment of the advantages for liquids.

> Liquid fertilizers are dependably free-flowing. They are well adapted to handling and application by mechanized, labor-saving methods. Precise metering and placement and uniform distribution are easier with liquids than with solids. Liquids are homogeneous, free from dustiness or caking, and unaffected by hygroscopicity. They are fully water soluble. With liquids, there are no sacks to lift, open, and dispose of; there is little delay in refilling applicators. Liquid fertilization may be combined with irrigation or with application of herbicides or pesticides.

These advantages and others, coupled with the high analysis and lower cost of suspensions, have led to the development of a dynamic and progressive segment of the fertilizer industry (7).

History of Suspensions

The highlight of the decade of the 1970s for fluid fertilizers was the continuing vigorous growth in production and use of suspensions. Growth was continuing in 1982, but in fact, suspensions were the only type of fertilizer showing real growth into the 1980s. By 1981 almost half of the 3,200 fluid fertilizer plants in the United States produced suspensions that accounted for more than 40% of the fluid mixed fertilizer market.

In the late 1950s and early 1960s, there were substantial efforts to break through the grade (solubility) ceiling imposed by liquid (solution) fertilizers of good quality. A main effort was through fluids that contained a large part of their nutrient content as finely divided solids. In the early years such fertilizers were commonly referred to as slurries. Later the term suspension came into use for higher analysis fluids that were much more dependable in storage, handling, and application. It may be well here to differentiate the terms suspension and slurry.

Suspension fertilizers are fluid mixtures of solid and liquid materials in which the solids do not settle rapidly and can be redispersed readily with agitation to give a uniform mixture. Certain types of clay are added as suspending agents. The suspension is fluid enough to be pumped and applied to the soil in application equipment commonly available for liquid fertilizers with little alteration of the equipment.

Slurry fertilizers are fluid mixtures of solid and liquid materials in which the solids settle rapidly in the absence of agitation to form a firm layer which is difficult to resuspend. Continuous agitation is required to ensure a uniform mixture that can be pumped and applied to the soil. Commonly available application equipment usually needs some modification to handle this type of product successfully (1).

Beginning dates for suspension fertilizers are difficult to identify, for various innovators have experimented with suspensions from time to time and produced material for distribution. The use of base suspensions presumably began when TVA shipped the first car of 12-40-0 in January 1963. This pioneering work by TVA, and continuing research, development, and demonstration work with industry during the next two decades, led to suspensions reaching a status in the United States approaching that of clear liquids (solutions) by 1980.

There were many problems and false steps along the way, and some people became discouraged. But the clear-cut advantages of suspensions spurred researchers, technologists, and industry innovators to find ways to deal with the problems. Here are some important main advantages for suspensions.

- The practical limit in concentration is much higher than for clear liquids (solutions), particularly when potash is a component. Solubility is not a limiting factor. When the $N:P_2O_5:K_2O$ ratio is 1:1:1, the suspension grade (14-14-14) is twice that of clear liquids.
- Adequate proportions of secondary and micronutrients can be readily incorporated, as can pesticides, herbicides, etc.

- Materials commonly used in formulating suspensions generally cost less and are more widely available than those required for clear liquids (8).

The growth of suspensions was spurred in the mid-1970s by the development of equipment and technique for readily incorporating solid intermediates such as mono-ammonium phosphate (MAP), diammonium phosphate (DAP), and nitrogen materials as major components in formulations (9). These solid intermediates were available in unlimited quantities and were substantially lower in cost than high-grade wet-process acid and polyphosphates required for high analysis liquids (solutions) (10).

Suspensions are likely to continue to grow, and because of important advantages, may ultimately dominate the fluid segment of the U.S. industry. Slurries, on the other hand, have essentially disappeared from the market.

Highlights of Fluid History

Table 1 lists a chronology of the history, development, and growth of the fluid fertilizer industry. This listing is primarily for the United States, but developments of lesser scope occurred in France, Belgium, the United Kingdom, and a few other countries.

Role of Polyphosphates

Polyphosphates are the "backbone" of clear liquid (solution) fertilizers. Polyphosphates are formed by removing (or eliminating during production) chemically combined water from orthophosphate molecules (figure 2).

The building block for phosphates, based on modern theories of electronic structure, is the PO_4 tetrahedron—a phosphorus atom surrounded by four oxygen atoms at the four corners of a tetrahedron. Multiple units (polymers) of PO_4 tetrahedra joined by shared oxygen atoms between the tetrahedra are called condensed phosphates. The simplest condensed phosphate is the pyrophosphate formed by the sharing of oxygens between two PO_4 groups. Polyphosphates are linear chain polymers that may contain from two to hundreds of PO_4 groups. Branching probably occurs in chains of more than about 500 PO_4 groups.

Polyphosphates were reported in the literature as early as 1816 when Berzelius heated ordinary phosphoric acid and showed that the products were different from orthophosphoric acid. They were considered to be mixtures of pyro- and metaphosphates and the idea of tripolyphosphate as a crystalline entity was not accepted until 1940. Proof of the existence of a homologous series of

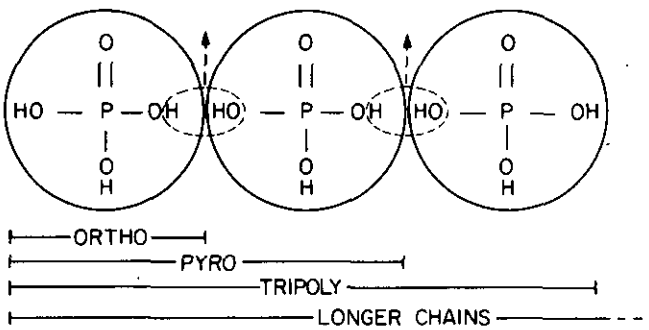

Figure 2. Diagram showing structural formation of polyphosphates

Table 1. Chronology of fluid fertilizers

400 B.C.	Fertilization of truck gardens and orange groves in Athens by city sewage in canals.
1843	Sir James Murray referred to "New" practice of using solid fertilizers.
1899	First liquid fertilizer patent obtained in U.S.
1923	First liquid mixed fertilizer plant in California.
1942	Injection of anhydrous ammonia into soil introduced (now a major fertilization practice of lowest cost).
1953	First liquid fertilizer production by neutralizing phosphoric acid with ammonia and dissolving potash.
1955	147 liquid fertilizer plants in the U.S.
1956	Superphosphoric acid introduced by TVA (now the "backbone" of liquid fertilizer production).
1963	Suspension fertilizers emerge in higher analysis (grades such as 15-15-15 and 7-21-21 practical).
1966	TVA develops wet-process superphosphoric acid.
1967	About 1,500 liquid and suspension fertilizer plants in U.S.
1968-70	Fluids developing slowly in France, Belgium, and United Kingdom.
1972	TVA pipe reactor process for high-polyphosphate liquids introduced (also a boon to wet-process superphosphoric acid production and use).
1974	2,800 fluid fertilizer plants in U.S.
1975-76	Use of solid MAP, DAP, etc., spurs growth of suspensions.
1976	3,000 fluid plants in U.S.
1980	3,200 fluid plants in U.S.
1980	Fluids (including NH_3 and N solutions) = 32% of U.S. fertilizers.
1981	More than 2 million tons of UAN solution used in U.S.
1981	Suspensions reach 40% of total fluid mixed fertilizers.

chain phosphates (polyphosphates) came only after the development of paper chromatography in the early 1950s. The progressive removal of water from orthophosphoric acid as shown in the diagram produces a series of polyphosphoric acids. The polyacids are obtained also when P_2O_5 from burning of phosphorus is hydrated with water short of the requirement for formation of orthophosphoric acid.

Mixtures of orthophosphoric and polyphosphoric acids are called superphosphoric acids (11).

Sequestration of Impurities

Sequestration of impurities in ammoniated wet-process phosphoric acid is an important phenomenon in the technology of preparation of clear liquid (solution) fertilizers of high quality. This is the process whereby polyphosphate ions form stable, soluble complexes with metal ions and hold them in solution. Ammonium polyphosphates are good sequestering agents and are added to wet-process phosphoric acid to hold in solution the iron and aluminum which otherwise would precipitate as orthophosphates when the wet-process acid is ammoniated. Ammonium pyrophosphates are more effective than the higher polyphosphates in sequestering iron and aluminum in fertilizer solutions, but the polyphosphates of longer chain length are better sequestrants for calcium and magnesium.

The sequestering power of ammonium polyphosphates also aids greatly in production of liquid fertilizers containing significant amounts of copper, iron, manganese, and zinc. These important micronutrient elements are almost insoluble in liquid fertilizers made from ammonium orthophosphates.

TVA has acquired most of its knowledge of ammonium polyphosphates since the introduction of electric furnace superphosphoric acid by TVA in 1955 (12).

TVA's pioneering research and development work on ammonium polyphosphates soon led to 11-37-0 ammonium polyphosphate solution (made by ammoniation of superphosphoric acid) that was provided to the industry for use in formulating high-quality liquids and for sequestration of impurities in ammoniated products of wet-process orthophosphoric acid.

TVA followed with the development of much more economical wet-process superphosphoric acid in pilot-plant work in 1961 (13). The industry followed in the mid-1960s with preparation of this acid by concentrating wet-process acid to 68% to 72% P_2O_5 content (14).

The real boost for wet-process acid-based polyphosphates came about 10 years later in 1974 with development by TVA of the simple pipe reactor and process for preparation of 10-34-0 ammonium polyphosphate solution (15). Ammoniation of wet-process superphosphoric acid of only 68% to 70% P_2O_5 content (20% to 30% of P_2O_5 as polyphosphate) in the pipe produces a melt of high polyphosphate content that is dissolved in water and ammoniated further to produce 10-34-0 with 60% to 75% of the P_2O_5 as polyphosphate.

The simple energy-conserving TVA pipe-reactor process caught on like wildfire in the industry. By 1980 at least 130 commercial plants were using this "revolutionizing" process (16). The pipe-reactor process also revolutionized the production of wet-process superphosphoric acid by industry, since acid of only 68% to 69% P_2O_5 content is needed. This acid can be readily produced in a single-stage stainless steel evaporator that requires only steam for heating. The much lower viscosity of this "low-conversion" superphosphoric acid also greatly simplifies its shipment and handling. It became a commodity in world trade by 1979 (17).

Higher Solubility With Polyphosphates

The polyphosphate system provides greater solubility, and higher grades can be produced as liquid (solution) fertilizers. In the orthophosphate system, maximum solubility at 32°F is 39% total nutrient content ($N + P_2O_5$). With about half of the P_2O_5 in polyphosphate form, the maximum solubility increases substantially to 46% total nutrients ($N + P_2O_5$). Wet-process superphosphoric acid is widely used to produce 10-34-0 ammonium polyphosphate solution (60% polyphosphate) that is a major commercial intermediate in production of finished liquid (solution) fertilizers. Two-component fertilizers with grades such as 18-18-0, 24-8-0, and 22-11-0 can be produced using 10-34-0. Lower solubility in the orthophosphate system limits $N:P_2O_5$ grades to 14-14-0, 18-6-0, and 18-9-0. When NPK grades are produced the polyphosphate system offers no grade advantage because solubility of KCl is limiting; the grade for a 1:1:1 ratio is 8-8-8 in either system.

Role of National Fertilizer Solutions Association

The National Fertilizer Solutions Association (NFSA) is the main trade association for the fluid fertilizer industry, with member companies in the United States and 14 other countries. It is dedicated to advancement of all aspects of fluid fertilizers. This very active organization was established in 1954—early in the history of the fluid industry, when there were less than 100 plants that produced mixed fluid fertilizers. Membership grew to about 1,700 companies in 1983, but NFSA remains fully as dynamic as during its formative years.

With headquarters in Peoria, Illinois, NFSA provides a range of services to members. These include assisting with the transfer of technology and information concerning the

production, marketing, application, economics, and agronomic aspects of fluid fertilizers. They also coordinate with other organizations, including governmental regulatory agencies and universities.

A general meeting each year is attended by more than 3,000, and the annual fluid fertilizer "Round-Up" draws large attendance and is a forum for timely technical presentations. NFSA publishes a bimonthly technical journal, *Solutions,* the leading journal of the fluid fertilizer industry. They also publish and update handbooks from time to time. The NFSA Foundation was established in 1982 to promote and assist in funding research vital to the industry. The Tennessee Valley Authority (TVA) and NFSA have worked actively together for more than 25 years in promoting the fluid fertilizer industry through technology transfer and other cooperative efforts.

Fluid Fertilizers in Other Countries

Fluid fertilizers also have found substantial use in France, Belgium, England, Mexico, Colombia, the U.S.S.R., and to a lesser extent in other countries.

In the United Kingdom, clear liquid mixtures have been used for several years with excellent results; commercial production of suspensions started in England in 1978. Since about 1970 liquids have been used extensively in France. Ammonium polyphosphate solution of grade 10-34-0 is produced from wet-process superphosphoric acid using TVA pipe-reactor technology. Test marketing of suspensions was underway in Belgium and the Netherlands in 1978. Fluids are expected to become popular in those countries. Other reports show that small amounts of fluids have been used in Spain, Sweden, China, India, and Japan (18).

The Soviet Union has conducted research on polyphosphates and liquid fertilizers since the late 1960s, and there is some production and use of NPK grades. There is substantial use of anhydrous ammonia and urea-ammonium nitrate (UAN) solution. There also is some activity with fluids in Czechoslovakia and Hungary. The Soviet Union started massive imports of wet-process superphosphoric acid from Florida in 1970 for general use in fertilizer production. The more concentrated superphosphoric acid (70% vs 54% P_2O_5) is imported mainly to save on shipping costs; substantial amounts are used in production of fluid fertilizers.

Solutions, in a 1980 account of the export of fluid fertilizer manufacturing and application equipment, shows U.S. firms marketing to a surprisingly large number of countries. Deliveries to the United Kingdom, Mexico, Netherlands, France, Belgium, Australia, South Africa, Spain, Malaysia, Colombia, Jamaica, Nicaragua, Venezuela, and the U.S.S.R. were reported. One manufacturer reported dealings with 23 countries.

Palgrave (20) has published an interesting account of the history of fluid fertilizer production and use in the United Kingdom.

Fluid fertilizers are not expected to reach the status in other countries that they have in the United States. The primary driving forces—convenience in handling and application and savings in farm labor—are not as important in other countries. Farms are smaller and dispersed, thus not very adaptable to high rates of custom application. In many countries there still is incentive for increased use of low-cost farm labor.

Development of Application Equipment

Fluid fertilizers were not only new from the standpoint of chemistry, physical form, and production equipment, but also required new types of application equipment. This was a major problem to early producers, along with their many other problems. Weed sprayers were adapted in some instances, but they were not entirely suitable. It was necessary to develop new types of equipment, first by the producers themselves to use in custom application (since the farmers usually had no suitable equipment) and later by farm machinery companies.

Early equipment was homemade or adapted. In one of the early types, a slit cut by hacksaw in a pipe provided a nozzle that effectively broadcast the solution, in about the same manner as the flooding nozzles used today (1).

With these makeshift but effective beginnings, design of application equipment has progressed until today there is a wide range of types available. There are gravity-flow types for use in planting, hose pumps, many varieties of nozzle types, special types for suspension application, and several others. Many farmers now have their own equipment, although custom application is still the major practice of the industry (21).

The modern "high-flotation" applicator vehicles, with huge rubber tires, can operate early on frozen or wet fields. When equipped with an 85-foot boom they apply fluid fertilizers at rates as high as 2.5 acres per minute (22, 23). (The development of application equipment and techniques is covered in depth in chapter 9.)

STATUS OF FLUID FERTILIZERS (EARLY 1980s)

Fluids—A Growth Market

Use of fertilizer in the United States has increased spectacularly in the past 20 years. In 1981 plant nutrient use ($N + P_2O_5 + K_2O$) totaled 23.5 million short tons—compared with only 7.5 million tons in 1960 (table 2). Nutrient use doubled from 1960 to 1970 and tripled from

Table 2. Selected data on U. S. fertilizer use

Plant nutrient consumption (1,000 tons) (24)

Year	Total nutrients	Fluid nutrients: Mixtures	Fluid nutrients: Materials (mainly N solutions)	Fluid nutrients: Total	Fluid mixtures % of: Mixtures	Fluid mixtures % of: Total fertilizers
1960	7,464	143	327	470	3	2
1970	16,068	823	1,150	1,973	10	5
1980	23,083	1,613	2,188	3,801	16	7
1981	23,451	1,767	2,329	4,096	17	7.5

Average annual growth rates for fertilizer nutrients (23)

Year	% total nutrients	% fluid: Mixtures	% fluid: Materials	% fluid: Total	% anhydrous ammonia	% dry: Mixtures	% dry: Materials
1960-70	8.0	19.1	13.4	15.4	17.2	4.6	8.9
1960-80	5.8	12.9	10.0	11.0	10.8	2.9	7.0
1970-80	3.7	7.0	6.6	6.8	4.7	1.3	5.2
1980-81	1.6	8.8	6.9	7.7	2.4	-0.1	0.2

Number and average production of fluid mix plants

Year	Estimated number of plants	Average throughput: Liquids	Average throughput: Suspensions
		tons per year	
1960	390	–	–
1970	2,751	–	–
1974	2,800	3,433	2,573
1976	3,000	2,606	3,252
1980	3,200	3,840	3,604

1960 to 1981. In 1981 fluid nutrient use (mixtures plus nitrogen solutions) totaled 4.1 million tons, more than doubling since 1970 and increasing from 6.3% to 17.5% of the total nutrient use since 1960. Fluid mixtures (NPK) use in 1981 totaled 1.8 million tons of nutrients–about 17% of total mixed fertilizers or 7.5% of total nutrients used.

The proportion of total fertilizer nutrients applied in fluid form increases greatly if anhydrous ammonia is included. The 4.6 million tons of nitrogen applied as anhydrous ammonia in 1981 increases total fluid nutrients to 8.1 million tons–34.5% of the total nutrients applied in the United States. Fluid fertilizer use has grown nearly twice as fast as total fertilizer use, averaging more than 15% per year increase between 1960 and 1970, and an 11% increase between 1960 and 1980. A large part of this increase occurred during the introductory stages of the new product form and was aided by rapid advances in technology. Although the growth rate has slowed–to 6.8% per year during 1970-80 and 7.7% from 1980-81–fluid fertilizer use is still increasing faster than total fertilizer use (table 2). In this table, fluid fertilizers include liquids and suspensions as either NPK mixtures or materials (28-0-0, 32-0-0, 10-34-0, etc.). Anhydrous ammonia is not included as a fluid material and is reported separately.

Nutrient use as mixed fluid fertilizers grew almost 13% per year from 1960 to 1980. The average nutrient content of mixed fluids also increased substantially. In 1981 fluid mixtures averaged 9.0-16.0-10.2, a total nutrient content of 35.2% compared with the estimated average of 28% for fluids in 1960. The increased use of suspension fertilizers has been responsible for the rapid rise in the analysis of fluid mixtures in the past few years. The average nutrient content for all U.S. mixed fertilizers in 1981 was 43.8%. Since their introduction in the late 1960s, suspensions have gained rapidly in market share. They moved from 25% of the mixed fluids market in 1974, to 33% in 1976, and to more than 40% in 1981.

Ten States–Iowa, Illinois, Nebraska, California, Texas, Indiana, Kansas, Ohio, Minnesota, and Georgia–account for 65% of the U.S. fluid fertilizer market. In these States, about 21% of the fluids used is applied as mixtures. Anhydrous ammonia consumed in these 10 States amounted to 75% of the total consumed in the United States (25).

Fluid Dealer Characteristics

Statistics compiled by TVA's National Fertilizer Development Center (NFDC) and the Association of American Plant Food Control Officials (AAPFCO) show the dramatic growth in the number of fluid mixed fertilizer plants from 1960 to 1980. Results (table 2) indicate that those plants having only liquid mix facilities have an average annual throughput of 3,840 tons. Comparable average throughput for suspension plants is 3,604 tons (5).

A typical fluid mix plant is difficult to characterize. It may distribute liquid and/or suspension mixtures, anhydrous ammonia, nitrogen solutions, liquid, and dry direct application materials. A frequency distribution of all fluid plants indicates the greatest number of plants in the 1,000- to 3,000-ton-per-year range. The mode—1,245 tons—is the value occurring with greatest frequency, and the median—2,067—represents the middle value for all fluid mix plants.

Ownership data relating to all fluid fertilizer plants show that 13% of these plants are sole proprietorships, 7% partnerships, 64% corporations, and 16% cooperatives (24).

Prospects for Future Growth

As the fertilizer market becomes more mature, consumption growth rates will tend to be lower than in the past. Total plant nutrient consumption in the United States is expected to grow at just over 3% per year through 1985, with total use reaching 26.5 to 27.0 million tons. Fluid fertilizers have been projected to increase by 4.5% per year reaching a total of 4.7 million tons—18% of total plant nutrient consumption in the United States. These projected growth rates are less than those of the 1970s. However, they represent a significant gain in the total amount of fluid fertilizers used.

Development of the suspension segment of the fluid fertilizer industry, which can use lower cost materials such as solid MAP or DAP and TVA base suspensions 13-38-0 and 9-32-0, has helped make fluids cost competitive with dry mixtures. This, plus the demonstrated advantages for fluids, gave rise to a sharp increase in use of suspensions in the late 1970s. There will be an increased use of lower cost solids to produce suspensions along with further improvements in suspension application equipment for row or starter fertilizer application. The narrowing of the retail price gap between fluids and dry fertilizers coupled with advantages to the farmer, such as overall convenience, relieving critical labor constraints, and better uses of limited investment capital, suggest that use of fluids will continue to grow more rapidly than the total market.

Growth of suspensions will continue higher than for clear liquid (solutions) mixtures because of their lower cost, and the increasing impurities content of wet-process acid that will make production of high-grade clear liquids more difficult and expensive.

Advantages of fluid fertilizers, including the lower investment for production facilities, ease of preparation and incorporation of additives, convenience of handling, and high reliability of fluid application systems will contribute to the continued strong growth of fluid fertilizers in the U.S. market. Growth will continue in several other countries, but fluids will not approach the status of practice by this dynamic segment of the industry in the United States.

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Chapter 2

Agronomic Aspects

By Eugene C. Sample and Gary W. Akin

In any discussion of fluid fertilizers, questions arise concerning the relative agronomic merits of various physical and chemical forms of fertilizers. Two common questions center on whether fluid fertilizers are agronomically better than their dry counterparts and whether polyphosphates are agronomically better than orthophosphates. The polyphosphate question is pertinent to a discussion of fluid fertilizers because polyphosphates are most often encountered in fluids. The answers to these questions are often confusing because responders tend to include nonagronomic factors such as ease of application, uniformity of application, and economics in their agronomic evaluations. The answer should be based solely on crop yields obtained when materials are compared using similar rates of plant nutrients under similar methods of application.

Agronomic Comparisons of Fluid and Dry Fertilizers

Although numerous field studies have been performed comparing fluid and dry fertilizers under similar conditions, very little of this research is reported in refereed journals. Rather, it is usually found in experiment station annual reports which are not widely available. The comparisons most often made have been among solid urea, solid ammonium nitrate, and urea-ammonium nitrate (UAN) fluids; between dry ammonium phosphates and fluid ammonium phosphates; and between ammonium orthophosphates and ammonium polyphosphates.

Experimental data from a wide range of studies overwhelmingly support the conclusion that there are essentially no differences among the liquid, suspension, and dry fertilizers when they are compared over the long term under conditions of similar nutrient rates, placements, and chemical forms. The latter is particularly important when comparing phosphate fertilizers. For instance, it would not be valid to compare a highly water-soluble phosphate in fluids with a solid phosphate of low water solubility. However, when solids such as diammonium phosphate (DAP), monoammonium phosphate, or ammonium polyphosphate were compared with fluids such as 10-34-0, 8-24-0, or 11-37-0 under similar conditions, long-term studies have shown these to be essentially equal in nutritive value. Similarly, long-term studies have shown solid urea or ammonium nitrate to be essentially equal to nitrogen solutions, such as urea-ammonium nitrate. Essentially the same conclusions would be reached with dry and fluid NPK mixes.

Cautions in Comparing Fertilizers

For valid comparisons, studies should be conducted for several years at the same location using the same experimental design to ensure that the variability inherent in field studies does not lead to faulty interpretations. If data are selected from one study, for one year, at one location, evidence can be cited to prove that solids are better than fluids, or vice versa, or that polyphosphates are better than orthophosphates, or vice versa. In the United States it is not unusual to encounter evidence in the marketplace or in advertising to support each of these claims.

Care must be exercised in comparing any fertilizers under field conditions, whether they be solids or fluids. For example, if one wanted to compare concentrated superphosphate (CSP) with either 10-34-0 solution or solid monoammonium phosphate (MAP) as sources of phosphorus, one cannot ignore the fact that both 10-34-0 and MAP also contain nitrogen. To be a valid comparison, equivalent amounts of nitrogen should be applied with the CSP to ensure that the materials are being compared for

their phosphorus supplying power, not confounded by the absence of nitrogen. Conversely, if one were comparing a solution, such as UAN, containing only nitrogen, with MAP, which contains both nitrogen and phosphorus, some source of phosphorus (such as CSP) should be applied with the UAN to equalize phosphorus.

Why are Fluids and Solids Equal Agronomically?

The relative equality of fluid and dry fertilizers should not be too surprising in light of the fact that the chemical constituents of the two physical forms are usually identical. For example, UAN solution or suspension contains both urea and ammonium nitrate, both popular dry materials. Likewise, 8-24-0 solution is an ammonium orthophosphate material, just as MAP and DAP are. Some of the ammonium phosphate fluids may contain ammonium polyphosphates; but this does not confuse the issue too much, as discussed below.

The matter of equality of various physical forms is even more predictable when one considers the limited variety of chemical forms presented to the plant root. Although a farmer may apply fertilizer nitrogen as anhydrous ammonia, urea, ammonium nitrate, UAN, calcium nitrate, or several other forms, the same farmer may be assured that, within a fairly short time, the roots of his crops will be confronted mainly with nitrogen in the nitrate form (NO_3^-). This is because various soil enzymes rapidly convert urea nitrogen to ammonium forms, and then soil microbiological processes fairly rapidly convert the ammonium forms to nitrate. So, for most of the growing season, plant roots "see" mainly nitrates.

Despite the fact that farmers are offered a wide array of phosphorus-containing fertilizers, these farmers are assured that their crops are really confronted with a very limited variety of chemical forms of phosphorus. First, the phosphorus in most fertilizers is present in the orthophosphate form. When an orthophosphate-containing fluid fertilizer is applied or an orthophosphate-containing dry fertilizer dissolves in the soil solution, the plant roots are confronted mainly with two phosphate species ($H_2PO_4^-$ and $HPO_4^=$). If a fertilizer material containing polyphosphates is applied, the polyphosphate is fairly rapidly converted in most agricultural soils to the orthophosphate form. So, regardless of the physical or chemical form of phosphate fertilizer, after a short while in the soil, plant roots "see" only two very similar forms of phosphate.

Potassium fertilizers are even more uniform than either nitrogen or phosphate fertilizers. The dominant source of potassium for both fluid and dry fertilizers is potassium chloride. Even when other sources, such as potassium phosphate or potassium nitrate, are used, it is the potassium ion (K^+) which the plant root deals with in the soil solution.

Implications of Equality

There are a number of logical reasons to expect fluid and dry fertilizers of comparable chemical makeup to be equal agronomically. Yet some proponents of either fluid or dry fertilizers feel that they are at a marketing disadvantage if they cannot claim agronomic superiority for their particular form. From a farmer's viewpoint, however, the equality of the various forms is a powerful management tool. It frees the farmer to choose from a wide variety of materials using a multiplicity of nonagronomic factors as criteria for the decision. For example, if he practices some form of no-till or minimum tillage agriculture, the farmer's primary concern may be to achieve a sod kill with a herbicide and fertilize by broadcast application, all in one operation. His most efficient and economical option may well be to apply a fluid fertilizer-herbicide tank mix. He can choose this option with the assurance that his fertilizer will perform about the same as it would have with a broadcast application of a comparable dry material, with a separate herbicide spray. There are numerous other technological or convenience advantages for fluid fertilizers, many of them discussed elsewhere in this manual, which he can take advantage of without worrying about sacrificing fertilizer quality. If the farmer is in a region of micronutrient deficiency and needs to apply relatively small amounts of these nutrients uniformly over relatively large areas, incorporation of the micronutrient into a fluid fertilizer is a way of assuring uniform distribution of the micronutrient in the fertilizer material and, hence, uniform distribution on the field. In fact, uniform distribution in the field, with or without micronutrients, is often cited as one of the advantages of fluid over dry fertilizers.

In summary, fluid and dry fertilizers of comparable chemical constituency are essentially equal agronomically when applied at equivalent nutrient rates under similar placements. This equality gives farmers a large number of options in choosing fertilizer materials based on economics, convenience, compatibility with other operations, dealer services, or regional availability.

Chapter 3

Physical Properties Evaluation

By T. M. Jones and H. L. Balay

The term, "fluid fertilizers," usually applies to all fertilizers that are capable of flowing. However, the fluid fertilizers in which the TVA National Fertilizer Development Center has been principally involved with are solutions and suspensions. Each of these classes of fertilizers has chemical and physical properties that significantly affect its production, transportation, storage, and application to the soil. Therefore, it is necessary that careful evaluations be made of the chemical and physical properties of the fluid fertilizers to determine their suitability for commercial use.

Both solution and suspension fertilizers cover two distinct types of fluid products. One type is mixed fluid fertilizer blends which are for direct application to the soil. The other type is base fluid fertilizers which may also be applied to the soil, but more often are used in production of fluid fertilizer blends of various $N:P_2O_5:K_2O$ ratios and grades which are then applied to the soil. These mixed fluid products can be produced very rapidly by cold blending different types of base solutions or suspensions. Since the mixed fluid blends are made for direct application to the soil, long-term storage is considered to be unnecessary and they are usually subjected to storage tests for only 2 weeks by TVA. Longer storage periods may be chosen by individual users to suit their own requirements.

The base fluid products usually are produced, then stored for various lengths of time before they are used to produce mixed fertilizer products; therefore, they must be capable of withstanding storage for long periods of time under various atmospheric conditions without deterioration in product quality. Some base fluid fertilizers are designed for storage in the colder regions of the country and others are not. Products that are considered to be satisfactory for cold weather storage do not solidify at temperatures above about -5°F (-20°C) and their viscosity at 0°F (-18°C) cannot exceed 2,000 centipoises (see section on viscosity for method of determining viscosity) because products of higher viscosity cannot be pumped satisfactorily. These base fluid products often contain significant proportions of urea, polyphosphate, or sulfate which act as solidification temperature depressants. However, orthophosphate base fluids usually do not contain significant proportions of these materials, and they, therefore, usually do not meet the solidification temperature and viscosity requirements for satisfactory storage in cold weather which restricts their winter storage in the colder regions of the country.

The evaluations of solution and suspension fertilizers overlap in that they are both rated for many of the same chemical and physical characteristics. In making these evaluations, much of the same equipment and procedures are used. However, some evaluations that are made apply only to solutions and others apply only to suspensions.

Solution Fertilizers

The major advantage of solution fertilizers over other fluid products is their freedom from troublesome precipitants which settle in storage tanks and distribution equipment and can stop up feed lines, orifice plates, and spray nozzles during application to the soil. A lesser advantage is that solutions usually have lower viscosities (50 to 250 centipoises) than most solids-containing fluid fertilizers which makes them easier to pump or otherwise transfer from one container to another. The principal disadvantages of solution fertilizers are that, generally, they are lower in plant food content and have higher production and shipping costs than other fluid products of similar $N:P_2O_5:K_2O$ ratios.

During production of solution fertilizers, measurements for pH and density are made to determine whether the products are of about the desired grade. Measurements are also made of the salting-out and saturation temperatures to determine the lowest temperature that solutions can be subjected to without crystallization of fertilizer salts.

After production and before storage, both base and mixed grade solution products should be evaluated chemically to obtain accurate determinations of their grade and $N:P_2O_5:K_2O$ weight ratio. The solutions should also be evaluated chemically for polyphosphate and for impurities (Al_2O_3, Fe_2O_3, MgO, and F) to indicate the expected stable impurity precipitating phases, the extent of precipitation, and the length of time that the solution would be expected to store satisfactorily. The solutions are evaluated physically for pourability, clarity, viscosity, crystal size, and solidification temperature to determine whether or not they are satisfactory initially. Mixed solution products are then stored for two weeks at 80°F (27°C) and 32°F (0°C) and then reevaluated for viscosity, pourability, large (+20 mesh) crystals, total volume of solids, and volume of adhering type solids (see specific sections on these subjects for methods of determining these physical properties). Base solutions are stored at temperatures of 32°, 80°, and 100°F (0°, 27°, 38°C) for periods of time up to about 180 days. Replicate samples of each solution are stored under quiescent conditions. Since base solutions may be either put into clean tanks or added to solutions that have been in storage for some time, some of the storage samples are seeded with a few small crystals of the expected crystallization phases and the other samples are unseeded. During storage, the samples are evaluated for pourability, crystal size, and volume of both adhering and nonadhering types of crystals. During the first month of storage, the samples are evaluated weekly; during the next 3 months, they are evaluated biweekly; and after 4 months they are evaluated monthly.

Solutions that are considered to be satisfactory are completely pourable at both 80°F (27°C) and 32°F (0°C), have viscosities that did not exceed 400 centipoises at 80°F (27°C) and 32°F (0°C), and have clarity of at least 25% light transmittance as compared with distilled water as having 100%. Satisfactory solutions also contain no crystals that exceed 20 mesh (850 μm), no more than 3% by volume of total solids, and no more than 0.1% of adhering type solids. Solutions that are to be stored in cold weather also must be completely pumpable at very low temperature; to meet this requirement, the primary nutrients must not salt out, the solutions must not solidify at temperatures above -5°F (-20°C), and the viscosity at 0°F (-18°C) must not exceed 2,000 centipoises.

Suspension Fertilizers

In past years, TVA has developed numerous types of suspension fertilizers. Most of the work has been directed toward development of base suspensions that can be stored until needed, then cold blended for production of mixed suspensions of various ratios and grades. During planting season, most of the farmers would like to get their fertilizer at about the same time, and production of mixed blends from base products is considered to be the most convenient way of rapidly producing premium-grade products of almost any grade or ratio desired by the farmer.

The principal base suspensions with which TVA is working in laboratory, pilot-plant, and demonstration-scale plant development are urea-ammonium nitrate, urea-ammonium sulfate, ammonium orthophosphate, ammonium polyphosphate, urea-ammonium polyphosphate, and potash base suspensions.

In production of satisfactory base suspensions, it is necessary that slurries containing an abundance of small crystals of the stable solid phase be first produced for prevention of excessive crystal growth during slow cooling and during fluctuations in temperature during storage. The abundance of small crystals is produced by quick cooling (quenching) solutions from the reactor to well below their saturation or salting-out temperature. Recirculation in the cooling-crystallization stage has been found to further promote production of small crystals. To suspend the abundance of small crystals, a gelling-type clay is added during or after the cooling step and incorporated in the slurry by mixing it thoroughly with a high shear stirrer or pump. Generally, during summer months, economics limit operation of the cooler to a minimum discharge temperature of about 100°F (38°C). In suspensions that are rated as satisfactory, the crystals remain suspended during transit and storage for indefinite periods of time.

After production, the suspensions usually are allowed overnight storage at room temperature (about 75°F [24°C]) for establishment of equilibrium. They are then evaluated chemically for primary nutrient content (N, P_2O_5, and K_2O) to determine the suspension grade and nutrient ratio. The suspension products are evaluated petrographically to determine the type and size of the crystals. The products also are evaluated physically for pourability, viscosity, solidification temperature, and settling of crystals during overnight storage at room temperature. Suspensions which are produced for shipment are also evaluated for vibrational settling such as occurs during transit by rail. The suspensions are then used in application to the soil, in production of mixed grade products, or are shipped and stored. For evaluation purposes, base suspension products usually are subjected to storage tests for 30, 60, and 90 days at 80°F (27°C) and 100°F (38°C). After each storage period, the base

suspensions are evaluated at 80°F (27°C) and 32°F (0°C) for pourability, viscosity, syneresis, crystal type and size, and settling of crystals during static storage.

Base suspensions that are considered to be satisfactory are at least 98% pourable when evaluated at 80°F (27°C) and 32°F (0°C), and have viscosities that do not exceed 1,000 centipoises at 80°F (27°C) or 1,500 centipoises at 32°F (0°C). Also, satisfactory base suspensions contain no large +20 mesh (850 μm) crystals, and no crystals that settle and pack on the bottom of the storage container. Suspensions for shipment also contain less than 2% by volume of crystals that settle during vibration tests. Syneresis, formation of clear liquid that sometimes collects either on top or within the suspensions, is undesirable because it may foster growth of excessively large crystals at the suspension-clear liquid interface. However, suspensions containing syneresis are not rated unsatisfactory if they can be remixed by recirculation or air sparging. Base suspensions for cold weather storage do not solidify at temperatures above -5°F (-20°C) and the viscosity at 0°F (-18°C) must not exceed 2,000 centipoises.

Mixed suspensions are for direct application to the soil; therefore, they are stored only for 14 days at 80°F (27°C) and are evaluated at 80°F (27°C) and 32°F (0°C). They are initially evaluated chemically for nitrogen, phosphate, and potash, and petrographically for crystal size. The mixed suspensions also are evaluated physically for pourability, viscosity, settling of crystals during overnight static storage, and syneresis. After 14 days of static storage, the suspensions are reevaluated for crystal size, pourability, viscosity, settling of crystals, and syneresis.

Mixed suspensions that are rated as satisfactory are at least 98% pourable at 80°F (27°C) and 32°F (0°C), contain no +20 mesh (850 μm) crystals, and no crystals that are settled and packed on the bottom of the storage container. Loose crystals on the bottom of the container or syneresis (clear liquid) are considered to be undesirable, but the suspensions are not rated as unsatisfactory if recirculation or air sparging will easily remix the suspension.

Laboratory Measurement of Physical Properties of Fluid Fertilizer

The laboratory methods used in making the evaluations are described below.

Pourability——Fluid fertilizers are evaluated in the laboratory for pourability to determine whether or not they can be drained from their container by gravity or pumped or otherwise transferred in the field from one container to another. This determination is made by rotating a stirring rod twice around the inside surface of the storage container, generally an 8- or 16-ounce sample bottle, to apply gentle agitation to the fluid. Rotation of the stirring rod is intended to supply no more agitation than would be supplied by air sparging. The container then is turned downward at a 45° angle for 1 minute and the content (% by volume) that pours out is determined. Field tests have shown that fluid products that are at least 98% pourable by this procedure will flow freely by gravity from their storage container and they easily can be transferred from one tank or container to another by pumping.

Viscosity——Fluid fertilizers are evaluated in the laboratory for viscosity to indicate their ability to flow. The viscosity generally is measured with a viscometer (figure 3). Before measuring the viscosity, all fluid fertilizers are agitated for 5 minutes with a stirrer operated at propeller-tip speed of 7 feet (2.1 m) per second. For fluids that are to be applied directly to the soil, the viscosity must not exceed 800 centipoises at 80°F (27°C) and 900 centipoises at 32°F (0°C). The viscosity of base fluids that are primarily for use in production of fluid blends must not exceed 1,000 centipoises at 80°F (27°C), 1,500 centipoises at 32°F (0°C), or 2,000 centipoises at 0°F (-18°C). Field tests have shown that fluid blends which do not meet the above viscosity specifications usually cannot be uniformly applied to the soil, and base suspensions that do not meet these viscosity specifications usually cannot be satisfactorily drained from storage tanks or transferred from one container to another by pumping.

Crystal Type and Size——Fluid fertilizers are considered to be unsatisfactory if they contain any crystals, either initially or after storage, that exceed 20 mesh (850 μm) in size, because the large crystals can stop up distribution pipelines, spray nozzles, orifice meters, and other types of flow metering or flow regulating equipment. In suspension fertilizers it is necessary that an abundance of small crystals of the precipitating phase be present for prevention of growth of crystals to excessively large size. The type of crystals in fluid fertilizer products is also important because crystals vary in shape from long needle-like to cubical blocks and to thin sheets (figure 4). The longer type crystals are avoided because they cause stoppages in equipment more readily than crystals of other shapes. The thin rectangular shaped crystals are preferred because they have a higher surface area-to-volume ratio and are therefore less difficult to suspend. The size and shape of the crystals are determined in the petrographic laboratory by microscopic analyses.

Settling of Crystals——It is desirable that all crystals in suspension fertilizers remain suspended at all times. The specifications require that for a suspension to be rated as satisfactory, no crystals can settle and pack on the bottom of the container during static storage and a maximum of only 2% by volume of crystals can be settled after the vibrational settling test which simulates vibration which occurs during transit by rail or truck. A suspension is measured in the laboratory for settled and packed crystals by pressing a stirring rod to the bottom of the storage container to determine if any resistance is encountered

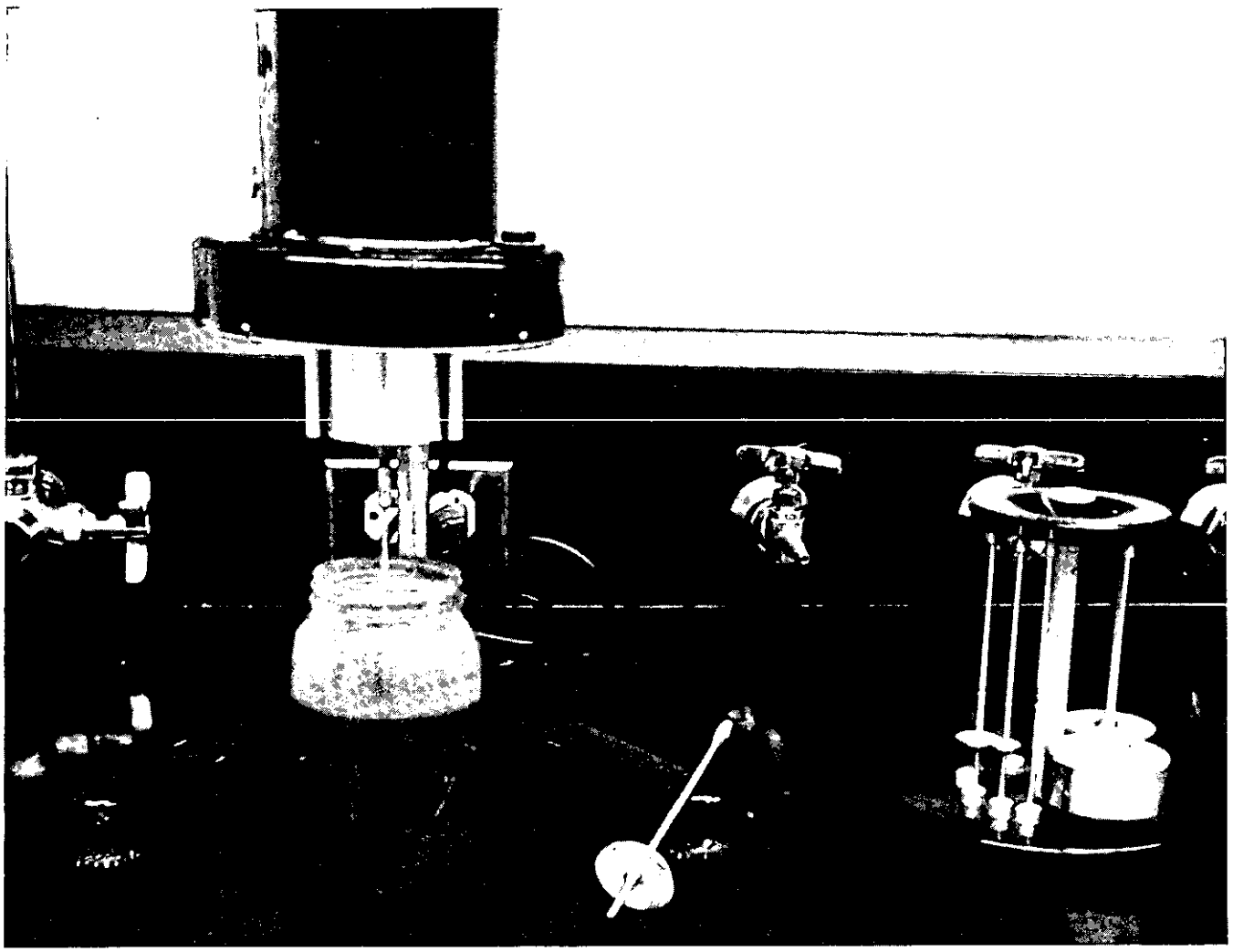

Figure 3. Viscosity measuring device

to reach the bottom of the container. If settled crystals are very loose and are capable of being redistributed in the suspension by recirculation or air sparging, the suspension is rated as satisfactory. If the settled crystals are packed and difficult to redistribute, the product is rated unsatisfactory.

Crystals of any type are undesirable in solution fertilizers. To ensure against nucleation and growth of fertilizer salt crystals in solution fertilizers, salt-out temperatures are determined, and the concentrations of the solutions are adjusted to enable production of the highest possible satisfactory solution grades. However, solutions that are prepared from wet-process phosphoric acids contain impurities that precipitate slowly as very fine crystals or sludge. Since precipitation of these impurity materials is almost impossible to avoid, some precipitated solids are permitted. Solution fertilizers are rated as being very good if they are completely pourable, contain no +20 mesh (850 μm) crystals and contain no more than 1% by volume of nonadhering type crystals (exclusive of carbonaceous matter) and less than 0.1% by volume of adhering type crystals. A solution is rated as acceptable if it contains no more than 3% by volume of loosely held precipitated solids. A solution is unsatisfactory if it is less than 100% pourable, contains any +20 mesh (850 μm) crystals, or contains more than 3% by volume of precipitated solids.

Syneresis—Suspension fertilizers sometimes are affected by syneresis, which is formation of clear liquid which usually occurs on top of the suspension with the remainder of the suspension being uniform throughout. The presence of the clear liquid layer does not necessarily cause a suspension to be unsatisfactory, but it is undesirable because with decrease or fluctuations in temperature or other conditions that cause changes in the concentration of the liquid phase, growth of excessively large crystals occurs at the clear liquid layer interface. Provided the crystals do not grow to exceed 20 mesh (850 μm) in size, syneresis is not objectionable if recirculation or air sparging will remix the clear

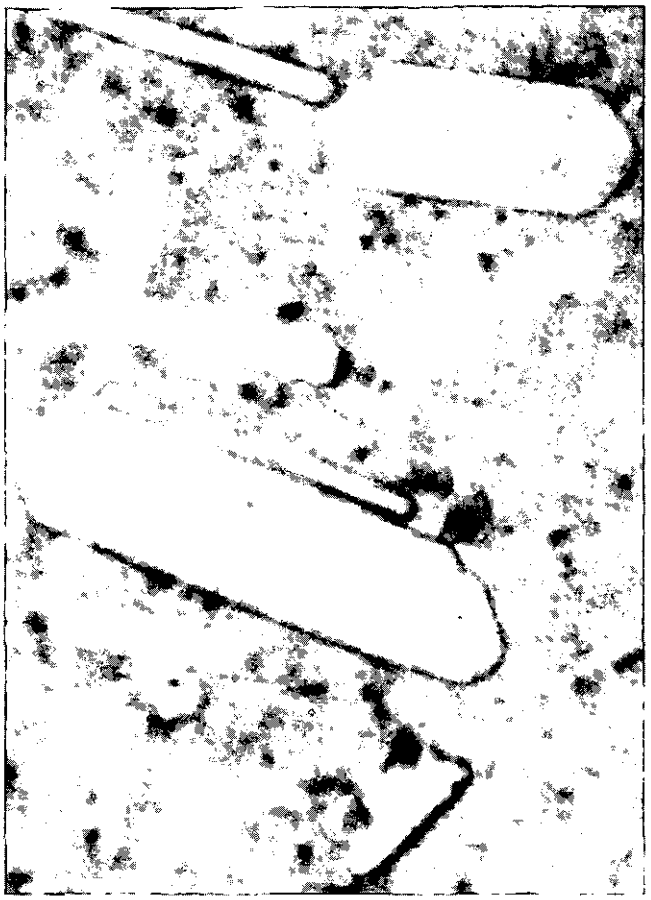

Figure 4. Mix of MAP and DAP crystals

liquid and suspension. Generally, syneresis is caused by either insufficient clay concentration or improper gelling of clay.

Clarity——Fluid fertilizers that are produced from wet-process phosphoric acids derived from uncalcined phosphate ores are black in color due to the presence of finely divided carbonaceous material. The black color has no effect on the nutrient value of the fertilizers but it does restrict the sight identification of solid material in solution fertilizers that could clog the equipment used for application. Solution fertilizers are often used for row application, whereas the larger part of suspension fertilizers is used for broadcast to the soil. Solution fertilizers often are gravity fed, and the distribution equipment, orifice meters, pipelines, and nozzles used for row application usually are smaller than those used for broadcast application of suspension fertilizers. Since the application equipment is smaller, it is more likely to get stopped up by large crystals or foreign particles; therefore, the need for being able to see these solid particles in the solution fertilizers is much greater than it is in suspension fertilizer.

In production of solution fertilizers, samples of the product are taken and measured for clarity, which is the amount of visible light that passes through the sample without being absorbed. Measurements for clarity are made with a spectrophotometer. The object of the measurement is to determine whether or not the fertilizer is clear enough for fertilizer producers, farmers, or others that handle or distribute solution fertilizers to the soil to see large crystals, or foreign matter, that might stop up orifice meters, or other equipment, that is used in handling or distributing the solution to the soil.

Clarity is expressed as the percentage transmittance of light at the desired wavelength of the liquid absorption spectrum. A liquid with 25% light transmittance, as compared with that of distilled water as being 100%, is considered as acceptable.

Solidification Temperature——If a fluid fertilizer is produced for winter-time storage in the colder regions of the country, its solidification temperature must not exceed -5°F (-20°C) and its viscosity at 0°F (-18°C) must not exceed 2,000 centipoises. Field tests show that fluids which meet these requirements can be transferred from one container to another throughout the winter weather of States located in the colder regions of the country. Field tests have further shown that some fluid products with solidification temperatures higher than -5°F (-20°C) solidified during winter storage and could not be removed from storage tanks in time for spring application. Solidification temperatures of fluid fertilizers are measured in the laboratory by cooling them to solidification over a period of 1-1/2 to 2 hours with an acetone or ethanol-dry ice bath. During cooling, the fluid fertilizer is agitated with a stirrer operated at a propeller-tip speed of about 7 feet (2.1 m) per second. The solidification temperature is recorded when a temperature rise occurs and with continued cooling the fluid product becomes semisolid or solid.

Salting-Out and Saturation Temperatures——Salting-out and saturation temperatures are determined by cooling the solution until crystallization occurs (salting-out temperature) and then warming it very slowly with continuous stirring until the last crystals disappear (saturation temperature). Usually the cooling and heating rate is about 2°F (1°C) per hour in the critical range. Such measurements are usually made in duplicate but occasionally are made in triplicate and the average is taken as the true value.

Nutrient Solubility——Ammonium phosphate solutions exhibit a high degree of supercooling. To obtain nutrient solubility in these solutions, 50 milliliters of a series of solutions of the ratio being tested differing by small increments in water content are stored at constant temperature, usually 32°F (0°C). Each solution is seeded with about 50 milligrams of crystals of a composition previously determined to be the salting-out phase of the particular ratio and agitated mildly in a shaking apparatus. The disappearance or growth of crystals in the different samples permits determination of the solubility at 32°F (0°C) within 0.1% to 0.2% of the plant nutrient content.

Specific Gravity--In the production of solution and suspension fertilizers, samples of the product are taken and measured for specific gravity to obtain estimates of the product grade. Specific gravity is the ratio of the weight of a given volume of solution or suspension compared with that of the same volume of water; when used together with pH it can give fairly accurate estimates of the grade of the product. Since specific gravity and pH are both affected by temperature, the measurements are made at 80°F (27°C). Specific gravity measurements are made at TVA by either actually weighing a volume of the fluid fertilizer and dividing the weight by the weight of an equal volume of water or it is obtained through use of hydrometers. A hydrometer is a calibrated instrument that will sink to various depths dependent upon the density of the fluid. The specific gravity is read directly from the calibrated scale.

Gel Strength--Suspension fertilizers are composed of a gelling agent dispersed in a solution of fertilizer salts--usually the solution is saturated and both crystals of fertilizer salts and impurities are present. In production of the suspension fertilizers, a suspending agent, which is usually a gelling-type clay, is incorporated in a slurry to form a gel that is strong enough to suspend the solids in the saturated solution, but is not too strong to prevent pumping, pouring, and distribution to the soil. Gel strength, which is the force required to break the gel, is measured with a gelometer developed at TVA several years ago (see chapter 7). Heretofore, there were no attempts to actually measure gel strength. The viscometer is used to measure viscosity (the resistance of a fluid to flow) once the gel has been broken. Viscosity is related to gel strength, and prior to development of the gelometer, the viscometer was considered to be the best available instrument for determining the ability of the suspensions to prevent settling of the solid particles.

In production of suspension fertilizers, gel strength measurements are made with the gelometer to determine the proportion of gelling-type clay that must be added and the degree of mixing that is required for producing a gel strong enough to keep the solids suspended in the saturated solution but weak enough to allow the suspension to drain by gravity or pumped from their containers. Factors that are known to affect the required degree of clay mixing are pH of the solution, proportion of solids, specific gravity, and the presence of polyphosphate and nitrate ions. Once the proportion of clay that should be added and the degree of mixing required have been established for production of a satisfactory suspension product, further gel strength measurements are only made as occasional spot checks or after changes in the process or in feed materials have been made.

Vibrational Settling--Some suspension fertilizers have been known to store satisfactorily for long periods of time under static conditions but, when they were subjected to vibration such as occurs during shipment by rail, the crystals settled excessively and packed on the bottom of the railroad tank cars. Settling of crystals during vibration was found to be related to the weight, size, and shape of the crystals; the specific gravity of the solution phase of the suspension; and to the strength of the gel. In order to estimate the proportion of crystals that would settle during transit by rail, a shaker was fabricated and calibrated at TVA to give approximately the same results during shaking for 2 hours that would be obtained by transit for several hundred miles by rail. TVA product specifications limit settling during vibration to less than 2% by volume of loose crystals. Vibration settling tests are made on all experimental materials that are produced in bench- and pilot-plant-scale equipment and on most of the materials that are shipped by rail.

Field Measurement of Physical Properties of Fluid Fertilizer

Measurements of physical properties made in the field are usually not as precise as those made in the laboratory but, with care, useful information can be developed.

Density--It is especially important to measure density because most fluid fertilizer application equipment in the United States is calibrated in gallons per acre and the weight of a gallon of fertilizer must be known fairly closely to obtain accurate application rates.

Two methods of measuring density are usually used. The most common is use of the glass hydrometer calibrated in appropriate units of specific gravity or density. A glass hydrometer calibrated at 60°F (16°C), a thermometer, and a suitable container (hydrometer jar) are required. The jar should be large enough to allow clearance between the sides and the bottom of the hydrometer and the jar. To measure the density, the hydrometer should be gently lowered into the fertilizer avoiding wetting the stem above the level of the liquid. The sample should be stirred with the thermometer until a constant temperature is reached. The hydrometer should then be given a slight spin and read when it comes to rest. When the hydrometer is read, it should not be touching the walls or the bottom of the container. The correct reading is the point at which the surface of the liquid touches the scale. The reading is recorded at the temperature of the sample compared to the temperature at which the hydrometer is calibrated. For example, if the fluid is at 77°F (25°C) and the specific gravity reading is 1.439, it should be recorded as 1.439 at 77°/60°F (25°/16°C). If the hydrometer is calibrated in specific gravity, the density of the solution can be determined by multiplying the specific gravity reading obtained from the hydrometer by the density of water at the temperature of the fluid being measured. If the density of water is not known at the exact temperature of the fluid, a close

approximation can be obtained by multiplying the specific gravity obtained times 8.34, the weight of 1 gallon of water at 62°F (17°C). For example, 1.439 times 8.34 equals 12 pounds per gallon.

A more accurate way to measure density, especially with dark colored fluids and suspensions, is to actually weigh a known amount of the mixture. In the laboratory, this can be done by using a triple beam balance reading in grams and a 100 milliliter volumetric flask. The balance is tared to the weight of the flask, or the empty flask is weighed. The flask is then filled to the mark with the fluid to be measured and the flask weighed. The weight of 100 milliliters of liquid can be read directly from the balance in grams if the flask has been tared, or can be determined by subtracting the weight of the empty flask from the weight of the flask plus the fluid. The density of the liquid at the temperature of the liquid in grams per milliliter can then be determined by dividing the weight of the liquid by 100. The approximate weight of the liquid in pounds per gallon can be determined by multiplying the grams per milliliter obtained times 8.34, as is done with the specific gravity determined by glass hydrometer. This can be done because the specific gravity and density in grams per milliliter of fluids are nearly the same.

A variation of this method is to weigh a known amount of material using a bucket of known volume and any scale available. Frequently a two-and-a-half-gallon bucket and dairy scale are used. The percentage error in this kind of measurement is less than might be supposed because of the large size of the samples being measured.

Saturation Temperatures--A system, similar to the laboratory method, is sometimes used to estimate the saturation temperature in a plant workroom. A sample of the liquid to be tested is put into a test tube and a thermometer is inserted into the tube. The test tube is then inserted into a container of ethanol mixed with dry ice and the fluid is frozen. Methanol-based automobile antifreeze can be substituted for the ethanol but if this is done, the experiment should be performed outside or in a well-ventilated area to prevent fumes from the antifreeze from collecting in the work area. The frozen fertilizer is then allowed to melt while stirring constantly with the thermometer. The temperature at which the last crystal disappears (as read from the thermometer) will give a close approximation of the saturation temperature of the fluid.

pH--It is important, when phosphoric acid is being ammoniated, to know the ammonia-to-phosphoric acid ratio to obtain the optimum solubility of the fluid being produced. This ratio can be obtained by measuring the pH of the fluid (figure 5). The pH can be obtained either with an electronic pH meter or pH paper.

The most accurate method of obtaining pH is with an electronic pH meter, but a pH meter is a precision instrument and must be used and maintained properly. The pH

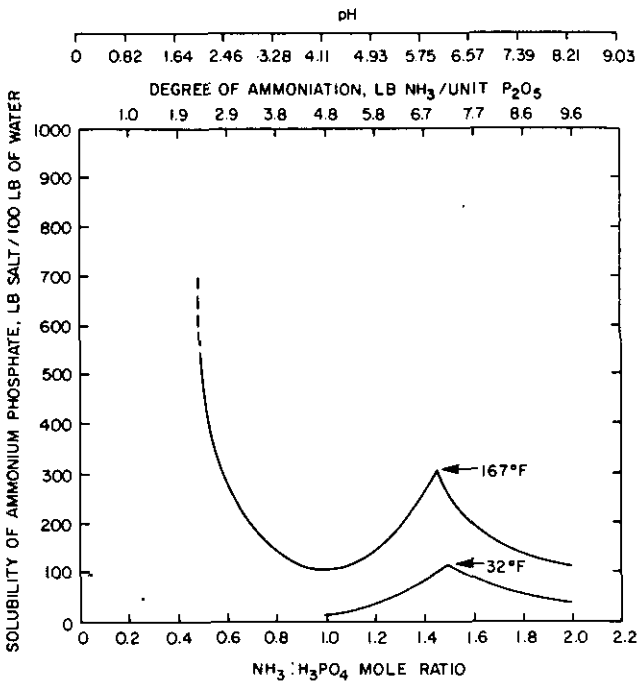

Figure 5. Effect of $NH_3:H_3PO_4$ mole ratio on solubility of ammonium phosphate

meter should have a standardization control, temperature compensation control function switch, and an electrode holder. The electrode can be the glass-calomel reference or a combination electrode type and, especially in a fertilizer plant, spare electrodes should be kept on hand. The pH meter should always be adjusted with a buffer solution (pH 6) and washed with deionized or distilled water before and after each use. The electrode should be stored in deionized or distilled water and not left dry or in fertilizer solution. The operating instructions of the pH meter supplied by the manufacturer should be read and followed closely.

To measure the pH of fluid fertilizer, the probe should be inserted into the fluid and the fluid swirled for about 5 seconds. A thermometer should then be inserted into the sample, the temperature read, and the temperature compensation setting adjusted to the temperature of the solution. After about 45 seconds the reading should be obtained. For accurate measurements, the reading should continue until a constant value is obtained.

Diluting the sample 4 to 1 with distilled or deionized water will sometimes give a more accurate reading. This is especially helpful in the case of suspensions where all soluble salts can usually be dissolved by a 4 to 1 dilution.

Because calibration and maintenance of pH meters in fluid fertilizer plants is a problem, pH paper is often used to control the ammonia:phosphoric acid ratio. With a little practice, pH paper can be used successfully. The pH paper should be chosen carefully. Some pH papers do not work

in fertilizer solutions. The paper should cover a pH range that has the expected pH near the center. For example, if the expected pH is about 6.0, the pH paper range should vary from about 4.5 to 7.5. If readings are difficult to obtain, satisfactory pH readings usually can be obtained with pH paper by diluting the sample 4 to 1 with distilled or deionized water.

The relationship between pH and $N:P_2O_5$ ratio in the pure systems at various polyphosphate levels is given in figure 6. Typical physical properties of some solution and suspension fertilizers are given in tables 3 and 4, respectively.

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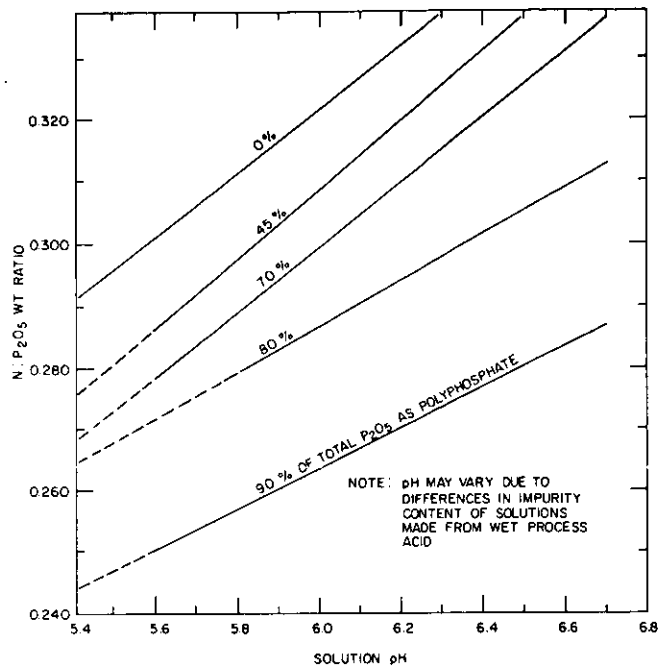


Figure 6. Effect of pH and polyphosphate level on $N:P_2O_5$ weight ratio of ammoniated ortho and superphosphoric acid solutions

Table 3. Typical physical properties of various solution fertilizers[a]

Grade	Specific gravity at 75°F	Density, lb/gal at 75°F	Viscosity,[b] cps at 75°F	Salting-out temperature °F (°C)	pH
8-24-0	1.26	10.5	30	18 (-8)	6.6
10-34-0[c]	1.37	11.4	50	<0 (<-18)	6.0
11-37-0[c]	1.40	11.7	80	<0 (<-18)	6.0
7-21-7[c]	1.33	11.1	50	8 (-13)	6.5
7-7-7[d]	1.24	10.3	40	23 (-5)	6.6
5-10-10[d]	1.25	10.4	40	33 (-1)	6.5
32-0-0[e]	1.33	11.1	50	32 (0)	7.5[f]
28-0-0[e]	1.27	10.6	23	1 (-17)	7.5[f]

[a]Based on thermal phosphoric acid.
[b]Brookfield viscometer, model RVT, No. 2 spindle at 100 rpm.
[c]Contains polyphosphate.
[d]Supplementary nitrogen from urea-ammonium nitrate solution.
[e]Urea-ammonium nitrate solution.
[f]Ammonia added to control corrosion.

Table 4. Typical[a] properties of various suspension fertilizers

Grade	Specific gravity at 75°F	Density lb/gal at 75°F	Viscosity, cps at 75°F	Solidification temperature, °F (°C)	pH
12-40-0[b]	1.44	12.0	700	0 (-18)	6.0
13-38-0	1.44	12.0	800	15 (-9)	6.4
9-32-0[b]	1.40	11.7	200	-7 (-22)	6.7
10-30-0	1.37	11.4	250	NA[d]	6.3
31-0-0[c]	1.32	11.0	150	NA[d]	8.0
18-0-18	1.37	11.4	160	NA[d]	7.4
13-13-13	1.40	11.7	600	NA[d]	6.3
4-12-24	1.41	11.8	400	NA[d]	6.3
0-0-31[e]	1.30	10.8	360	NA[d]	6.8

[a]Based on wet-process orthophosphoric and polyphosphoric acids. Properties may vary with impurity content of raw materials used and amount of suspending clay added.
[b]Contains polyphosphate.
[c]Urea-ammonium nitrate suspension.
[d]Not available.
[e]Potash suspension.

Chapter 4

Chemical Properties

By A. W. Frazier

The chemical knowledge of fluid fertilizers has increased from a few pure system studies prior to 1960 to the present development of multicomponent systems including micronutrients and impurity components in ammoniated wet-process polyphosphoric acids. Initially, relatively pure soluble materials were available for the production of clear liquid fertilizers. Even though their physical properties, such as ease of transport and distribution, lack of dustiness, and compatibility with herbicides and pesticides, were very desirable, the low solubility of these products (1) limited their fertilizer value. This set the stage for high-analysis liquids which later became available from ammoniation of electric-furnace superphosphoric acid. The chemistry of these four-to-five component ammonium polyphosphate systems was not extremely complicated and the saturation isotherms of the pure systems were developed (2). The addition of micronutrients complicated the chemistry to some extent and led to a significant quantity of knowledge about the solubilities and characteristics of many new compounds. These included both the saturating micronutrient compounds (3) and the compounds of ammonium polyphosphate (4) dissolved in these solutions. This information described the limits of nutrient levels that could be obtained from the pure systems. The development of chromatographic analysis for the polyphosphate species provided a method by which the chemistry of the hydrolysis of polyphosphates and their ultimate return to orthophosphate could be monitored.

Advances made in the polyphosphate chemistry of liquids prepared from highly pure electric-furnace acid were impressive and provided a background for understanding similar products prepared from the less expensive wet-process superphosphoric acid (WPSA). However, there was a gap in needed fundamental knowledge presented by the use of these highly impure multicomponent acids. The precipitation and gelling problems presented by the redistribution and interaction of the iron, aluminum, magnesium, and fluorine needed study. Considerable progress has now been made in defining the large number of compounds (3, 5, 6, 7, 8, 9, 10) that can be present in experimental ammonium phosphate fluids. However, a fundamental application of chemical methods on the complex multicomponent phase systems is needed before long-term storage of stable fluids can be guaranteed. An applied research approach is being directed toward such problems as acid purification, solid phase identification, impurity sequestration, and others which have resulted due to the use of wet-process phosphoric acids. Since wet-process acids are now being supplied with increasingly higher impurity concentrations, a major effort is now directed toward the production of stable suspensions; the precipitated impurities will be more acceptable among other suspended material than in a clear liquid.

A primary problem in the study of suspensions is isolating and determining the chemical and physical properties of the impurity precipitates. These characteristics such as citrate solubility, crystallite size, water solubility, and gel-forming properties will be reflected in the overall properties of the suspension. Liquid and suspension fertilizers, in essence, are very similar—a liquid approximates a suspension with solids removed whereas a suspension is a liquid that contains solids. Both have a liquid base that is almost saturated with fertilizer salts. Thus, knowledge gained from one type of fluid can be applied to the other. In order to compete with solids, fluids must have a high plant food content and provide a guaranteed stable storage life over a given period of time. These are the goals of the chemical research being conducted today.

PHOSPHATE SOURCES FOR FLUID PRODUCTION

The initial phosphate source for the production of fluid phosphate fertilizers was orthophosphoric acid prepared from elemental phosphorus in excess of that required by U.S. industry for use in food products and detergents. This excess elemental phosphorus was burned, hydrolyzed, and converted to phosphoric acid for ammoniation to 8-24-0 base solution. The basic NH_4-H_3PO_4-H_2O isotherms (11) provided data for selection of a satisfactory base solution. Many pure systems of mixed fertilizer components have been reported (1, 12, 13, 14, 15). The additional fertilizer materials included in these studies were ammonium nitrate, urea, potassium chloride, and ammonium sulfate. The plant nutrient values for these systems at 32°F (0°C) ranged from 15% for saturated KCl to 38% for liquids at the invariant point between $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$.

Real progress for fluid fertilizer production began with the development of electric-furnace superphosphoric acid. The production of this acid follows the stepwise oxidation of elemental phosphorus with subsequent limited hydrolysis. Oxidation of phosphorus can occur at three levels:

$$P_4+O_2 \rightarrow 2P_2O \text{ hypophosphite} \quad (1)$$

$$P_4+3O_2 \rightarrow 2P_2O_3 \text{ phosphite} \quad (2)$$

$$P_4+5O_2 \rightarrow 2P_2O_5 \text{ phosphate} \quad (3)$$

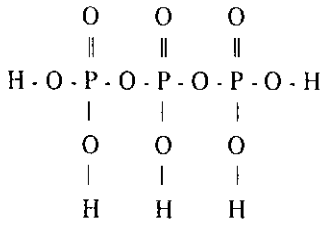
The first two oxides are unstable and oxidize stepwise to the stable P_2O_5 form with phosphorus having a valence of +5. The phosphorus oxides are hygroscopic and react readily with water to produce the three acids:

$$P_2O+3H_2O \rightarrow 2H_3PO_2 \text{ hypophosphorous acid} \quad (4)$$

$$P_2O_3+3H_2O \rightarrow 2H_3PO_3 \text{ phosphorous acid} \quad (5)$$

$$P_2O_5+3H_2O \rightarrow 2H_3PO_4 \text{ phosphoric acid} \quad (6)$$

These equations provide the basic reactions for the electric-furnace acid process. For polyphosphoric acid, the water in equation 6 is limited to a value between 1 and 3 so that condensed phosphoric acids are the final product. These acids have the general formula of $H_{n+2}P_nO_{3n+1}$ where n for practical purposes varies from 1 to about 15 (theoretically infinity) and their weight percentage distribution varies with the final P_2O_5 analysis (16). Acids with P_2O_5 values above 80% are syrupy viscous liquids with more of the longer chain length acids whereas acids around 75% P_2O_5 are more fluid and contain a mixture of polyphosphates mostly having a chain length from 1 to 4. These are named orthophosphoric acid (H_3PO_4), pyrophosphoric acid ($H_4P_2O_7$), tripolyphosphoric acid ($H_5P_3O_{10}$), and tetrapolyphosphoric acid ($H_6P_4O_{13}$). The bonding configuration for tripolyphosphoric acid, as an example, is:



Phosphate Rock Sources

The impurity load in WPSAs reflects the concentrations found in the phosphate rock source and varies widely among the phosphate raw materials of North Carolina, Western United States, and the various fields in Florida. The primary rock source in the United States used for research on fluid fertilizer production is central Florida; most fluid processes have been developed to accommodate the impurities in this rock. Merchant-grade acids (54% P_2O_5) produced from this rock have typically contained about 1.5% Al_2O_3, 0.5% MgO, and black carbonaceous matter, all of which interfere with the production of clear, stable liquids. However, suspension processes using Florida acid are well developed and can result in a stable suspension fertilizer (17). North Carolina phosphate rock is high in CO_2 and organic matter, and is usually calcined prior to acidulation to remove organics and prevent foaming. This process is beneficial in preventing the formation of black carbonaceous material in fluid fertilizers. The high magnesium content of this rock is being controlled in the acid product to the extent that it is the most acceptable phosphate source in this country for successful liquid fertilizer production. A contributor to this success was the development of the pipe-reactor process by TVA for the production of very high polyphosphate (up to 80% of the P_2O_5) products (18).

Western U.S. phosphate rock sources are high in most impurities including organic matter and are less suitable for fluid production. However, when extensive research studies are applied, similar to those on Florida rock, a suitable suspension fertilizer should result.

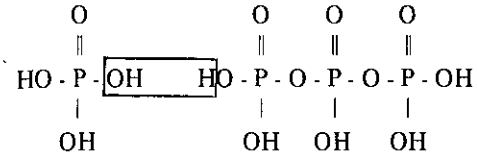
Wet-Process Acid

The advent of wet-process phosphoric acid (WPA) and its condensation product, WPSA, as an economical source of P_2O_5 for fluid fertilizers significantly increased the need for chemical information to control the various types of precipitates that are detrimental to the fluid properties of these fertilizers. The impurities in WPA play a significant role in determining the final grade and quality of both fluid and solid fertilizers. The cations of iron, aluminum, magnesium, and sodium will reduce the possible nitrogen grade, whereas sulfate and fluoride lower the P_2O_5 grade. It is possible to produce standard fluid grades, such as 10-34-0 liquids or 13-38-0 suspensions, at higher impurity concen-

trations but the resulting liquid will have a higher salting-out temperature and the suspension will have a higher viscosity. In both cases the increased impurities will be replacing some of the water used to fluidize the fertilizer.

Early in the study of WPSA liquid products, attempts were made to reach higher and higher levels of polyphosphate (18) in the ammonium polyphosphate liquid using only a WPA phosphate source. Also, numerous reports and patents were issued for the purpose of defluorinating wet-process acids in order to prevent $MgAl(NH_4)_5(P_2O_7)_2F_2 6H_2O$ from precipitating in the liquids. This cure was only partially effective because the stable precipitate now became $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$. Consequently, the next effort to obtain a stable, clear liquid fertilizer was magnesium removal from the original phosphate rock or from the WPA intermediate. Like the fluorine removal processes, a large number of processes for magnesium removal were proposed and patented but primarily for economic reasons most did not prove to be adaptable to fertilizer systems. The two most promising processes appear to be the precipitation of $MgH_2P_2O_7$ from 70% P_2O_5 WPSA (6) or the precipitation of $MgSiF_6 \cdot 6H_2O$ from 55% P_2O_5 acid (19). Considerable effort is still being applied to the purification of WPA, especially since there is increased use of lower-grade rocks containing larger quantities of cation impurities notably Mg, Al, and Fe. Probably, some of these purified acid products will be more applicable to feed- and detergent-grade products with the by-product sludge fraction going to the solid fertilizer industry.

As the cost of electric-furnace superphosphoric acid to produce 11-37-0 increased, a more cost-effective approach was developed whereby mixtures of 11-37-0 and ammoniated merchant-grade wet-process acids were produced. This provided two desirable effects: (1) the impurities in the WPA were diluted to help prevent precipitation, and (2) the polyphosphates from the 11-37-0 sequestered the impurities. Later the economics of electric-furnace acid limited the use of even this process for making clear liquid products. WPSA was developed to obtain the polyphosphate components necessary for sequestration. This new acid form was produced by continuing the concentration process of filter grade (30% P_2O_5) acid to merchant grade (54% P_2O_5) and on to superphosphoric acid (70% P_2O_5). An example of condensation with heat is shown below for an orthophosphoric acid and a tripolyphosphoric acid going to a tetrapolyphosphoric acid as they lose a mole of water. Other polyphosphoric acids are formed in a similar manner.



The primary chemical problem associated with concentrating WPSAs was directly related to the use of submerged combustion which resulted in localized overheating and caused $(Fe, Al)H_2P_3O_{10}$ and $(Al, Fe)(PO_3)_3$ to precipitate (6). These solids not only interfered with the concentration process but also are citrate insoluble and remained as stable precipitates in ammoniated products. The concentration process for these acids effectively eliminated the precipitation problem caused by fluoride since any unevolved fluoride is so strongly complexed with the aluminum that it is unavailable for any other reaction. For example, figure 7 is a plot of the Al_2O_3 and F content of 11-37-0 high polyphosphate fertilizers prepared from several commercial WPSAs. This fluoride was not available for the precipitation of $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ even though it ranged up to 0.18%. On the other hand, as little as 0.02 F as NH_4HF_2 would cause the precipitation of this compound in these liquid products. The MgO content of the liquids was around 0.6% and $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$ eventually formed in all samples as the higher polyphosphate species hydrolyzed to pyrophosphate.

The process of increasing the polyphosphate values for sequestration purposes in 10-34-0 and 11-37-0 liquids reached a practical limit with the use of 68%-70% P_2O_5 WPSAs and anhydrous ammonia in a pipe reactor (18). The polyphosphate content reached 85% of the total P_2O_5 (15% orthophosphate, 35% pyrophosphate, 30% tripolyphosphate, 10% tetrapolyphosphate, and 10% greater than tetra) and the storage life was extended to about 3 months. However, eventually $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$ precipitated in these high poly liquids and it was difficult to increase this 3-month value or to predict any finite storage life for any particular acid product.

SOLUBILITY DIAGRAM FOR MACRONUTRIENTS

The maximum fertilizer grade of liquid materials depends on the saturation composition of the major nutrient components at temperatures down to 32°F (0°C), which are likely to be encountered in cooler climates. Likewise, in order to obtain maximum grade, it is necessary to understand the interaction of components with each other; the best known example of which is the use of ammonium nitrate and potassium chloride. Both materials have reasonable solubilities in fluid fertilizers when used alone. However, attempts to saturate a fluid with either material in the presence of the other, results in salting out of potassium nitrate. Numerous studies have been reported (1, 2, 20) describing the solubility relationships in liquid mixed fertilizer systems with and without polyphosphate. Many other reports are now available describing the phase systems involved in the ammonium polyphosphate mixtures with

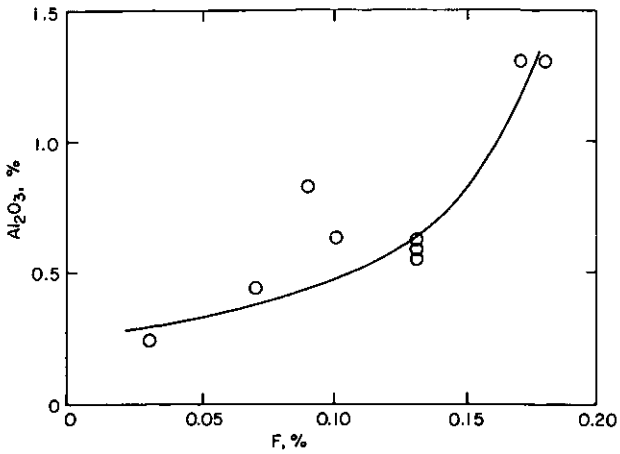


Figure 7. Relation between aluminum and residual fluorine contents of ammoniated superphosphoric acids prepared from wet-process acids

and without urea amendments (21, 22, 23), and with potassium values (24). The heat of ammoniation of electric-furnace superphosphoric acid from which these fertilizers are obtained is also available (25). All these reports have extensive literature references to earlier reports which describe simpler systems, frequently at 32°F (0°C), 77°F (25°C), and 122°F (50°C), so that the basic descriptions of the solution and solid phases in fluid fertilizers are available including the optical, X-ray, and infrared properties of the solid components. An examination of these phase systems shows that higher analysis fluids can usually be obtained from multicomponent mixtures and from mixtures of several polyphosphate species.

Interaction of the macronutrients is demonstrated by comprehensive diagrams (20) which are reproduced in figures 8 and 9. The total plant food content (%N + $\%P_2O_5$ + $\%K_2O$) is shown on lines of equal concentration and is greatest in solutions of pure ammonium polyphosphates. Since chloride is a diluent for all three macronutrients and KCl has a low solubility, the use of this component results in a very low grade liquid fertilizer.

The data in figures 8 and 9 (20) show that plant food values up to 45% could be obtained in pure ammonium polyphosphate systems. The addition of other nutrients such as urea, NH_4NO_3, and especially KCl reduced the total nutrient concentration. Because of high shipping costs and the low analysis of these trinutrient systems, these solutions are useful at small mixing plants close to application sites where one-time applications of special ratios are required.

Fundamental solubility diagrams (23, 26, 27, 28, 29, 30, 31) are available that give the maximum grade possible at various pH values and nutrient ratios for pure systems. The highest N + P_2O_5 value reported was 57.45% at pH 5.61 (27) in the system NH_3-H_3PO_4-$H_4P_2O_7$-$H_5P_3O_{10}$-$H_6P_4O_{13}$-H_2O at 32°F (0°C). Similar systems including urea (21) but without the benefit of $H_6P_4O_{13}$ reached a

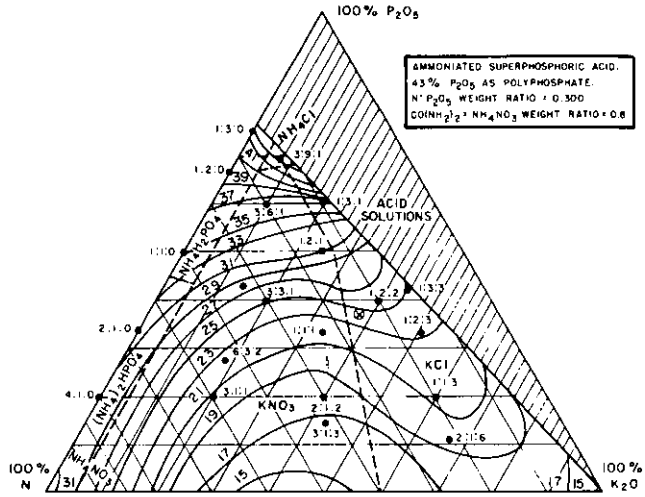


Figure 8. System: ammonia-superphosphoric acid-urea-ammonium nitrate-potassium chloride-water at 32°F

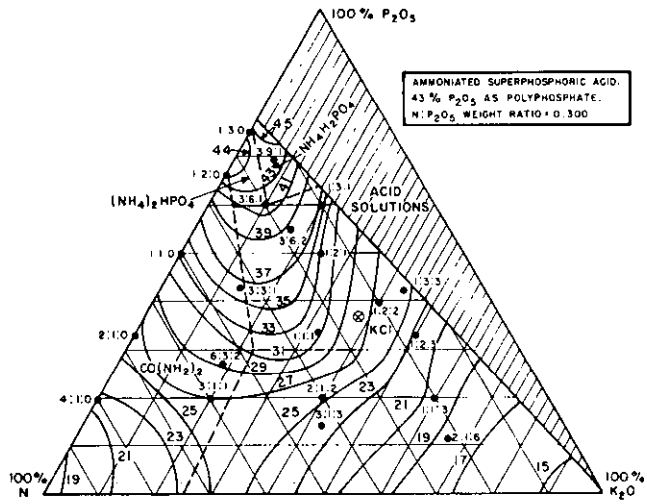


Figure 9. System: ammonia-superphosphoric acid-urea-potassium chloride-water at 32°F

plant food value of 53%. Systems involving potassium ortho- and pyrophosphate (no KCl) with and without urea and ammonia (22, 24, 26) showed that on the high potassium side, nutrient values up to 64% could be obtained at 32°F (0°C). Many new compounds (4, 24, 26, 32) were isolated, identified, and characterized during the determination of these phase systems. The precipitating solids that are in equilibrium in the ammonium potassium polyphosphate system are shown in table 5. Some of the conditions under which these compounds are encountered in production processes for fluid fertilizers have been reported (33), and others are described elsewhere in this text.

The complexity that can be encountered in a simple four component fertilizer system is shown in figure 10 where the system K_2O-NH_3-$H_4P_2O_7$-H_2O at 77°F (25°C) is projected on the K_2O-$(NH_4)_2O$-H_2O face. The figure

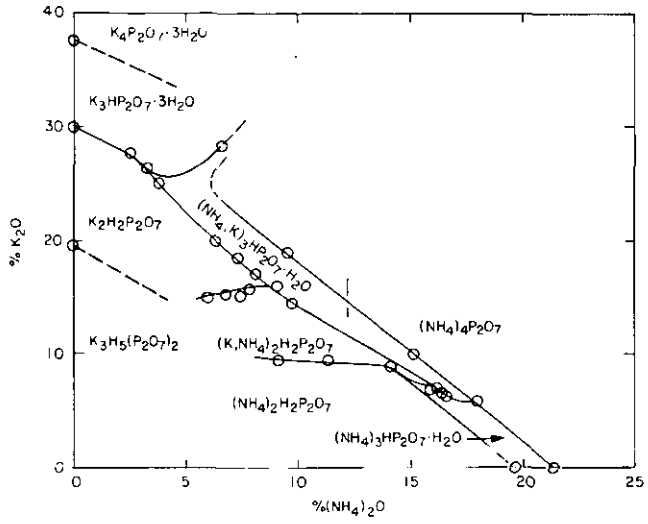


Figure 10. The system NH_3-K_2O-$H_4P_2O_7$-H_2O at 25°C projected on the $(NH_4)_2O$-K_2O-(P_2O_5 + H_2O) face

shows that each di, tri, and tetra substituted compound of ammonia and potassium with pyrophosphoric acid has its own field of stability as well as the more acid salt $K_3H_5(P_2O_7)_2$. Not only is there a lack of isomorphous substitution between the ammonium and potassium end-members, but also the mixed ammonia potassium di and tri substituted pyrophosphates have different crystalline structures from these end-member compounds and consequently their own unique stability fields.

INFLUENCE OF PRODUCTION METHODS

Electric-Furnace Acid

Tank-type reactors were originally used for the ammoniation of 80% P_2O_5 electric-furnace superphosphoric acid to produce 11-37-0 solution and 12-40-0 suspension grades with a very high polyphosphate content (34). The high-analysis acid with its multicomponent polyphosphate composition was readily obtained by limiting the water of hydration during the process of converting elemental phosphorus to polyphosphoric acid. The 12-40-0 grade, after 1 to 3 days, would frequently contain a voluminous precipitate of $(NH_4)_5P_3O_{10} \cdot 2H_2O$ (34). This did not restrict the maximum grade of these suspension fertilizers since these thin plate crystals would not settle. Likewise, a redistribution of the polyphosphate species due to hydrolysis would quickly eliminate tripolyphosphate as a saturating component and the crystals would redissolve after 20 to 30 days. After about 2 or more years' storage, continued hydrolysis of the polyphosphate species in solution eventually resulted in the precipitation of $(NH_4)_2HPO_4$ and naturally this occurred more rapidly at higher analysis and higher temperatures. Otherwise, these products were trouble free.

Electric-Furnace Pipe-Reactor Products

The success of liquid fertilizers produced in a pipe reactor from WPSA precluded extensive studies using the more expensive electric-furnace acid. However, several tests were conducted with this high-purity acid, and variations in the process resulted in some unusual redistribution of the polyphosphate species in the ammonium polyphosphate (APP) melt (4, 35). The parameters causing this redistribution have not been fully researched but limited tests have shown that a preheated, 78.1% P_2O_5 acid with 45% of the phosphate at $P_2O_7^{4-}$ results in an APP melt having 82% of the phosphate as pyrophosphate. Likewise, an 83.5% P_2O_5 acid with 9% of the P_2O_5 above a chain length of 9 was converted, after preheating, to an APP melt having 36% of the P_2O_5 above nonapolyphosphate. This high-poly ammonium phosphate fraction is water insoluble (~0.1g/100 cc H_2O) and has the formula, $(NH_4)_{n+2}P_nO_{3n+1}$ where n was estimated from the chemical ratio of N/P to be 51 (4, 36). Studies of pipe-reactor products, which became polymerized solely by the temperatures of ammoniation (~400°-700°F, 204°-371°C), have shown polyphosphate distributions comparable to acids having the same polyphosphate level rather than the unusual distributions described above (18).

Tank Reactor WPA

The use of tank reactors to produce stable liquid grades (10-34-0 or 11-37-0) from anhydrous ammonia and high conversion WPSA was reasonably successful (37). At the low fluoride concentrations found in these products, all the fluorine is complexed with aluminum so that it cannot precipitate as $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$. Thus, the stable solid phase is $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$, which precipitates at about 0.2% MgO in these liquids but can remain supersaturated at about 0.3%-0.4% MgO for a few weeks.

The developmental program for 13-38-0 orthophosphate suspension in tank reactors has been successful (17) with only small applications of chemical parameters. Fluosilicic acid was developed as a crystal modifier for $NH_4H_2PO_4$ for the purpose of producing thin needles instead of the thick rods that tend to settle rapidly (38). The major emphasis on developing 13-38-0 suspensions was limited to central Florida acid. Several exploratory tests using North Carolina acid having a high magnesium and a low aluminum content required chemical control (39) to prevent the formation of gelatinous precipitates. A simple relationship between the cation impurities and fluorine

concentration in suspensions (17) was developed in order to meet the viscosity limitation of 1,000 centipoises.

The important parameters that control the types of solids during ammoniation of WPA are time and temperature. Two- and three-stage reactors (17, 40, 41) and long retention times in first stages at elevated temperatures cause the iron to precipitate as the citrate-insoluble compound $FeNH_4(HPO_4)_2$ in an orthophosphate or low polyphosphate (<10% of total P_2O_5) system. To prevent this, fluoride in excess of that complexed with the aluminum, which precipitates as the stable crystalline form of $AlNH_4HPO_4F_2$, will result in precipitation of the iron compound, $Fe(NH_4)_2(HPO_4)_2F$. Magnesium precipitates as well crystallized $MgNH_4PO_4 \cdot H_2O$, which after cooling in storage, will slowly recrystallize as $MgNH_4PO_4 \cdot 6H_2O$ and consume a small quantity of the free water.

Table 5. Stable compounds in the ammonium potassium polyphosphate systems

Compound	pH range in pure system	Occurrence in fertilizers (reference)
$NH_4H_5(PO_4)_2$	<1	Forms in slightly ammoniated acid solutions above 59% P_2O_5 (32)
$(NH_4)_3H_9(PO_4)_4$	<1	
NH_4HPO_4[a]	1-6	Forms in concentrated fluids (23)
$(NH_4)_2HPO_4$[a]	6-8	Forms in concentrated fluids (23)
$(NH_4)_3PO_4 \cdot H_2O$	>8	Forms during localized overammoniation (23)
$(NH_4)_2H_2P_2O_7$	<4.8	Comprises the stable crystalline phase when pipe reactor solids are saturated in water (without additional NH_3) (4, 23)
$(NH_4)_3HP_2O_7$[a]	5.0-6.1	Precipitated from high analysis fluids high (>50%) in P_2O_7 content (4, 23)
$(NH_4)_3HP_2O_7 \cdot H_2O$[a]		
$(NH_4)_4P_2O_7$[a]	>6.1	
$(NH_4)_4P_2O_7 \cdot H_2O$		
$(NH_4)_3H_2P_3O_{10}$	<3.7	Precipitates in ammonium tripolyphosphate system at 9% N and 43% P_2O_5 (4, 31)
$(NH_4)_3H_2P_3O_{10} \cdot H_2O$		
$(NH_4)_4HP_3O_{10}$	3.7-5.0	Precipitates in high poly fluids having a tripolyphosphate content above 38% (4, 31)
$(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O$	4.9-5.4	Stable compound in the NH_3-$H_5P_3O_{10}$-H_2O system at 37% P_2O_5 (4, 31)
$(NH_4)_5P_3O_{10} \cdot 2H_2O$[a]	>5.4	Forms in high poly fluids having a tripolyphosphate above 35% (4, 31)
$(NH_4)_5P_3O_{10} \cdot H_2O$[a]		
$NH_4NO_3 \cdot (NH_4)_3HP_2O_7 \cdot H_2O$	← 6 →	Forms when NH_4NO_3 is used to augment the N content of ammonium polyphosphate fluids high in pyro content (4)
$NH_{4\,n+2}P_nO_{3\,n+1}$	0-6	Precipitates on dissolution of pipe reactor solids made from 80%-90% P_2O_5 acid (4)
$(NH_4,K)_2H_2P_2O_7$	4.6-5.2	Forms in the mixed ammonium-potassium pyrophosphate system (24)
$(NH_4,K)_2H_2P_2O_7 \cdot 0.5H_2O$		
$(NH_4,K)_3HP_2O_7 \cdot H_2O$	4.9-8.6	Forms in the mixed ammonium-potassium pyrophosphate system (24)
$KH_5(PO_4)_2$	<1	Forms when KH_2PO_4 is charged to reagent H_3PO_4 (26)
KH_2PO_4	1-9	Forms in potassium orthophosphate systems (26)
$K_2HPO_4 \cdot 3H_2O$	9-13	
$KH_3P_2O_7 \cdot H_2O$	<0.43	Stable phase in the potassium pyrophosphate system at 35% P_2O_5 and 12% K_2O (26)
$K_3H_5(P_2O_7)_2$	0.43-2.1	Stable phase in the potassium pyrophosphate system at 29% P_2O_5 and 12% K_2O (26)
$K_2H_2P_2O_7$	3	Forms when heated (500°C) K_2HPO_4 is charged to acetic acid (26)
$K_2H_2P_2O_7 \cdot 0.5H_2O$	2.1-6.4	The stable potassium pyrophosphate in a potassium polyphosphate mixture (26)
$K_3HP_2O_7 \cdot 3H_2O$	6.4-10.1	The stable potassium pyrophosphate salt in a potassium polyphosphate mixture at 35% K_2O and 30% P_2O_5 (26)
$K_4P_2O_7 \cdot 3H_2O$	>10.1	The stable pyrophosphate is the potassium polyphosphate system at 38% K_2O and 28% P_2O_5 (26)

[a]Compounds most commonly found in fluid fertilizers.

In a single-stage continuous reactor, the acid and ammonia are added simultaneously to a tank of the fluid product at a pH above 6. The impurities are very insoluble and precipitate rapidly as a colloidal gelatinous form of $FeNH_4(HPO_4)_2 \cdot nH_2O$ and $AlNH_4HPO_4F_2 \cdot nH_2O$ which trap and retain a large amount of water. Recent data (42, 43) indicate that the fluoride compound is stable and does not change. However, the $FeNH_4(HPO_4)_2 \cdot nH_2O$ is unstable and this amorphous form undergoes dissolution with precipitation of the lesser soluble and more gelatinous $FePO_4 \cdot nH_2O$ which has a strong affinity for water and forms as a very viscous gel. This reaction appears to continue slowly during storage and depending on the crystallinity of the $FeNH_4(HPO_4)_2$ may require years to reach stability. These amorphous precipitates are frequently gel-like and tend to form after the viscosity has been adjusted with clay prior to storage. The fine-grained form of $AlNH_4HPO_4F_2$ and $Fe(NH_4)_2(HPO_4)_2F$ contributes to the overall surface area of the solids.

Pipe Reactor

Products obtained by feeding ammonia, superacid, and water simultaneously to a tank of 10-34-0 product will, at best, maintain the same polyphosphate distribution as the original acid (44). The use of tank reactors for ammoniating phosphoric acid does not take advantage of the heat of ammoniation which is removed by heat exchange or evaporative cooling.

The advent of the pipe reactor (18) greatly enhanced clear liquid fertilizer growth. Prior to this, batch ammoniation of 70% P_2O_5 WPA to produce 10-34-0 liquids containing approximately 50% of the P_2O_5 as pyrophosphate resulted in liquids with precipitation problems. While pyrophosphate is effective in preventing the precipitation of iron, aluminum, and magnesium orthophosphates, the high $P_2O_7^{4-}$ usually caused precipitation of $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$ after an unpredictable incubation period varying from 2 days to 2 months. As discussed above, the total magnesium content is an important factor in limiting this time period but several other factors are also involved. The worst condition of precipitation occurs when a small residual fluoride concentration (0.7% to 0.9%) is present in the starting acid.

Anhydrous ammonia reacted with 68%-70% P_2O_5, WPSA in a pipe reactor produces liquids having a higher polyphosphate content than the original acid, and the 10-34-0 and 11-37-0 APP liquid products have superior storage properties as compared to batchwise, tank ammoniation of the same acids (18). As described elsewhere, these liquids contain polyphosphate concentrations up to about 85% and remain free of precipitates for 1 to 3 months at 100°F (38°C) with one pilot-plant product being satisfactory for 6 months at 80°F (27°C). Three factors contribute to the extended storage life of these samples as tested. The magnesium concentration in the final products was only 0.3% to 0.4%, the fluoride content was 0.1% or less, and the $P_2O_7^{4-}$ concentration was 40% or less of the total P_2O_5. Since the precipitating phases of $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$ and $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ are both pyrophosphate, the lower $P_2O_7^{4-}$ in these products, as compared to 50% $P_2O_7^{4-}$ in tank products, tends to reduce the rate of precipitation. However, hydrolysis of the higher polyphosphates to pyrophosphates is rapid as compared to the hydrolysis of pyrophosphate itself (45). Thus, the long-term storage value of these very high polyphosphate solutions is limited by the buildup of pyrophosphate. One test sample from a commercial acid reached a level of 70% pyrophosphate after 3 months and contained a solid phase comprising both $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ and $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$.

The "direct pipe-reactor process" in which merchant-grade WPA is preheated and reacted with anhydrous ammonia in a pipe reactor has been researched (46, 47). The heat of ammoniation of this reaction supplies 80% of the heat required for condensing about 30% of the orthophosphate to pyrophosphate. However, when made from acid produced from Florida rock, these liquid products have a moderate fluoride concentration, a low polyphosphate concentration (all P_2O_7), a very limited storage life, and result in a voluminous precipitate of $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ after 2-3 days. They are also reported to contain citrate-insoluble P_2O_5 (46). Two factors contributed to the failure of the direct process to produce a stable clear liquid 10-34-0 product: the low solubility of the fluoride compound $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ and the higher residual fluoride content (~0.6% F) of merchant-grade acid as compared to the very low quantity (~0.2% F) left in WPSA. Research data (7) show that the quantity of $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ that can precipitate in these liquid fertilizers is only limited by the least abundant component. Either magnesium, aluminum, or fluoride in solution can be reduced to 0.01% by precipitation if the other two exceed this value.

Pipe-Reactor Scale Formation and Corrosion

In early development of the pipe reactor for the production of liquid fertilizers from high-conversion WPSA (containing about 50% or more polyphosphate), an insoluble precipitate was encountered in the melt within 1 to 2 seconds after mixing. Rapid dispersion of the hot melt in a tank of 10-34-0 at pH 6 prevented the formation of this compound. Research studies showed that the iron and aluminum crystallized in the melt and on the inside walls of the reactor as $(Fe, Al)NH_4P_2O_7$ which is not only citrate insoluble but has a very slow rate of solution in hot concentrated acids. It is readily soluble in hot caustic solu-

tions. The parameters controlling the formation of this compound were thoroughly studied (5) and several factors were effective in reducing its formation, i.e., higher nitrogen to phosphate ratio, lower temperature, higher fluoride content, lower poly levels, and lower retention time. None of these variables could be applied to pipe-reactor products so that a solid high polyphosphate APP, free of citrate-insoluble P_2O_5, could be produced. A lower temperature resulted in lower polyphosphate, a higher nitrogen to phosphate ratio could not be obtained except under pressurized conditions, the retention time was already very small, and an economical source of fluoride was unavailable. The lower temperature parameter was eventually achieved in the form of a water jacket around the pipe reactor to retard the formation of (Fe, Al)-$NH_4P_2O_7$ on the inside wall of the pipe. This skin-effect cooling did not significantly affect the polyphosphate content but did extend the useful life of the pipe reactor before clean-out time was required for the removal of the deposit in the pipe. APP melts from the pipe reactor, containing lower polyphosphate concentrations (~25%), could be granulated successfully without the formation of insoluble solids. At lower poly levels, iron and aluminum (mainly the iron form) still deposited inside the pipe, not as the pyrophosphate, but as (Fe, Al)$NH_4(HPO_4)_2$ in the form of dense crystalline spheres up to 5 mm across. This compound also is citrate insoluble and very slowly acid soluble but does not form in the cooled melt. One method for removing these pipe deposits is to heat the removed section of pipe at 600° to 700°C so that frothed glass of iron and aluminum polyphosphate can flow from the pipe. The stable aluminum fluoride complex in these hot melt systems is $Al_3(NH_4)_5H_2(PO_4)_4F_4$ (5); however, the short retention time in a pipe reactor prevents its formation.

In contrast to WPSA, electric-furnace superacid reacted in a pipe reactor resulted in rapid corrosion of a Type 316L pipe at the same zone where deposits form with WPA. Mixing the two acids to obtain an optimum iron content was beneficial to both problems by depositing a small controlled quantity of (Fe, Al)$NH_4P_2O_7$ as a protective coating.

Fluids from Solids

Solid ammonium phosphates from WPA have become popular fertilizers because of their ease of manufacture, high analysis, and good storage properties. The production of diammonium phosphate (DAP) at the nominal grade of 18-46-0 has become a standard in the industry and allows for a total impurity content of 15% (41, 48). This grade is readily obtained from high-grade rock sources or from clarified WPA products. However, acids from low-grade rocks or sludge acids cannot meet grade for DAP and are more suitable for a nonstandard monoammonium phosphate (MAP) grade such as 10-50-0 which allows for 18%-19% total impurities. The final form of the impurities in these ammoniated products has recently been determined by Dillard, *et al.* (41, 42, 48) who have identified the impurity compounds that are in equilibrium with MAP and DAP and their effect on suspension grades prepared from them (table 6) (43). The production of suspension mixtures from granular ammonium phosphate (43, 49, 50) eliminates the problems associated with long-term storage of fluids because they can be processed as needed from the stored solids. Recent studies using solid ammonium phosphates from different acid sources showed that 11-33-0 suspension grades made from MAP without polyphosphates became excessively viscous and completely solidified after 1 week of storage. These results could not be correlated with operating parameters and varied widely depending on the MAP source. Two chemical controls previously applied to suspensions produced directly (17, 43) were effective in maintaining their fluid property. A controlled fluorine concentration solubilized some of the iron and aluminum and changed the stability region in which hydrated gel formation (Fe, Al)$PO_4 \cdot nH_2O$ occurred to one in which $AlNH_4HPO_4F_2$ and $Fe(NH_4)_2(HPO_4)_2F$ are stable. At

Table 6. Impurities in 11-33-0 prepared from wet-acid MAP

Compound in MAP		Fate in 11-33-0 suspension
$FeNH_4(HPO_4)_2$ (citrate-insoluble)	→	$FePO_4 \cdot nH_2O$ gel
$Fe_3KH_{14}(PO_4)_8 \cdot 4H_2O$	→	$FePO_4 \cdot nH_2O$ gel
$Fe(NH_4)_2(HPO_4)_2F$ (crystalline)	→	No change
$AlNH_4(HPO_4)_2$ (citrate-insoluble)	→	$Al(NH_4)_2H(PO_4)_2 \cdot 4H_2O$ (crystalline)
$AlNH_4HPO_4F_2$	→	No change
$Mg(NH_4)_2(HPO_4)_2 \cdot 4H_2O$	→	$MgNH_4PO_4 \cdot 6H_2O$
$CaHPO_4$ } $CaSO_4$ }	→	$Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$
(Mg,Fe,Al)-NH_4-P_2O_7-F (gel)	→	$MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ or gel Clear solution (controlled F) $(NH_4)_3AlF_6$ (excess F)
$MgAl(NH_4)_2H(PO_4)_2F_2$	→	No change

higher concentrations of iron, aluminum, magnesium, and other impurities, the limit of fluoride sequestration is exceeded and it becomes necessary to reduce the grade to 10-30-0. It is conceivable that with the use of low-grade phosphate rocks and sludge acid products, it may be necessary to reduce the grade to 8-25-0 and still need fluorine in order to produce an acceptable fluid. Similar controls may be required for mixed systems such as 8-8-8 or 6-6-6 grades with or without micronutrients.

Limited unpublished TVA data (42, 43) for several suspensions prepared with granular ammonium phosphates from different acid products has provided a correlation for controlling the viscosity of these suspensions. These results show that it is necessary to add fluorine, as HF, NH_4HF_2, or similar source, until the weight ratio of $(Fe_2O_3+Al_2O_3+MgO+CaO/F)$ is near 3 or less. This ratio produces the maximum solubility of impurities and prevents the formation of gels which may become stable at other fluoride values. The highest possible grade can then be determined by the total impurity concentration including weight percent $Fe_2O_3+Al_2O_3+MgO+CaO+SO_3+F$. When the total impurities in the fluid fertilizer sum to 7.5 to 8.0%, an 11-33-0 product, stable for at least 10 weeks, can be produced. Experience has demonstrated that this relationship is acceptable for MAP suspensions prepared from Florida, Western United States, or North Carolina acids. Other acids, such as spent pickling acids or sludge products abnormally high in Al_2O_3 (>2.5%) or MgO (>1.2%), may require further testing to determine the optimum fluoride content.

The production of acceptable orthophosphate suspension fertilizers from granular ammonium phosphate must begin with chemical control of the granular intermediate which is usually MAP rather than DAP. Water removal should be accomplished by concentrating the acid prior to ammoniation because removing water between pH 2 and 5 causes the citrate-insoluble compound $FeNH_4(HPO_4)_2$ to form and results in a serious loss of phosphate availability in the MAP and resulting suspension fertilizer. Sufficient fluorine will be necessary to provide for the stoichiometry of $AlNH_4HPO_4F_2$ and $Fe(NH_4)_2(HPO_4)_2F$ so that both $FeNH_4(HPO_4)_2$ and $(Fe, Al)PO_4 \cdot nH_2O$ will be insignificant (42, 48). This would require roughly 1% F for each percentage of $R_2O_3(Al_2O_3+ Fe_2O_3)$—more at high calcium or magnesium contents.

Suspensions prepared from granular materials containing 20% of the total P_2O_5 as pyrophosphate will not require additional fluoride to prevent formation of the citrate-insoluble compound, $FeNH_4(HPO_4)_2$, since this component does not form in the melt from the pipe reactor. Fluids prepared from these solids contain a significant quantity of the impurities as solubilized complexes sequestered by pyrophosphate and fluorides. The ultimate limit of this sequestration is the production of clear stable liquids in which the proper ratios of impurities, pyrophosphate, and fluoride are obtained (7, 51). Without this chemical control, the potential for deterioration is great. At high pyrophosphate concentration (30-50), the low residual fluoride is insufficient for the formation of soluble complexes, and $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ will precipitate as thin needle crystals with a large surface area. At low pyrophosphate levels ($\lesssim$ 10%), the R_2O_3 (especially the iron) will precipitate as $(Fe, Al)PO_4 \cdot nH_2O$ in the form of an amorphous gel-like material that immobilizes a large fraction of the water needed to fluidize the product. Experience with these polyphosphate liquids has shown that redistribution of the impurities can result in semi-solidification of the solution to give a nonflowing, clear gel. Some of these gel-forming characteristics are known (7, 17, 39, 43), but most have only been encountered but not studied. These gels can form in low-grade mixed fluids such as 4-8-4, 6-6-6, and orthophosphate suspensions, and if detected in the early stages of gelling when they are still lightly thixotropic, can be fluidized again by air sparging. Long-term storage at summertime temperatures and the use of acids having higher impurity levels will eventually make this gelling problem unbearable.

CHARACTERISTICS OF SOLID PRECIPITATES

The potential for precipitation of solids in fluid fertilizers is indicated by the phase rule property of "stable salt pairs" which in any chemical system, at any one time, provides for the possibility of one less solid phase than the total number of ionic components. Table 7 shows the significant components involved in the study of fluids from wet-process phosphoric acids. Although this group provides for the presence of 12 solid phases at one time, the fluid products, except for DAP in suspensions, are undersaturated with respect to the soluble compounds of ammonium and potassium sulfates and phosphates. This eliminates 6 of the 12 possibilities, and calcium can be removed by proper control of the WPA filtration process. The number of precipitating solids is further reduced by the isomorphous substitution of aluminum and ferric iron (also the divalent

Table 7. Significant components affecting the chemical and physical properties of ammonium polyphosphate fluid fertilizers

Cations	Anions	Neutral
Ca	SO_4^{2-}	H_2O
Mg	PO_4^{3-}	
Fe^{2+}	$P_2O_7^{4-}$	
Fe^{3+}	$P_3O_{10}^{5-}$	
Al	F	
NH_4^+		
K		

micronutrients zinc, ferrous iron, and manganese) which sometimes coprecipitate as the same compounds. This helps explain why there are only one or two solids present at a time in most APP liquids.

However, a given impurity can be present in an ammonium phosphate fluid in many chemical forms. The large variety of solution complexes, discussed elsewhere, can be in equilibrium with solid precipitates which exist as crystalline compounds having a multitude of compositional arrangements. For example, in a simple ammonium orthophosphate system, mono, di, and trivalent substitutes will exist for each metal impurity; also, double salts between these impurities and ammonia will exist—likewise various hydrates of all these can be encountered at different temperatures. The addition of just one polyphosphate, the tetravalent pyrophosphate, can increase the possible crystalline solids by a formidable amount. This extensive complexity is the primary reason that so little is known about the chemistry of fluid fertilizers. Even with the expert use of a polarizing microscope, which is mandatory for recognizing and identifying the solid phases, the study of a four component system is difficult and a six component system study is essentially impossible. Consider now that a fluid fertilizer made from WPA effectively contains Fe^{3+}, Fe^{2+}, Al^{3+}, Mg^{2+}, NH_3^+, H_3PO_4, $H_4P_2O_7$, F^-, and H_2O—nine active components. It is not surprising that "thinking research scientists" have hesitated to attack this problem from a fundamental standpoint. To simplify these types of studies, the solutions that have been studied were limited to N:P compositions—mainly from a high analysis point of view. For example, very little research has included fluids with potassium chloride (this introduces two more components) or dilute fluids such as 6-6-6 or 4-8-4 and similar grades.

Several major phase diagrams are now available which identify many of the compounds encountered due to impurity components exceeding saturation limits in ammonium phosphate fluid fertilizers. Most of these have been reported within the past 20 years. They include $CaO\text{-}NH_3\text{-}H_3PO_4\text{-}H_2O$ (52); $CaO\text{-}NH_3\text{-}H_4P_2O_7\text{-}H_2O$ (53, 54); $CaO\text{-}K_2O\text{-}H_4P_2O_7\text{-}H_2O$ (53, 54); $MgO\text{-}NH_3\text{-}H_3PO_4\text{-}H_4P_2O_7\text{-}H_2O$ (55, 56, 57); and $Fe_2O_3\text{-}Al_2O_3\text{-}NH_3\text{-}H_3PO_4\text{-}H_2O$ (58, 59). The magnesium phase diagram is given in figure 11 (55) to demonstrate the ease in which the precipitating magnesium compound can change with only slight compositional changes. The solid lines represent equilibrium conditions at 77°F (25°C), and along these isotherms the solid fraction consists of two or three ammonium phosphates and one magnesium ammonium phosphate. The position of the dashed lines can vary slightly depending on the ratio of ortho- to pyrophosphate. This relationship is shown in figure 12 which again shows a compositional change and demonstrates the effect of pH and pyrophosphate content on determining the precipitating solid phase. Note that a much lower MgO content will saturate the solution for precipitation of $Mg(NH_4)_6\text{-}(P_2O_7)_2\cdot 6H_2O$ as compared to $Mg(NH_4)_2P_2O_7\cdot 4H_2O$. In contrast to this solubility variation in APP, the six hydrate has a relatively high rate of solution and dissolves in water, whereas the four hydrate is water insoluble. On the other hand, neither compound will ever be theoretically in equilibrium with a water solution since pyrophosphate, albeit slowly, will always be hydrolyzing to orthophosphate. Similar data for zinc is shown in figure 13.

The phase relationships shown in figures 11 and 12 will be encountered when WPSAs (fluorides vaporized away) are ammoniated to ammonium polyphosphate fluids. The tripolyphosphate generated by the pipe-reactor process has no detectable effect on the solubility of MgO at saturation for the invariant points shown at points A (pH 6.30) and B (pH 5.70) in figure 11. In these tests, 13% tripolyphosphate gave MgO saturation of 0.03 vs 0.02 (pH 5.7) and

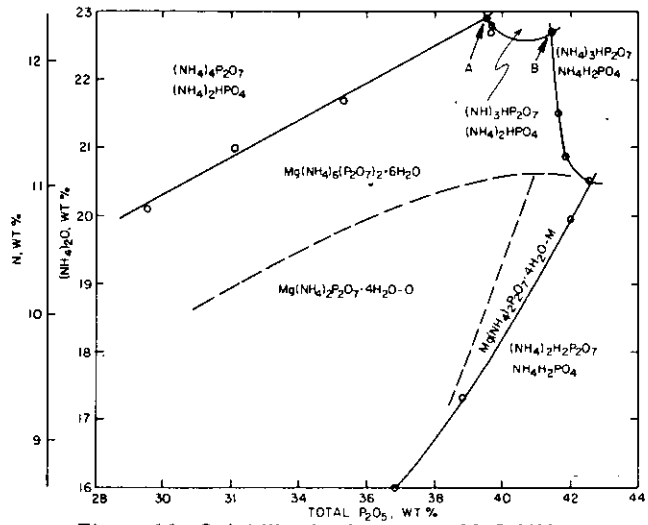


Figure 11. Solubility in the system $MgO\text{-}NH_3\text{-}H_3PO_4\text{-}H_4P_2O_7\text{-}H_2O$ at 25°C

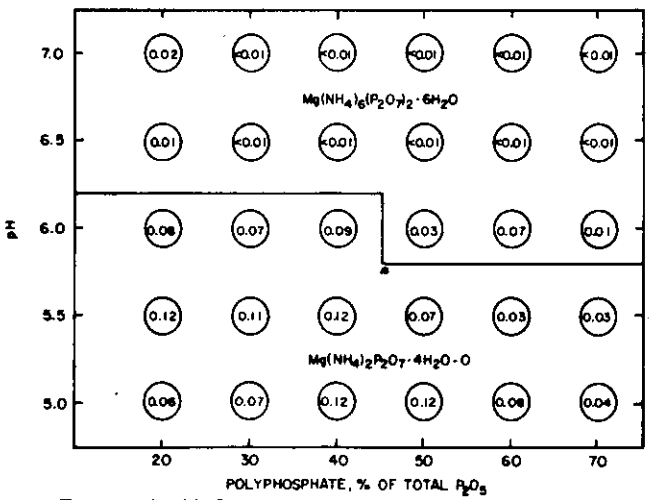
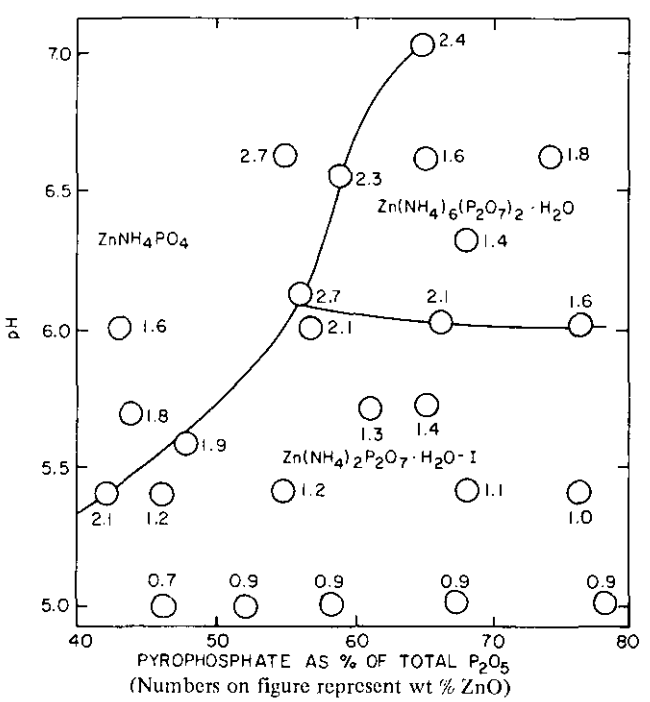


Figure 12. MgO saturation levels vs polyphosphate content and pH in liquid fertilizers

0.01 vs 0.01 (pH 6.30) demonstrating that ammonium tripolyphosphate does not sequester MgO–in fact, it probably has less effect than nitrate or chloride ions. Other similar phase systems may be more complicated than the magnesium one shown here. For example, the zinc system (8) shows five zinc compounds instead of three and tables 8 and 9 show that numerous water soluble and insoluble iron and aluminum compounds can be expected in these systems. This is the primary reason that these two phase systems have not been studied. Because of the complex chemical nature of ammoniated WPSA, many of the precipitating salts cannot be represented by the simple phase systems above; three of the best examples are $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$, $Mg_3Fe(NH_4)_{12}(P_2O_7)_4F_2 \cdot 12H_2O$, and the mixed crystal $(Fe, Mg, Zn)(NH_4)_6(P_2O_7)_2 \cdot 6H_2O$.

Although the potential for isomorphous substitution is great, it is remarkably absent much of the time in fluid fertilizers. It appears that substitution is greatest in compounds such as $(Mg, Fe, Mn, Zn)(NH_4)_6(P_2O_7)_2 \cdot 6H_2O$ which are water soluble like the ammonium pyrophosphates indicating that, in this compound, crystalline structure is affected very little by the size of the divalent cation. On the other hand, substitution is restricted by size and affinity for water of the divalent cation in compounds such as $Me^{2+}(NH_4)_2P_2O_7$, which are water insoluble and precipitate as various hydrates depending on the divalent cation. The magnesium compound is a tetrahydrate with no significant substitution, ferrous iron and manganese substitute as the dihydrate, and zinc and calcium each



(Numbers on figure represent wt % ZnO)

Figure 13. Solid phases in ammonium orthopyrophosphate liquid fertilizers saturated with ZnO

precipitate as the monohydrate but do not substitute–calcium forms as a monoclinic crystal while the zinc compound is orthorhombic. Thus, instead of having one precipitate that contains numerous impurities–as in $(Mg, Fe, Mn, Zn)(NH_4)_6(P_2O_7)_2 \cdot 6H_2O$–we encounter several different precipitates when $Me^{2+}(NH_4)_2P_2O_7 \cdot nH_2O$ is the stable phase.

Iron and aluminum do not coprecipitate in fluids except under limited conditions. The formation of $(Fe, Al)NH_4PO_4F_2 \cdot nH_2O$ (48) is a rare occurrence when fresh orthophosphoric acid is ammoniated before the fluoride has evolved. Ferric iron does not substitute in $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ even at increasing fluoride concentrations. Less is known about the compound $Fe_3Mg(NH_4)_{12}(P_2O_7)_4F_5 \cdot 12H_2O$ but chemical analysis shows only a trace of aluminum. Similar comparisons exist for other iron and aluminum compounds; one major reason for the difference is the high degree of complex ion formation between aluminum and fluoride which is not true for ferric iron and fluoride. In the pure system Fe_2O_3-NH_3-$H_4P_2O_7$-H_2O, there are many highly soluble iron ammonium pyrophosphates (table 8) which precipitate at about 3% to 4% Fe_2O_3. In contrast, the comparable aluminum system becomes saturated at about 0.5% Al_2O_3 and the stable precipitates are unlike the iron compounds (compare tables 8 and 9). Similarly, many aluminum ammonium orthophosphates have been encountered in fertilizer research but only a few comparable iron ammonium orthophosphates.

Another solid phase, crystallographic phenomenon that is encountered in fluid fertilizers is that of dimorphic forms. This is a condition where a compound can exist in either of two or more (polymorphism) crystalline structures. This property is exhibited by $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$, which forms both as elongated orthorhombic blade crystals (most common form) or as rectangular monoclinic plate crystals both of which have their own fields of stability as shown by figure 11. This phase diagram shows why the orthorhombic form is more common as demonstrated by the more extensive compositional range over which it exists. Three other less familiar compounds have been found in fluids as dimorphic forms. These are the orthorhombic and hexagonal forms of $ZnNH_4PO_4$ (60), the two monoclinic forms of $Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$ (52), and the orthorhombic and monoclinic forms of $Zn(NH_4)_2P_2O_7 \cdot H_2O$.

The precipitated impurities in fluid fertilizers have been identified and characterized as individual compounds along with many of the compatible compounds with which they can form a stable salt pair in the same liquid (3, 5, 7, 41, 61). The calcium, aluminum, magnesium, ferrous iron, ferric iron, and fluoride compounds which have been encountered in ammoniated phosphoric acids are shown in tables 8, 9, 10, and 11. The pure ammonium salts that may

Table 8. Reaction products of iron with ammonium phosphate fluid fertilizers

Precipitate	Solubility properties	Occurrence in fertilizers	Reference
$FePO_4 \cdot NH_2O$[a]	Water insoluble, citrate soluble	Precipitates during rapid ammoniation of orthophosphate acid to pH 6.	3, 41
$FeNH_4(HPO_4)_2$[a]	Citrate insoluble, V.S. soluble in acid, soluble in hot caustic	Forms as scale in low poly pipe reactors; forms in ammoniation processes at pH 3-5.	3, 41
$FeMg_3(NH_4)_{12}(P_2O_7)_4F_5 \cdot 12H_2O$[a]	Water soluble	Precipitates in fresh APP.	Unpublished TVA data
$FeNH_4P_2O_7$[a]	Citrate insoluble, acid insoluble, soluble in hot caustic	Forms as scale in high poly pipe reactors. Precipitates in cooled APP melts.	3, 5, 18
$Fe(NH_4)_3HPO_4P_2O_7$	Water insoluble, citrate soluble	Forms in cooled APP melts below 240°C.	3, 5
$Fe(NH_4)_3HPO_4P_2O_7 \cdot H_2O$	Water insoluble, citrate soluble	Crystallizes slowly (6 mo.) in 10-34-0 APP solution at 1.5% Fe.	3
$Fe(NH_4)_5(P_2O_7)_2 \cdot 4H_2O$	Water soluble	Stable Fe salt at pH 6 in the system Fe^{3+}-NH_4^+-$P_2O_7^{4-}$-H_2O.	7
$Fe(NH_4)_9(P_2O_7)_3 \cdot 9H_2O$	Dissolves incongruently in water with pptn. of $Fe(NH_4)_5(P_2O_7)_2 \cdot 4H_2O$	Stable in Fe^{3+}-NH_4^+-$P_2O_7^{4-}$-H_2O at pH 7.	7
$Fe(NH_4)_2P_2O_7OH \cdot 2H_2O\}$ $Fe(NH_4)_2P_2O_7OH \cdot 3H_2O\}$	Dissolve incongruently in H_2O	Stable in Fe^{3+}-NH_4^+-$P_2O_7^{4-}$-H_2O above pH 8.5.	7
$Fe(NH_4)_2P_2O_7 \cdot 2H_2O$[a] (ferrous)	Water insoluble, citrate soluble	Precipitates at 0.1% Fe^{2+} in 10-34-0 APP fluids.	3, 51
$FeNH_4PO_4 \cdot H_2O$ (ferrous)	Water insoluble, citrate soluble	Stable in Fe^{2+}-NH_4^+-PO_4^{3-}-H_2O at pH 6.	63
$Fe(NH_4)_6(P_2O_7)_2 \cdot 6H_2O$ (ferrous)	Water soluble	Stable in Fe^{2+}-NH_4^+-$P_2O_7^{4-}$-H_2O above pH 6.	3
$Fe(NH_4)_2(HPO_4)_2F$[a]	Water insoluble, citrate soluble	Forms in ammoniated WPA when fluoride is sufficient for both the aluminum and iron.	41, 48

[a]Compounds most commonly found in fluid fertilizers.

Table 9. Reaction products of aluminum with ammonium phosphate fluid fertilizers

Precipitate	Solubility properties	Occurrence in fertilizers	Reference
$Al_2(NH_4)_3(PO_4)_3 \cdot H_2O$	Water insoluble, citrate soluble	Corrosion product from storage of fertilizers in aluminum tanks.	68
$Al(NH_4)_2H(PO_4)_2 \cdot 4H_2O$	Water insoluble, citrate soluble	Reaction between aluminum tanks and fluid fertilizer.	59, 68
$AlNH_4KH(PO_4)_2 \cdot 4H_2O$	Water insoluble, citrate soluble	Reaction of aluminum tanks and three component fluid fertilizer.	68
$Al_5(NH_4)_3H_6(PO_4)_8 \cdot 18H_2O$	Water insoluble, citrate soluble	Occurs in the acidic (pH~3) zone of the Al^{3+}-NH_4^+-PO_4^{3-}-H_2O system.	59
$AlNH_4PO_4OH \cdot 2H_2O$	Water insoluble, citrate soluble	Forms in dilute Al-NH_4-PO_4 systems at pH 8.	58, 59
$AlNH_4PO_4OH \cdot 3H_2O$	Water insoluble, citrate soluble	Forms in concentrated Al-NH_4-PO_4 solutions above pH 8.	59
$Al_2(NH_4)_3(PO_4)_3$	Citrate insoluble	Forms from aluminum in medium poly APP melts without fluorine.	5
$Al(NH_4)_3HPO_4P_2O_7$	Citrate soluble	Forms from aluminum in low poly APP melts without fluorine.	5
$Al_3(NH_4)_5H_2(PO_4)_4F_4$	Citrate soluble	Forms from aluminum in APP melts with fluorine.	5
$AlNH_4P_2O_7$ [a]	Citrate insoluble, acid insoluble, soluble in caustic	Forms from aluminum high poly melts. Forms scale in pipe reactor.	3, 5
$Al(NH_4)_2P_2O_7OH \cdot 2H_2O$	Water insoluble, citrate soluble	Forms from 10-34-0 solutions at pH 8.	3, 7
$Al(NH_4)_2P_2O_7OH \cdot 3H_2O$	Water insoluble, citrate soluble	Forms in dilute 10-34-0 solutions at pH 6.	7
$AlMg(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ [a]	Water insoluble, citrate soluble	Major sludge component in commercial APP fluid fertilizers.	7, 9, 10, 51
Al-Mg-NH_4-P_2O_7-F-H_2O [a] variable composition gel	Soluble	Major gel forming component in APP fluids having mole ratio Mg/Al $\gtrsim$ 1.5.	7, 9, 10, 39
$AlNH_4HPO_4F_2$ [a]	Water insoluble, citrate soluble	Major aluminum compound in orthophosphate suspensions.	41, 48, 69
$AlNH_4(HPO_4)_2$	Citrate insoluble	Rare but does form in hot orthophosphate fluids with low fluorine.	41, 48
$Al_2(NH_4)_2(HPO_4)_4 \cdot H_2O$	Water insoluble, citrate soluble	Forms from aluminum in 135°C $NH_4H_2PO_4$ solution.	61
$Al_2NH_4(PO_4)_2OH \cdot 2H_2O$	Water insoluble, citrate soluble	Forms from aluminum in 1M DAP solution at 95°.	61

[a]Compounds most commonly found in fluid fertilizers.

Table 10. Reaction products of calcium with ammonium phosphate fluid fertilizers

Precipitate	Solubility properties	Occurrence in fertilizers	Reference
$CaHPO_4 \cdot 2H_2O$ $CaHPO_4$	Water insoluble, citrate soluble	Soil-MAP reaction product	15
$Ca_4H(PO_4)_3 \cdot 2.5H_2O$ $Ca_{10}(PO_4)_6(OH)_2$	Water insoluble, citrate soluble	Soil-DAP reaction product	15
$CaNH_4PO_4 \cdot H_2O$ $Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$[a]	Dissolves incongruently	Soil-DAP reaction product	15, 52
$Ca(NH_4)_2P_2O_7 \cdot H_2O$[a] $Ca_3(NH_4)_2(P_2O_7)_2 \cdot 6H_2O$	Water insoluble, citrate soluble	Calcium in contact with ammonium polyphosphates	15, 53

[a]Compounds most commonly found in fluid fertilizers.

Table 11. Reaction products of magnesium with ammonium phosphate fluid fertilizer

Precipitate	Solubility properties	Occurrence in fertilizers	Reference
$MgHPO_4 \cdot 3H_2O$	Water insoluble, citrate soluble	Soil reaction products and magnesium impurity in MAP, DAP, and APP.	3, 15, 41, 56, 57, 70
$Mg_3(NH_4)_2(HPO_4)_4 \cdot 8H_2O$ $Mg(NH_4)_2H_2(PO_4)_2 \cdot 4H_2O$ $MgNH_4PO_4 \cdot 6H_2O$[a]	Dissolves incongruently in water	Magnesium precipitate in MAP and DAP	3, 15, 41, 56, 57, 70
$MgAl(NH_4)_2H(PO_4)_2F_2$	Citrate insoluble	Forms in MAP fertilizers.	Unpublished TVA data
$Mg(NH_4)_2P_2O_7 \cdot 4H_2O$[a] $Mg(NH_4)_6(P_2O_7)_2 \cdot 6H_2O$	Dissolves incongruently in water	Soil-APP reaction product. Magnesium impurity in APP.	3, 7, 15, 41, 55
$MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$[a]	Water insoluble, citrate soluble	Major sludge component in APP fluid fertilizers.	7, 9, 10, 51
$Mg_3Fe(NH_4)_{12}(P_2O_7)_4F_5 \cdot 12H_20$	Water soluble	Forms in fresh 10-34-0 liquids at 50% polyphosphate.	Unpublished TVA data
Mg-Al-Fe-NH_4-P_2O_7-F[a] gel variable composition	Soluble	Forms in APP fluids having Mg/Al mole ratio $\gtrsim$1.5.	7, 9, 10, 39

[a]Compounds most commonly found in fluid fertilizers.

form in ammoniated wet-process phosphoric acid (6, 19), or partially ammoniated acids, are given in table 5 along with the potassium phosphates that have been identified from phase system studies. The most common compounds identified in fluids are noted. Although unusual, as many as six compounds have been found together in an 11-37-0 or 10-34-0 polyphosphate liquid at one time. These included $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$, $Mg(NH_4)_6(P_2O_7)_2 \cdot 6H_2O$, $Fe(NH_4)_2P_2O_7 \cdot 2H_2O$, and $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$, which are also known as "stable salt pairs," i.e., any two or all of them can exist together in the same solution without interacting.

The possible compounds range from very soluble in water to citrate insoluble. Some form as crystalline anhydrous compounds and have little effect on the solvent water while others are amorphous or even gels (very viscous, clear liquids) which can totally destroy the fluidity of the fertilizer products by consuming the (so called) free-water. Others are intermediate such as the thin needle crystals (0.5 x 0.5 x 10 microns) of $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ which not only have a tremendous surface area for thickening the fluids but also remove 6 moles of solvent water for each mole of magnesium. All of these compounds have an effect, some profound, on the chemical and especially physical properties of the fertilizer products and they can be encountered during simple unit processes.

MICRONUTRIENTS IN FLUIDS

With the exception of boron and molybdenum, which do not present solubility problems, the micronutrient cations that are desirable in fluid fertilizers are mainly zinc, ferrous iron, manganese, and copper. Crop response and greenhouse studies have demonstrated the value of these nutrients (62, 63); however, the lack of fundamental chemical or physical controls for stabilizing micronutrients in liquid grades, or providing nongelling components in suspensions produced from wet-process phosphoric acids, seems to have reduced the interest in providing and storing fluids with micronutrient additives. This depressed interest is most obvious at the production level but is less so at the distribution site where the mixtures can be applied to the soil before interaction problems arise. Chemical controls are needed to provide sequestration of these cations both during formulation, storage, and distribution of the fluid products.

Limited progress in the use of micronutrient sources has demonstrated that essentially all of them are unstable when mixed with the components in fertilizers. The interaction with fluid grades occurs rapidly because of the gross difference between the micronutrient mineral and the saturated ammonium phosphate solution. Figures 12 and 13 show the reaction products and saturation composition for magnesium and zinc in liquid polyphosphate products. Micronutrient sources such as sulfates or oxides are frequently added as a powder to solid granular fertilizers where the same reactions occur but at a much slower rate. This may result in caking problems with the reaction products serving as the bonding phases between granules. The micronutrient fertilizer reaction products which have been isolated in fertilizer mixtures are shown in table 12. More compounds have been characterized for zinc than the others, primarily because much more research has been performed in trying to use fertilizers as zinc carriers for corn fertilization. Also, a complete phase system study ($Zn\text{-}NH_3\text{-}H_3PO_4\text{-}H_4P_2O_7\text{-}H_2O$) (8) is available for the region of interest to fluid fertilizer scientists.

Table 12. Micronutrient precipitates in fluid fertilizers (2, 60)

Composition	Estimated solubility	Remarks
$CuNH_4PO_4 \cdot H_2O$	<0.1% Cu^{2+}	A slow-release fertilizer
$Cu(NH_4)_2P_2O_7 \cdot H_2O$	~1.0% Cu^{2+}	Less soluble in dilute solutions
$Fe(NH_4)_2P_2O_7 \cdot 2H_2O$	<0.1% Fe^{2+}	A common precipitate in APPs from acids exposed to reducing conditions
$FeNH_4PO_4 \cdot H_2O$	<0.1% Fe^{2+}	A slowly available fertilizer
$MnNH_4PO_4 \cdot H_2O$	<0.1% Mn^{2+}	A slowly available fertilizer
$Mn(NH_4)_2P_2O_7 \cdot 2H_2O$	~0.2% Mn^{2+}	Coprecipitates with Fe^{2+} and Zn^{2+}
$ZnNH_4PO_4$ (73)	<0.1% Zn^{2+}	A slowly available fertilizer solubility is ~1% Zn in polyphosphates
$Zn(NH_4)_2P_2O_7 \cdot H_2O$ (37)	~1% Zn^{2+}	A slowly available fertilizer
$Zn(NH_4)_6(P_2O_7)_2 \cdot 6H_2O$ (37)	~2% Zn^{2+}	Water soluble, coprecipitates with Mg^{2+} and Fe^{2+}
$Zn_3(NH_4)_2(P_2O_7)_2 \cdot 2H_2O$ (73, 37)	~2% Zn^{2+}	Forms in APP liquids below pH 5
$Zn_2NH_4H(PO_4)_2 \cdot 2H_2O$ (73)	~1% Zn^{2+}	Precipitates when ZnO is charged to $NH_4H_2PO_4$

Most of the solubility data available for micronutrients in fluid fertilizers (table 12) are metastable values obtained from multicomponent commercial fluids as opposed to the equilibrium solubilities that are obtained in pure systems. These values can vary widely depending on several factors: the micronutrient source (i.e., ZnO vs $ZnSO_4$), the point in the fertilizer process at which it is added, the quantity of coprecipitating elements, the quantity of sulfate or fluoride, and the temperature environment of the fluid after the micronutrient is added. These saturation concentrations are usually higher than the equilibrium values, most likely because of supersaturation due to elevated temperatures or ligand complexing. All of these conditions can change during storage and cause undesirable precipitation or gelling.

The type of micronutrient source can introduce unsuspected problems which cannot be foreseen. For example, $ZnSO_4$ is readily soluble, while ZnS is essentially insoluble in fluids, and ZnO has been observed in fluids with a coating of reaction product, the thickness of which controls the dissolution rate of the residual zinc oxide. Also, some metallic oxides have a varying rate of solution depending on the degree to which they have been "dead burned" during preparation. Another problem can result from isomorphous substitution of one element for another. For example, if ferrous iron is substituted for zinc in $(Zn, Fe)SO_4$, a ferrous iron precipitate will result. Ferrous iron from corrosion of storage tanks or reduction of ferric iron and magnesium impurities from WPA sources will reduce the saturation solubility of zinc (and vice versa) in fluids where $(Fe, Mg, Zn)(NH_4)_6(P_2O_7)_2 \cdot 6H_2O$ is the stable solid phase. This effect is similar to "mass action" where a high concentration of one constituent will reduce the saturation level of another. This interaction of divalent cations also results in micronutrient deficiencies in soils even when sufficient quantities of a given element are present. High levels of calcium and magnesium in a well-limed soil will prevent zinc uptake (62) for this reason. Simple solubility values for single micronutrients in fluid fertilizers are only relative and must be considered along with coprecipitating ions.

The solubility of a micronutrient in ammonium pyrophosphate is higher than the comparable metal ammonium orthophosphate at the same pH. However, this gain is usually minimal or influenced greatly by the other factors mentioned above to the extent that high solubility values for micronutrients cannot be guaranteed in polyphosphate fluids. The primary advantage gained by polyphosphates, in this respect, is available in high poly, pipe-reactor fluids where a high quantity of polyphosphate above pyrophosphate is present and will not precipitate the cation components at the concentrations found in fluids.

The solubilization of the divalent micronutrient elements in fluid fertilizers is an important chemical phenomenon that needs more research study. This goal may be more successful by the fluoride sequestration phenomenon but other aspects should be studied also. It should be remembered that elevated quantities of several micronutrients will be accomplished at the expense of the nitrogen grade of the fluid. It may be necessary to apply a purification process to remove the unwanted ferric iron and aluminum so that the fertilizer can accommodate the more desirable divalent metallic nutrients.

STABILIZING FLUIDS BY FLUORINE SEQUESTRATION

The saturation compositions for any given compound in fluid fertilizers depend on the solubility product and activity of the component ions. In fluid fertilizers, these values are impossible to obtain at our present level of knowledge because the precise ionic formations that are present at any given impurity concentrations in these systems are not known. Also in order to determine the activity of a complex ion, its equilibrium constant relative to its ligand and other complexes having the same ligand are necessary. Theoretical approaches to defining the chemistry of fluid fertilizers have largely been ignored primarily because of the magnitude of these complex ion formations. At the present state-of-the-art, saturation limits for each element have to be reported with limiting conditions because chemical principles have not been determined to predict precipitation reactions. Many simple phase systems have been reported but none of them include the sensitive element fluorine which is always present in WPA fluid fertilizers and has a profound effect on the other impurities and on the ultimate physical properties of the product. Solubility products can be applied to pure fertilizer systems in order to predict precipitation concentrations. For example, in systems such as $MgO\text{-}NH_3\text{-}H_3PO_4\text{-}H_2O$, the specific complex formation is controlled mostly by pH value which also controls the composition of the precipitant and its level of saturation. Because of the low level of magnesium over most of the system, the ratio of magnesium to ammonia is not an effective parameter. However, when a fifth and/or sixth component such as pyrophosphate or fluoride is added, the type of saturating complex is more controlled by the MgO/F and $P_2O_7^{4-}/F$ ratios. Varying ratios provide different complex formations in solution and have a major effect on the saturation composition and, more importantly, the actual composition of the equilibrium solid phases, some of which are very soluble while others are very insoluble. At certain combination of ratios, the five component fertilizer system ($MgO\text{-}H_3PO_4\text{-}H_4P_2O_7\text{-}F\text{-}H_2O$) can result in a water-white, clear, almost solid gel which is extremely difficult to bring to a fluid condition. These problems can become impossible

when iron, aluminum, and an unknown quantity of sulfate are also added.

In order to relate to the astronomical chemical variations that may be encountered in fluid fertilizers prepared from WPA, it is necessary to limit many of the parameters that are involved. For example, in fluorine sequestration studies we limit pH to 6.0-6.2, plant nutrient content to 10-34-0, polyphosphate content to 15%, 30%, or 50% of the total P_2O_5, and we eliminate sulfate as a problem because of its low concentration level. Under these restrictions and others such as an aluminum to magnesium mole ratio of about 1.8 (wt % Al:Mg ~ 2 as in Florida rock), several chemical relationships have been determined to help control the physical properties of the fluid products. Ferrous iron is very insoluble and frequently encountered in these polyphosphate fluids as $Fe(NH_4)_2P_2O_7 \cdot 2H_2O$ which can be easily prevented by oxidizing to the ferric state in hot acid prior to ammoniation. Tests of typical acids show that 0.5% NH_4NO_3 or even less HNO_3 is sufficient for this reaction. In one study, it was determined that the proper ratio of fluoride to iron, aluminum, and magnesium in solution would maintain the clear liquid property of the polyphosphate liquid. This relationship was expressed as a sequestration ratio (S.R.) thusly (7, 51):

$$\text{S.R.} = \frac{\text{wt \% F}}{\text{wt \% MgO} + 2.5\ Al_2O_3 + 0.33\ Fe_2O_3}$$

where the proper value of S.R. for stabilizing a liquid fertilizer is a function of the pyrophosphate level, the aluminum to magnesium ratio and the total ionic strength, i.e., the effective S.R. would be higher at higher pyrophosphate concentrations and in dilute fluids such as 4-8-4 as compared to 10-34-0. This fluoride sequestration required about 1.2% F for a typical 50% polyphosphate liquid prepared from Florida phosphate rock. Lower polyphosphate concentrations require less fluoride (7, 51). This same chemical relationship can be applied to suspension grades to control viscosity values during storage since fluoride can control both precipitation and gel formation which are the primary problems associated with suspensions. Since it is known that very small (sometimes 0.1%) fluorine increases can cause a heavily precipitated gelled product to be a clear, free-flowing fluid, a solubility product relationship cannot be used to explain this effect. However, an equilibrium shift from a very insoluble magnesium complex to one that is soluble can occur; this is similar to changing from a stability field of an insoluble compound to one of a soluble salt in a phase system study. Thus, the ratio of the impurities which determined the type of complex present is more important for understanding precipitation and gelling mechanisms than is the total impurity composition.

Impurity ratios were also found to be important in determining the catalytic effect of iron and aluminum on the hydrolysis of polyphosphates above pyrophosphate (45). The half-life formula (presented in the hydrolysis section) to determine the degree of hydrolysis of polyphosphate above pyrophosphate ($P_3O_{10}^{5-}$ and higher) shows that uncomplexed iron and aluminum are detrimental to the storage life of the higher polyphosphates. However, fluorine can control part of this effect by complexing the iron and aluminum into ions that are not effective as catalysts for the reaction.

Another chemical study involved the use of fluorine to change the impurity ratios in suspension grades to maintain a stable viscosity value below 1,000 centipoises (17). Again, it was found that the ratio of F/Al + Fe + Mg on a mole basis was more important than the total quantity of the cation impurities. Even though a mole ratio of one was recommended, the study was limited to Florida acids and variations in the ratios of Al:Fe:Mg were not tested. For example, it is not known if the fluoride addition solved a magnesium, iron, or aluminum problem or what effect other parameters such as pH, temperature, or fertilizer grade have on the fluoride requirement.

All these examples are given to show that saturation limits required for maintaining a stable fluid fertilizer do not provide an explanation for solving the physical problems encountered. Notice that in the sequestration ratio equation and the suspension stabilization study above total impurity concentration is not a factor. Solubility products for the very slightly soluble components can be used to define the extent of the precipitating problem when it occurs; however, the saturating solids and their solubility products are not known for fluid fertilizer under the most favorable conditions such as a clear liquid fertilizer. For example, in a clear, sequestered liquid fertilizer the stable solid phases, with respect to the impurities of iron, aluminum, and magnesium, are not known. The reported phase systems data for these metals in ammonium polyphosphate solutions cannot be remotely applied to similar systems containing fluoride. These data in the presence of fluorine will be necessary before the chemistry of fluid fertilizers and the corresponding physical properties can be controlled.

Experience has shown that the residual fluoride in fluid fertilizers is usually insufficient to provide the benefits described above. Thus, an inexpensive source is needed to augment the 0.5% fluoride that is usually present in commercial fluid products. The use of purified HF or NH_4HF_2 is economically prohibitive and the inexpensive H_2SiF_6 is not suitable. However, technology is available (64) for readily converting off-gas scrubber solutions from phosphate rock dissolution processes to concentrated solutions of NH_4HF_2 by simple ammoniation. This not only provides pollution abatement but also produces a useful fluoride by-product.

HYDROLYSIS OF POLYPHOSPHATES IN FLUID FERTILIZERS

A theoretical discussion on the hydrolysis of polyphosphate chains and rings with many references to early data is available in Van Wazer's *Phosphorus and Its Compounds* (65). Considerable updated information (2, 30, 31, 33, 34, 45) is available for polyphosphates in special environments such as strong ammonium and potassium phosphate solutions or strong sodium and potassium phosphate detergents. The surfactive and peptizing properties of both chain and ring polyphosphate solutions have been developed for use by the detergent industry but the hydrolysis characteristics of these products, which are usually available as the sodium salts, will not be discussed here.

One of the most desired properties in detergent and fertilizer applications is the ability of polyphosphates to solubilize and prevent the precipitation of di and trivalent metallic orthophosphate compounds. These properties have been developed for fluid fertilizers where iron, aluminum, and magnesium precipitates and gels at relatively low levels of impurity concentrations are almost impossible to control without this polyphosphate sequestration effect.

Hydrolysis of Polyphosphates Above Pyrophosphate

Early in the study of polyphosphate sequestration of iron, aluminum, and magnesium, it was apparent that better storage properties could be obtained at higher polyphosphate concentrations. However, when the polyphosphate was mainly pyrophosphate as obtained in a tank reactor, precipitation of $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$ or $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ occurred within a few days. On the other hand, when pipe-reactor products (18) were available with a high proportion of the polyphosphate above pyrophosphate, storage was extended appreciably before precipitation started. Maintaining this high polyphosphate content above pyrophosphate is desirable for long-term storage of fluid fertilizers. Several properties of these longer chain phosphates contribute to this. They are produced at the expense of the pyrophosphate which precipitates insoluble compounds; they do not react with the impurities as insoluble solids; they do not form gelatinous materials with the impurities, and each one is much less concentrated than the pyrophosphate and thus less susceptible to precipitation as water-soluble compounds. These higher-chain-length polyphosphates are produced in abundance by the pipe-reactor process using 70% P_2O_5 WPSA (18). The polyphosphate content above pyrophosphate can be as high as 50% of the total P_2O_5 in these 11-37-0 liquid fertilizers and storage periods of 4 months are possible at room temperature with some acids.

At the water content required for fluid fertilizers, the polyphosphate components are metastable and eventually hydrolyze (react with water) to the stable orthophosphate form. The scission of chain polyphosphate in fluid fertilizers usually (not always) occurs at the end-member phosphate and results in one orthophosphate and the chain member next lower down. Since the higher species have a faster hydrolysis rate, the initial effect is for each chain length to increase in quantity at the expense of the next higher species until a balance between the total quantity and hydrolysis rate is attained for each succeeding species. This hydrolysis of polyphosphates is measured as a half-life time period in which one-half of a given species is hydrolyzed to lower chain length polyphosphates at a given set of environmental conditions. This half-life value can be calculated from chromatographic analysis which gives the percentage change in concentration of a given species during a time period, i.e.,

$$\text{Half-life} = \frac{0.301t}{\log C_o/C_t}$$

where this half-life equation is a fundamental rate relationship based only on the initial concentration, C_o, and the final concentration, C_t, after time, t. The hydrolysis reaction rate varies for each polyphosphate species and is faster at higher chain lengths. The value for the very high chain length ammonium polyphosphate (4) $(NH_4)_{n+2}P_nO_{3n+1}$ (where n may be as high as 2,000) has not been determined; however, Van Wazer (65) states that a similar chain length found in Graham's salt $(NaPO_3)x$, hydrolyzes at a rate that is of the same order of magnitude as those for pyro- and tripolyphosphates under equivalent environmental conditions. Nevertheless, since its solubility in liquid fertilizers is very low compared to the solubility of tripolyphosphate, the total quantity hydrolyzed in a given time period would be extremely small compared to the quantity of tripolyphosphate hydrolyzed during the same time period. The rates at ambient conditions and pH 6 are sufficiently slow that the fertilizer and detergent industry can take advantage of the complexing and surfactive properties of these interesting ions.

Every component ion in a polyphosphate solution has an effect on the rate of hydrolysis of the polyphosphate to a lower chain length species. This effect is negligible for components that are insoluble and incapable of attaining a significant concentration. For example, in an ammonium pyrophosphate solution, ferrous iron, calcium, and magnesium precipitates as $(Fe, Ca, Mg)(NH_4)_2P_2O_7$ and reduces the divalent metal to 0.2% or less; thus their effect on the hydrolysis of pyrophosphate is negligible. These same cations would be temporarily soluble in an ammonium tripolyphosphate solution and can be expected to have a large effect on the hydrolysis of the tripolyphosphate—at least until enough pyrophosphate was formed to precipitate

them (55). For fluid fertilizers produced from wet-process phosphoric acid, the most significant factors controlling the hydrolysis rates are pH, NH_3, K, Fe, Al, F, and temperature. Since the desirable properties of polyphosphates are limited by their hydrolysis, understanding the processes by which these parameters affect these reactions is necessary in order to stabilize this species as long as possible.

The inverse pH effect (higher pH = lower hydrolysis rates) and direct temperature effect (high temperature = higher hydrolysis rates) are well-known and compensated for whenever possible by the fertilizer industry. During production of fluids, the pH is maintained at 6.0 to 6.2; above this value ammonia vapor pressures become excessive. Hot polyphosphate solutions are provided with evaporative coolers; however, temperatures cooler than ambient usually are not economically justified during storage to obtain slower hydrolysis. Likewise, the industry cannot take advantage of decreased hydrolysis due to decreased ammonia or potassium concentrations since high analysis fertilizer grades are mandatory to reduce shipping cost. The effect of the ammonium ion has been determined for polyphosphates above pyrophosphate and for tripolyphosphate itself (45). The results of these studies show wt % N to be about equivalent to wt % K and are presented below.

Hydrolysis rates vs concentration

wt % N or K	Half-life, days
21	50
11	160
5	400
0.1	1,000

Effect of N or K on hydrolysis rate of tripolyphosphate at pH 6 and 25°C

These data show that the 160-day half-life for polyphosphates above pyrophosphate is the upper limit that can be expected for concentrated fluid fertilizers at pH 6. However, this value is further limited by the positive catalytic effect of iron and aluminum on the hydrolysis of these higher polyphosphates as shown by the half-life formula (45):

$$\text{H.L.} = 2.19 - 0.313\,(\text{wt \% } Fe_2O_3 + \text{wt \% } Al_2O_3) + 0.119\,(\text{wt \% F}[2\,\text{wt \% } Al_2O_3 + Fe_2O_3])^{1/2}$$

This relationship shows that without fluorine, a value of 1.5% each of Fe_2O_3 and Al_2O_3 will reduce the 160-day half-life for these higher polyphosphates to only 18 days. At a typical fluorine content of 0.5% F, the second part of the formula shows that fluoride complexing with part of the iron and aluminum will bring the hydrolysis rate back up to 27 days. Extending this compensating effect of fluorine to higher concentrations is limited by the empirical formula:

$$\text{wt \% F} \leq 1.5\,\text{wt \% } Al_2O_3 + 0.5\,\text{wt \% } Fe_2O_3$$

When the fluorine concentration exceeds the value required to complex with the iron and aluminum, the excess is present as free fluoride which provides a scission of P-O-P linkages that is far too fast for a practical half-life value to be determined. However, this quantity of fluoride is well above the amount that may be present or added for sequestration purposes, i.e., in our hypothetical liquid at 1.5% Fe_2O_3 and 1.5% Al_2O_3 without magnesium, fluoride would have to exceed 3% before free fluoride would be available for scission of the polyphosphates. With magnesium present, this value would be higher before the accelerated hydrolysis started. In an attempt to study this fluoride scission, a slurry of $(NH_4)_3HP_2O_7 \cdot H_2O$ and NH_4HF_2 was mixed with water. The precipitation of $(NH_4)_2PO_3F \cdot H_2O$ was almost immediate and neither reactant could reach saturation as long as the other was present. The hydrolysis of the $PO_3F_2^-$ ion (65) controls the rate at which fluoride is freed again to cause the scission of another polyphosphate ion.

The relatively low level of pyrophosphate in very high polyphosphate fluids is desirable since the common ion effect (lower pyrophosphate) retards the precipitation of the magnesium pyrophosphates. However, this environment deteriorates rapidly with hydrolysis of the higher chain length members which on the average produce one pyrophosphate and one orthophosphate, thus the wt % of pyrophosphate increases twice as fast as the orthophosphate (31). Since the half-life for the higher polyphosphates averages 27 days for a typical wet-acid, high-poly, pipe-reactor liquid fertilizer, the major to bulk fraction of these species will be gone after 2 to 3 months. The resulting liquid will contain 60% to 70% of the phosphate as pyrophosphate, and precipitation of magnesium will be excessive unless fluorine sequestration has been maintained.

Thus in an impure fluid fertilizer, every soluble ion contributes toward the rapid hydrolysis of the higher (>pyrophosphate) polyphosphate species to the extent that only a few months of their desirable properties can be obtained. Technology is available which provides relief from R_2O_3 catalytic hydrolysis. The iron and aluminum can be effectively removed from 50% to 54% P_2O_5 acid by adding potassium and precipitating $(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$ (6). This not only provides a longer life for the polyphosphates above pyrophosphate but also removes these elements as diluents.

Hydrolysis of Pyrophosphates

Except for its rapid reactions with excess fluoride, pyrophosphate is unlike the higher polyphosphates in its hydrolysis mechanisms. The primary reason for this is the ability of pyrophosphate to form stable complexes with the di and trivalent cations. Pyrophosphate hydrolyzes more slowly than the other polyphosphates and this reaction is

reduced further by the pyro ions being bonded with the di and trivalent impurities. A multiple nonlinear regression program was used to evaluate the data from an experiment designed to test the effects of nitrogen, iron, aluminum, fluorine, and phosphate on the half-life value of pyrophosphate hydrolysis. These data were used to determine an empirical formula relating the hydrolysis rate to these factors.

$$\ln \text{half-life} = 1.6620 + 0.1932\ \text{wt\% N} - 0.0696\ \text{wt\% } P_2O_5 + 0.2987\ \text{wt\% } Fe_2O_3 + 0.2054\ \text{wt\% } Al_2O_3 - 0.1332\ \text{wt\% F}$$

Although the interaction terms have not been developed, the equation reveals that iron, aluminum, and nitrogen decrease the hydrolysis rate of pyrophosphate while phosphate and fluoride increase it. These data were determined at fluoride concentrations (0%, 1.0%, and 2.8% F) which were below the level required to complex with all the iron and aluminum. Fluorine complexed with iron and aluminum is effective in reducing the ln value about half the quantity that iron and aluminum increase it. Under conditions of fluoride sequestration (7), magnesium and probably other divalent elements (fluoride sequestration of Fe^{2+}, Zn, Ca, or Mn has not been researched) are solubilized as fluoride complexes and, like the iron and aluminum fluoride complexes, are expected to have a negligible effect on hydrolysis.

The slow hydrolysis of pyrophosphate as shown by the equation does not limit the storage properties of fluid fertilizers. In fact, since the divalent metallic impurities, micronutrients, and aluminum form insoluble components or gels with pyrophosphate, only a limited quantity of this phosphate species is desirable for long-term storage of fluid fertilizers. Ferric iron is the only metallic impurity in wet-process phosphoric acid that forms soluble pyrophosphates in fluorine-free ammoniated products around pH 6 (7).

COMPLEX FORMATIONS

Complex formation is the important mechanism by which impurities are sequestered in fluid fertilizers. Since PO_4^{3-}, $P_2O_7^{4-}$, and F^- are very strong ligands in these systems, essentially no free ions of the impurity components are present. Each type of complex acts as an independent component with its own chemical and physical effects on the other components. The low level of solvent water and the types and multivalent nature of the component ions in solution are naturally productive of numerous complex ions. Each additional component, i.e., the condensation of orthophosphate to pyrophosphate, creates another distinct group of complex multicomponent ions which must establish an equilibrium with the others already in the system. The simplest system involved in the production of fluids is the initial wet-process acid where complex formation has already occurred before ammoniation begins (19, 66). In orthophosphoric acids, the complexes are sometimes manifested by the various colors that can be observed; i.e., a yellow coloration is believed to be due to vanadium complexes; green may be caused by one of the valence states of chromium; and ferric iron complexes with orthophosphoric acid to give a purple color. Chemical analysis has also demonstrated that a complex formation exists between aluminum and fluorine in hot commercial WPSAs (~76% P_2O_5). Higher aluminum concentrations will retain higher fluorine values at any given temperature (figure 7). This relationship is not simply between aluminum and fluorine since the other ions likewise have an affinity for the fluorine. Many stability constants have been reported (67) for various cations and orthopolyphosphates in solution but they cannot be applied to strong acids or fluid fertilizers in such a manner that we can predict the conditions under which various ones can be expected to precipitate. Sometimes these data can be used in conjunction with the types of solid compounds that are in equilibrium with the liquid phase to predict the types and properties of the ions in solutions. For example, as mentioned elsewhere, $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$, $Mg(NH_4)_6(P_2O_7)_2 \cdot 6H_2O$, and $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ can exist together in the same ammonium polyphosphate solution; consequently they must be formed from similar complexes in solution such as:

$$MgP_2O_7^{2-} + 2NH_4^+ + 4H_2O \rightarrow Mg(NH_4)_2P_2O_7 \cdot 4H_2O \quad (7)$$

$$MgP_2O_7^{2-} + 3NH_4^+ + (NH_4)_3P_2O_7^- + 6H_2O \rightarrow Mg(NH_4)_6(P_2O_7)_2 \cdot 6H_2O \quad (8)$$

$$MgP_2O_7^{2-} + 2NH_4^+ + (NH_4)_3P_2O_7^- + AlF_2^+ + 6H_2O \rightarrow MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O \quad (9)$$

When the solubility products of these ions are exceeded, these compounds precipitate. This occurs regularly in APP fluids when the MgO content exceeds 0.2% and free fluorine exceeds 0.01% (7). Notice that other complexes have been proposed for equations 8 and 9 so that advantage can be gained from phase chemistry results (55) and experimental observations. For example, the precipitate in equation 8 forms at higher pH values and higher pyrophosphate concentrations both of which are shown for No. 8 as compared to 7. In No. 9, an aluminum fluoride (insoluble) is needed and AlF_2^+ fits nicely relative to equations 7 and 8.

The sequestration ratio effect that ammonium fluoride has on solubilizing all three compounds can be applied to these reactions. Since aluminum requires more than twice the fluoride that magnesium requires, the solution reactions can be visualized as:

$$Mg(NH_4)_2P_2O_7 + NH_4F \rightarrow MgF^+ + (NH_4)_3P_2O_7^- \quad (10)$$

$$Mg(NH_4)_6(P_2O_7)_2 + NH_4F \rightarrow MgF^+ + 2[(NH_4)_3P_2O_7]^- + NH_4^+ \quad (11)$$

$$MgAl(NH_4)_5(P_2O_7)_2F_2 + 3NH_4F \rightarrow MgF^+ + 2(NH_4)_3P_2O_7^- + 2NH_4^+ + AlF_4^- \quad (12)$$

Thus we have gone from a solution with insoluble (low solubility) complexes, $MgP_2O_7^{2-}$ and AlF_2^+, to one with soluble (high solubility) complexes, MgF^+ and AlF_4^-. The complex AlF_4^- is postulated as the soluble form of aluminum since both the aluminum fluoride (AlF_2^+) and aluminum orthophosphate ($AlHPO_4^+$) complexes are insoluble, indicating that $MgP_2O_7^{2-}$ is the species which causes precipitation in fluid fertilizers. Also, as indicated above, the sequestration equation required twice the fluorine for aluminum as for magnesium.

Exploratory studies in the system Al-NH_4-$H_4P_2O_7$-H_2O have shown that several double salts are stable between pH 3 and 8, and all precipitate at low levels of aluminum. The saturating Al_2O_3 concentration in pure ammonium pyrophosphate solutions is 0.3% to 1.4% whereas with small quantities of fluorine, a saturation level with respect to an aluminum ammonium pyrophosphate was never reached. As more fluorine is charged more aluminum dissolved until saturation is reached with respect to $(NH_4)_3AlF_6$ (7). This occurs at about 1% Al_2O_3 and 1.5% F without forming a double salt between pyrophosphate and fluoride. It is apparent that aluminum ammonium pyrophosphate fluorides are very soluble and cannot be expected to precipitate at concentrations encountered in fluid fertilizers. Aluminum in orthophosphate fluids prepared from WPA (17, 41) is almost always complexed with fluorine, probably as AlF_2^+, and precipitates as the insoluble compound $AlNH_4HPO_4F_2$ which can be easily visualized as a combination of the two complexes AlF_2^+ and $NH_4HPO_4^-$.

A major anomaly exists in fluid fertilizer systems between iron and aluminum. Use of the singular term "I and A" (iron and aluminum) or R_2O_3 indicates a similarity which does not exist for these elements in fluid fertilizers. Ferric iron is totally unlike aluminum except for products prepared from defluorinated WPSA. The iron fluoride complex is relatively weak and can be decomposed by the heat of ammoniation. When fluorine is in excess of that required by the aluminum, the citrate soluble salt $Fe(NH_4)_2(HPO_4)_2F$ can form; however, the most commonly found orthophosphate is $FeNH_4(HPO_4)_2$ which in the absence of fluoride can coprecipitate aluminum. Unlike aluminum, which precipitates readily in ammonium pyrophosphate solutions as $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$, iron forms strong soluble complexes with $P_2O_7^{4-}$ (67); in fluids it is most probably $FeP_2O_7^-$ since this form can be readily applied to the stable iron ammonium pyrophosphates (7) shown in table 8. Except in the special case of $Al(NH_4)_2P_2O_7OH \cdot 2H_2O$ which forms in the absence of fluorine, a pure aluminum ammonium pyrophosphate has not been encountered. Although the iron ammonium pyrophosphate phase system has not been studied, exploratory tests show the salts in table 8 precipitate at about 4% Fe_2O_3. The exception being $Fe(NH_4)_3HPO_4P_2O_7 \cdot H_2O$ which forms slowly in ammonium polyphosphate liquids at 2%-3% Fe_2O_3. This compound was still precipitating from commercial liquids high in ferric iron after 2 years and demonstrates a slow shift in equilibrium between a soluble and an insoluble complex since the same study showed that increasing the iron content to 4%-5% Fe_2O_3 did not accelerate the precipitation. Several complex formations are obviously required for precipitating $Mg_3Fe(NH_4)_{12}(P_2O_7)_4F_4OH \cdot 12H_2O$. One of them is sufficiently short-lived to the extent that the salt forms in fresh high polyphosphate 10-34-0 solution but later (up to one month) redissolves.

In many cases, complexes are formed that are soluble but have a strong affinity for water which causes the fluid fertilizer to become a clear liquid gel. This can be easily demonstrated (7) by starting with a pure 10-34-0 solution with 33% of the P_2O_5 as pyrophosphate and adding 0.7% MgO, 0.5% Al_2O_3, and 0.3% F (1.5% total impurities). After equilibrating 1-2 days at 140°F (60°C), the product will be a clear gel capable of being sliced into stable cubes. The types of complexes responsible for this will be similar to those that cause precipitation but obviously quite different since a new physical feature (gelling) has now been encountered. Other gels have also been encountered in strong phosphoric acids, dilute fertilizers, and in ammonium orthophosphate systems, but none have been researched. Indeed the solution chemistry of fluids is more complex than the standard phase system chemistry indicates where crystalline solids are in equilibrium with a given liquid phase. Gel formation in fluid fertilizers is a serious problem which occurs slowly and without warning, resulting in a clear jello-like product with an ever increasing rigid structure. These gels consist of soluble complexes which have an affinity for more water than is available in the fertilizer product. Limited studies have shown that up to a point, small increments of dilution with water result in gels of even higher viscosities indicating that simply lowering the grade of the fluid will not solve this gel problem.

Gelled fluid fertilizers have been encountered from many sources and since little is known about them it became common practice to search for empirical solutions to each without researching its chemical characteristics. It was determined that some gels could be broken by adding small quantities of fluoride whereas some required ammonium pyrophosphate while others were susceptible to small additions of aluminum. The undesirable element, magnesium, was never tried but probably would also have

worked. Again, as with sequestration of solids, the solution to the gel forming problem was the elimination of solution complexes that have a strong affinity for water. Both problems seem to be susceptible to variations in impurity ratios as well as pyrophosphate content. For example, in one study the aluminum content effective in preventing gel formation was 1-2 times the magnesium content (39). Likewise, the sequestration ratio equation (7) was effective in gel control; however, it was necessary to make allowances for the aluminum-to-magnesium effect. Many of the gels encountered in fluid fertilizers were never broken by single exploratory testing, and quantitative records were not maintained on those that did work since processing data was rarely available for comparison. While gel formation can occur in all orthophosphate systems, it seems to be especially prevalent in polyphosphate mixtures containing pyrophosphate. Recent exploratory results (42) have shown that many simple mixtures are capable of gelling. For example, in a factorial study of 9-32-0 fluid fertilizers, the simple systems containing 2% Fe_2O_3 and 2% F at 25% pyrophosphate resulted in a purple colored (pyrophosphate) gel but was yellow colored (orthophosphate) in the absence of fluorine and pyrophosphate indicating two different types of complexing, both of which are capable of gelling the fluid fertilizer. Similar gelling, without coloration, was encountered with aluminum at 3% Al_2O_3, 1% F, and 25% pyrophosphate. The complex formations responsible for these observations will have to be controlled before a stable storage life for fluids can be guaranteed.

SUMMARY

Fluid fertilizers made from wet-process phosphoric acid are complex, multicomponent chemical systems for which the stable matrix component is ammonium orthophosphate. As produced, the ammonium phosphates are in a quasi-equilibrium state with the other components and are actively trying to reach an equilibrium condition. The rate of approach to equilibrium is partially controlled by a large number of stability constants which affect both the rate of formation and the rate of decomposition of each complex encountered. The quantity and ratio of the impurity components predetermine the equilibrium path that will be followed. The complex molecules in solution are continuously reacting to form more stable complexes since those stable in the original acid must rearrange to others that are stable in the hot ammoniated products. Redistribution and new complex ion formation is controlled by many parameters and proceeds slowly. Three physical parameters which impede equilibrium are easily recognized: (1) insoluble complexes removed by precipitation cannot react until redissolved, (2) diffusion of dissolved impurities is slowed by precipitated solids and also by added suspending agents, and (3) massive gel formation will virtually stop any further reaction.

The presence of polyphosphates greatly retards the rate at which the systems reach equilibrium since the final stable forms must wait for the polyphosphates to hydrolyze to the ultimate orthophosphate form. The many different complex ions that will be encountered with time will cause a wide variation in the chemical and physical properties of the fertilizer products. Some complexes will be very soluble with very little affinity for water and have little effect on the fertilizers; some are insoluble and will precipitate as complex chemical compounds having a wide range of particle sizes and shapes; and some will be soluble with a strong affinity for water and reduce the product to a clear, nonflowing viscous liquid or gel.

Very little is known about the soluble, nonhydrated ions since their saturation concentrations have not been exceeded and they have not represented a problem to the development of fluid fertilizers. These are the ionic forms present in the so-called "sequestered" products which are stabilized for periods up to 5 to 7 years with proper fluoride control.

The role of fluoride in fluid fertilizers has been well defined. This element acts as a strong ligand with other ions—consequently, there is no effective quantity of free fluoride present in fertilizer solutions.

GOALS FOR FUTURE RESEARCH

The growth of fluid fertilizers has been retarded by the persistent storage problems that continue to exist. The attributes of these fertilizers are desired by the industry and the problems are being solved. Background factorial data covering the range of impurity concentrations that will be encountered from all types of acids are needed to predict the consequences of changing the various chemical parameters. The lack of these data prevents development of fluid fertilizers to their full potential. At the present economic status of the fertilizer industry, WPSA of low impurity content and purified WPA are unavailable as a solution to the precipitation of impurities in fluid fertilizers. Likewise, as learned early in the study of fluids, diluting the products with water to obtain less viscous, more fluid materials is not desirable below 10-34-0 grades. Less expensive and less energy consuming chemical controls must provide the answers that are needed to continue the upward development of fluid fertilizers. Since other industries are willing to pay higher prices for purified phosphoric acid, an opportunity will be available for the fertilizer industry to find a use for the low cost reject acids from these purification processes. These reject acids along with settled sludge acids, WPAs from low-grade phosphate rocks, and spent pickling acids from industry sources can be consumed as an economi-

cal source of phosphate fertilizer—if the technology is available for controlling a wide range of impurity concentrations.

Basic research, experimentation, computer modeling, and theorizing must continue before the industry can feel confident in providing long-term storage for fluid fertilizers. In this respect, fertilizer scientists are in a position to benefit from several years of detailed study performed on most all aspects of these fertilizer materials. An impressive level of achievement which describes the parameters controlling the precipitation of impurities in fluids from wet-process phosphoric acid is available now (see references).

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Chapter 5

Production, Handling, and Use of Anhydrous Ammonia

By G. M. Blouin, H. L. Kimbrough, and W. J. Sharratt

Nitrogen is an essential element in supplying the burgeoning world population with adequate food and fiber. Fortunately, it is in abundant supply in the Earth's atmosphere, but, unfortunately, is essentially useless in intensive agriculture because of its inherent inertness to most growing organisms. Aside from very small amounts available in naturally occurring minerals such as Chilean "caliche" ($NaNO_3$ and KNO_3) and the large but still completely inadequate amounts absorbed directly from the atmosphere by a complex biological process occurring in certain legumes, elemental nitrogen must be converted in large quantities to reactive chemical compounds that are available to growing plants. This process is often referred to as nitrogen fixation. Because of an equal abundance of water on this planet, the logical and most economical route to fixed nitrogen is through the production of highly reactive hydrogen from water and its subsequent reaction with atmospheric nitrogen to produce anhydrous ammonia.

PRODUCTION PROCESSES

HISTORY

Today anhydrous ammonia is a basic industrial chemical, ranking in annual tonnage production with sulfuric acid and oxygen. However, reaching this status has required over 200 years of painstaking development since its discovery in the laboratory by Priestly in 1754. It was some 30 years later that the composition of this laboratory curiosity was established by Bertholet. In the meantime, atmospheric nitrogen was identified by Rutherford in 1795. However, it was not until the period 1795 to 1823 that consideration was given by Hildebrand and Dobereiner to the possible synthesis by the catalytic reaction of atmospheric nitrogen and hydrogen. Others continued this work—possibly given impetus by the knowledge expounded by the work of Lord Dundonald in 1795 and that of Sir Humphrey Davy in the early 1800s that nitrogen-bearing materials were essential to plant growth—but it remained to Fritz Haber in the period 1902-09 and later to Carl Bosch in the period 1910-13 to develop the first commercial ammonia synthesis process, using promoted iron oxide catalyst for reaction of nitrogen and hydrogen, at Oppau, Germany; that plant soon reached a production rate of 30 tons per day. In 1917 a 100-ton-per-day unit was built at Leuna (1).

During the painful development of the Haber-Bosch process in Germany, the fixation of atmospheric nitrogen took other directions as well. By 1905 Berkeland and Eyde had put into operation in Norway their electric arc process for direct oxidation of atmospheric nitrogen to form nitric acid. Also in 1906 the Frank-Caro calcium cyanamide process, under development since 1898, was commercialized, first in Italy in 1906 and in the United States in 1918. After World War I, these processes were rapidly discarded in view of the successful Haber process development in Germany.

Thus the era 1920-30 saw the rapid increase in world synthetic ammonia capacity. In the United States alone, the capacity increased to over 380,000 tons per year by 1932 and again, during World War II, to about 1.4 million tons per year. This increased capacity, for the most part, was not due to increasingly larger plants—most were of a

200- to 350-ton-per-day capacity, or smaller—but to a doubling in the number of plants (1).

The period 1950-70 saw an amazing series of developments—first came new technology involving large single-stage converters and multistage centrifugal compressors—and then a rapid expansion of numbers of plants and plant capacities. In 1950, U.S. capacity was about 1.7 million tons per year. By 1960 it had risen to about 5.5 million, almost a fourfold increase (1, 4). Between 1960 and 1970, capacity increased to 16.9 million tons, another threefold increase. Current (1982) capacity is about 19.5 million tons per year in 144 plants. (About half of these plants were closed or idle in mid-1983 because of the general recession or because of their low capacity and efficiency.)

CHEMISTRY

The ultimate exothermic, catalytic reaction involved in the formation of anhydrous ammonia (NH_3) is:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(l) + 32 \text{ kcal}$$

This seemingly simple reaction is, however, only the final step of four major steps involved in the production of more than 95% of the tremendous annual tonnage of anhydrous ammonia throughout the world. Only where relatively pure hydrogen is available (certain electrolytic processes, including water electrolysis, or petroleum refining processes) can the single process (reaction) above be utilized.

Four basic unit operations are required in the production of nearly all anhydrous ammonia processes (1). These steps, together with the chemical reactions involved, are described briefly as follows:

1. Raw synthesis gas (hydrogen + carbon monoxide) production by:
   a. Reforming hydrocarbons with steam; catalytic; endothermic; air added in secondary reformer to burn out residual methane and to provide the required nitrogen for synthesis.
      (1) Methane

      $$CH_4 + H_2O \rightleftarrows 3H_2 + CO - 49.3 \text{ kcal}$$

      (2) Naphtha

      $$2C_7H_{15} + 14H_2O \rightleftarrows 14CO + 29H_2 - 520 \text{ kcal}$$

   b. Partial oxidation of coal or residual oils in presence of steam; endothermic (emperical formula of a typical coal macromolecule; SiO_2 equivalent to ash content).

      (1) $C_{50}H_{60}O_{10}S(SiO_2) + 40\,H_2O \rightleftarrows 70\,H_2 + 49\,CO + COS + SiO_2 - 2400$ kcal (approximate)

2. Shift conversion—catalytic reaction of carbon monoxide with steam; exothermic.

   $$CO + H_2O \rightarrow H_2 + CO_2 + 9.8 \text{ kcal}$$

3. Synthesis gas purification
   a. Acid gas (CO_2, H_2S, COS, or H_2S) removal—scrubbing of raw synthesis gas by preferential basic chemical (promoted potassium carbonate, ethanolamines, etc.) absorbent solutions or physical absorbent liquids (methanol or other organic liquids) in packed or plate towers. Major energy requirements are in regeneration of sorbent solutions.
   b. Methanation-catalytic reaction of residual carbon oxides from acid gas removal with hydrogen to form methane (CO_x are synthesis gas poisons, methane is not); exothermic.

      $$CO + 3H_2 \rightarrow CH_4 + H_2O + 49.3 \text{ kcal}$$
      $$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O + 39.3 \text{ kcal}$$

   c. Liquid nitrogen wash (in lieu of methanation)—residual CO_x and CH_4 are scrubbed out of synthesis with liquid nitrogen; generally used only with partial oxidation processes that require oxygen; also provides nitrogen required for synthesis.
4. Ammonia synthesis—catalytic reaction of hydrogen and nitrogen; exothermic.

   $$N_2(g) + 3H_2(g) \rightarrow 2NH_3(l) + 32 \text{ kcal}$$

It must be noted that the above reactions are the preferred reactions in each step but that in the raw synthesis gas production numerous side reactions occur and must be suppressed by the optimum adjustment of pressure, temperature, air, or oxygen: feedstock ratio, space velocities, catalyst composition and age, steam:carbon (feed) ratio, feedstock H:C ratios, etc. Details of this optimization procedure are beyond the scope of this text and are covered thoroughly in the literature (2, 4, 6). Computerized operation of ammonia plants is of significant benefit because of the high degree of interaction of these many variables.

One aspect of the chemistry of ammonia synthesis, the thermodynamic (thermal) efficiency of the various processes, is not widely discussed in the literature. However, Hignett (4) provides basic thermodynamic data that permits calculation of process thermal efficiency. He developed the overall theoretical reaction in the methane steam reforming process as being:

$$7\,CH_4(g) + 10\,H_2O(l) + 8N_2(g) + 2O_2(g) \rightarrow 16NH_3(l) + 7CO_2(g)$$

Using standard heats of formation, the reaction is found to be exothermic to the extent of 1.6×10^6 Btu/ton NH_3 (liquid). However, the high heating value (HHV) of the 7 moles of CH_4 given in the equation is equivalent to 1,489 kcal, or 93.1 kcal per gram mole NH_3, or 19.7 million Btu per ton liquid NH_3. The HHV usage here is believed to be justified in that the efficient alternate use of the gas as a fuel would, by preheat units, recover the latent heat of vaporization of the water formed in combustion reaction. This serves as the theoretical base for determining the thermal efficiency of all ammonia synthesis processes, that is

$$\text{Thermal efficiency, \%} = 100\left(\frac{19.7 \times 10^6}{10^6 \text{ Btu process energy input}}\right)$$

The theoretical energy content, 19.7×10^6-Btu-per-ton liquid NH_3, is verified in an approximate manner by calculating the heat of reaction (combustion) of liquid NH_3 with O_2:

$$2NH_3(l) + 4O_2(g) \rightarrow N_2O_5(g) + 3H_2O(l) + 172.4 \text{ kcal}$$

Using standard heats of formation, the heat of reaction of this equation is 172.4 kcal, or 18.3×10^6 Btu per ton NH_3. The higher theoretical value (19.7×10^6 Btu per ton) is normally used in estimating process efficiency (1).

RAW MATERIALS FOR HYDROGEN PRODUCTION

Virtually any hydrocarbon or carbonaceous material can be converted to hydrogen (plus CO_2) by reaction at high temperature with water (steam). Water itself may be considered as a "feedstock" through the electrolytic process.

Methane—Natural gas (methane) is, however, by far the most economical and widely used feedstock in the world (1, 4). About 75% of the world capacity and about 95% of the U.S. capacity is based on the catalytic reforming of methane with steam. Only those countries having no indigenous gas go to other feedstocks. It is very nearly the ideal feedstock in that it provides both the carbon for reduction of the hydrogen ions in water to elemental hydrogen and an equal amount of hydrogen by the simultaneous oxidation of the carbon in the methane molecule. The overall reaction, in its simplest form, is:

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$$

In addition, the simple molecular structure requires less energy to drive the endothermic reaction to the right than any other readily available feedstock.

Liquified natural gas (LNG) is a growing world commodity and, in spite of the huge investments required both in the exporting and importing countries, is beginning to displace naphtha as indicated below.

Naphtha—Naphtha (emperical formula C_7H_{15}) is the most widely used feedstock in those countries that have no indigenous natural gas. However, in recent years, the world price of naphtha has increased to the point where LNG is beginning to displace naphtha as a feedstock in existing reforming plants. It is estimated that about 15%-20% of the world ammonia capacity is based on naphtha (4).

Naphtha is a straight-run, light petroleum distillate fraction with a final boiling point of about 265°F (130°C); it is primarily a saturated hydrocarbon (95% by weight). Unlike natural gas, which is desulfurized at the production field, naphtha may contain as much as 0.15% sulfur (1). As a result, it must be desulfurized at the ammonia plant. On the other hand, like methane, it can be steam-reformed to produce the required hydrogen for NH_3 synthesis. In fact, the two feedstocks are interchangeable provided the specially promoted iron oxide synthesis catalyst required for naphtha is used.

Naphtha plant investment costs are about 10% higher than comparable natural gas plants because of the desulfurizing unit and the somewhat larger acid gas removal system required for the former.

Coke-Oven Gas—The production of coke by the reductive pyrolysis of coal (coking) yields by-product offgas that contains hydrogen, carbon monoxide, methane, and nitrogen as well as numerous impurities (H_2S, COS, CO_2, tars, phenols), and some NH_3. The gas can be used in the reforming process after purification by acid gas removal or cryogenic separation and liquid nitrogen wash (1). This feedstock is economically feasible when used in a large metallurgical operation where tonnage oxygen is required and thus liquid N_2 is also available. Its major drawback is high-compression energy requirements since the feedstock is normally at atmospheric pressure. Its use is dwindling because of the competition from large natural gas-based plants.

Heavy Oil—Raw petroleum, heavy distillates, and residual fuel oils (Bunker C) are widely available, but have been used only to a limited extent—perhaps 5% to 10% of world capacity. The primary reason for its past limited use (future use may tend to increase as indigenous gas reserves dwindle in some areas) is the high plant capital investment required for the associated air liquifaction plant, the large feedstock storage facility, and the much larger acid gas removal system for a given capacity (1, 4). The future of the partial oxidation process required by these heavy feedstocks will depend upon the future complex relationships of natural versus synthetic pipeline gas (SNG), petroleum refining demands (gasoline versus naphtha or other petroleum

products), and the degree of concentration of world market supplies from the "gas-rich" areas such as the Persian Gulf, Indonesia, and the North Sea—as well as on the future results of the vastly increased gas/oil exploration in the United States, Canada, Mexico, etc.

Coal—Partial oxidation of coal is a technically viable but expensive process for hydrogen (ammonia) production. It is even more costly—investment and operating—than the oil partial oxidation process because of the still larger air liquifaction and gas purification systems. The basic advantage is to those countries with large indigenous coal reserves, among which is the United States.

There are only a small number of coal-based plants in the world—Turkey, South Africa, and India, to name the most prominent. However, the ammonia plants at Modderfontein and Sasolburg, South Africa, are large units and, at Sasol, are part of a large complex wherein modified Fischer-Tropsch synthesis processes yield synthetic petroleum products of a wide variety. Their operation has been quite successful after an initial period of trials and unit modifications. This approach, i.e., the inclusion of an ammonia plant in a very large scale coal-based chemical complex, appears to offer the best chance for economic viability in the near term.

The current or first-generation plants operate at low pressure in the gasification section. As a result, compression costs are high (1). TVA, at its National Fertilizer Development Center, has undertaken on a relatively small scale (130 tons per day) the demonstration of the integration of a second-generation coal-gasification and gas purification unit (figure 14, left center) with its existing gas reforming ammonia plant (figure 14, right center) (6). The purpose is to demonstrate the high-pressure (500 $lb/in^2 g$, 3.4 x 10^6 Pa) Texaco gasification process and the means of retrofitting a coal gasification system compatible with existing downstream gas-reforming plant purification and synthesis units. Successful demonstration could lead to the savings of hundreds of millions of dollars in the event that depleted gas reserves or exorbitant gas costs force a change to plentiful coal reserves in this country as an alternative petrochemical feedstock. The TVA unit, which is in the early stages of operation (figure 15), has completed the 5-day performance test and has produced ammonia at full design rates.

Other Feedstocks—Among other alternative feedstocks—all requiring the partial oxidation process—are coke and waste celluloses such as paper and wood dust. Their use is extremely limited; they are mentioned only to emphasize the wide range of potential feedstocks for ammonia synthesis.

Water, of course, may be disassociated into hydrogen and oxygen, in separate streams, by electrolysis. A few small plants in remote areas produce ammonia from hydrogen obtained in this manner.

PROCESS AND DESIGN DETAILS

Feedstock Purification

1. Natural gas reforming—Natural gas from the well-head invariably contains unacceptable levels of sulfur compounds, generally H_2S, and carbon oxides, both of which are poisons to the nickel oxide reformer catalyst. In the United States, these impurities are nearly always reduced to a few tenths of a part per million before introduction to the pipeline system. In other areas, this must be done at the ammonia plant site. Since virtually all of the acid-gas removal systems can be designed to be equally effective for H_2S and CO_2, descriptions of these processes will be covered under the Acid Gas Removal section.

In some areas, pipeline gas may contain a few parts per million of sulfur compounds. In this case, a sulfur guard may be placed in the ammonia plant gas inlet line. Either alternating beds of activated carbon at ambient temperature or zinc oxide beds at about 600°F (316°C) (gas preheated) are effective in reducing the sulfur to undetectable levels (1).

2. Naphtha reforming—Nearly all commercial naphthas contain significant amounts—up to 1,500 ppm—of sulfur as delivered. Thus the ammonia plant must include naphtha desulfurizer upstream of the primary reformer. The naphtha is vaporized and mixed with a sufficient amount of hydrogen from the synthesis section to ensure reduction of all sulfur compounds to H_2S in a catalytic converter. The H_2S is removed by a combination of steam stripping of the recondensed naphtha and iron or zinc oxide sulfur guards for the revaporized naphtha (1, 4).

3. Most other hydrogen production for ammonia synthesis involves noncatalytic partial oxidation of the feedstock with relatively high-purity oxygen from an air separation plant that also supplies the high-purity nitrogen for syngas makeup and for the liquid nitrogen syngas wash in the final purification step.

Under these conditions, the feedstock cannot be purified; therefore, the feedstock impurities such as ash, sulfur, and chlorine compounds, and volatile, condensable tars, hydrocarbons, phenols, etc., are present in the raw gasifier offgas and must be removed from this stream prior to its undergoing shift conversion. This purification process is described in more detail later in this section.

Primary Reforming

As previously indicated, the most widely used primary reforming reaction is that of methane with steam:

$$CH_4 + H_2O \rightleftarrows 3H_2 + CO$$

The reaction is endothermic, thus requiring a large amount of heat energy to drive the reaction to the right. Addition-

Figure 14. Coal-gasification and gas-purification unit and gas reforming ammonia plant

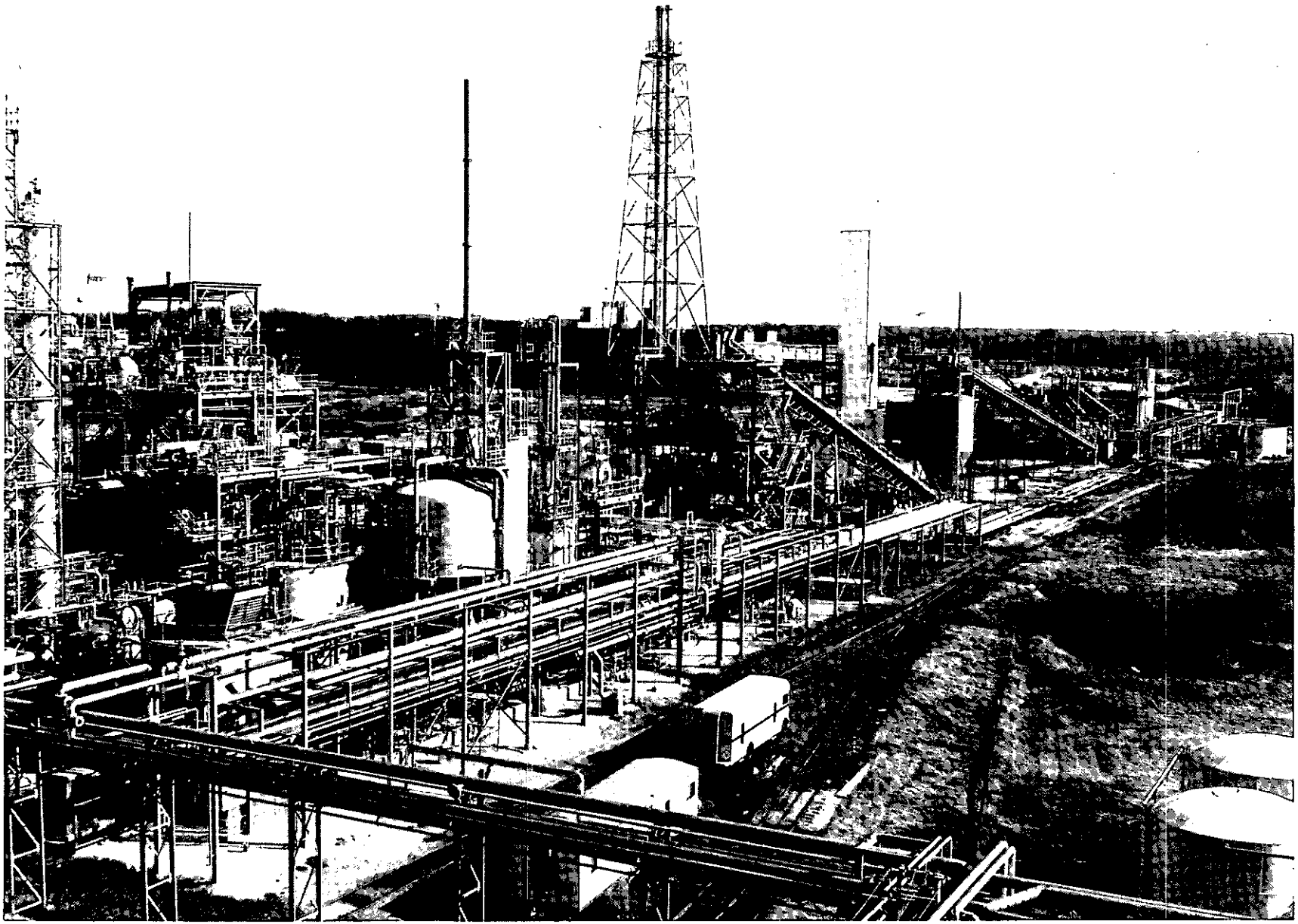

Figure 15. TVA ammonia from coal project

ally, a catalyst is required to increase the rate of reaction to an acceptable level. Further, the typical reformer, and subsequent unit operations prior to syngas compression, is operated at about 500 lb/in^{2}g (3.4×10^6 Pa) by compressing the methane, as necessary, prior to reforming and utilizing high-pressure steam generated by waste heat recovery. The moderately high pressure favors CO shift conversion kinetics and acid gas removal, not reforming, but it requires less compression energy to compress the methane (and secondary reformer air) than the larger volume of raw reformer offgas (2). The primary reformer catalyst generally consists of small (5/8 x 3/8 x 1/4 inch, 1.6 x 1 x 0.6 cm) rings of alpha alumina base impregnated with activated nickel; the catalyst is packed in nickel alloy tubes (gas side) that are externally heated (fire side) by gas flames in the reformer furnace. Catalyst temperature is generally about 1472°F (800°C). An excess of steam—about 3.5 mols per mol CH_4—versus the theoretical 1 mol—is used to control tube temperature and to prevent carbon (soot) formation due to incomplete methane cracking (2).

The primary reforming of vaporized naphtha is quite similar to that of methane. The basic difference is in the catalyst employed. While still an activated nickel-on-alumina ring, the base is "promoted" with potash. Kalsilite ($K_2O{\cdot}AL_2O_3{\cdot}2SiO_2$) is a typical base, or support, for the nickel catalyst. A somewhat higher steam:carbon ratio (4-5:1) is generally required to guard against carbon deposition (1, 2).

Secondary Reforming

The gas leaving the natural gas or naphtha primary reformer contains unreformed methane (methane is an intermediate in naphtha reforming). The same nickel catalyst (somewhat lower nickel content) is used, but it is deposited in a packed tower bed rather than in tubes; potash addition is not required. Compressed, preheated air is added in sufficient quantity at the gas inlet to provide the final 1:3 $N_2:H_2$ mol ratio in the syngas. A relatively small amount of additional high-pressure steam is added to carry out some additional methane reforming. The oxygen in the added air reacts, of course, with all of the constituents of the gas so that a net exothermic series of reactions occur. Thus the reformer temperature rises to about 1800°F (982°C) (1, 2).

Partial Oxidation (Gasification)

In lieu of steam reforming of light hydrocarbons, the partial oxidation of heavy hydrocarbons or coal is generally the source of hydrogen and carbon monoxide for ammonia synthesis. This general process was described briefly in the Raw Materials for Hydrogen Production section. On one hand, it is a simpler and more rugged process than steam reforming in that no pretreatment of the feedstock is required and no sensitive catalysts are involved. On the other hand, it is a much more complex process mechanically and much more costly because of the necessity of liquid or solid feedstock storage and handling; of the need for an air separation plant; and of significant problems in gaseous, liquid, and solid waste disposal (1, 2, 4).

Extreme detail in process description is covered in the literature (1, 2, 4, 6) and is beyond the scope of this text. Briefly, the endothermic conversion of steam to hydrogen by reaction with carbon (coal) or heavy hydrocarbon involves the respective reactions:

$$C + H_2O \rightarrow H_2 + CO$$

and

$$C_nH_m + nH_2O \rightarrow nCO + (\tfrac{m}{2} + n)H_2$$

Thus, as in steam reforming, the principal products important to ammonia production are H_2 and CO, the latter being convertible to additional H_2 by the shift conversion process.

The significant differences between the ' catalytic reforming process and the noncatalytic partial oxidation process are (1) the endothermic heat of reaction of the carbon or hydrocarbon and steam is supplied by complete combustion of part of the feedstock with oxygen within the gasifier rather than by indirect firing in the catalytic reformer, (2) the required nitrogen (and combustion oxygen) is supplied by a costly air separation plant rather than directly from the atmosphere as in the secondary reformer, and (3) feedstock purification prior to gasification (reforming) is not required as in natural gas or naphtha reforming. However, the raw gas from the gasifier does require extensive cleanup, namely, venturi and/or packed tower scrubbing and electrostatic precipitation for solids removal, condensation and separation of condensable vapors, and absorptive removal of sulfur compounds and some carbon dioxide, both before and after shift conversion.

Carbon Monoxide (Shift) Conversion

The formation of carbon monoxide (CO) in the first stage of either the steam reforming or partial oxidation processes is unavoidable. However, it is relatively simple to convert the carbon monoxide to additional hydrogen by the catalytic reaction:

$$CO + H_2O \rightarrow H_2 + CO_2$$

This is generally carried out in two stages. The first is a "high temperature," packed tower catalytic converter containing chromium promoted iron oxide catalyst tablets and operating at about 780°F (416°C). The second unit ("low temperature") is similar except the catalyst is a zinc copper oxide catalyst, sometimes promoted with aluminum oxide,

operating at about 500°F (260°C). The exit gas from the first stage is cooled somewhat by heat-exchange prior to entry into the second stage (1, 2).

The first-stage catalyst is reasonably tolerant to sulfur; as much as 200 ppm H_2S can be tolerated. The low temperature catalyst, however, is very sensitive to sulfur; so often a zinc oxide-sulfur guard may be placed upstream of the unit.

Recently a shift conversion catalyst was developed specifically for use in partial oxidation processes where feedstock sulfur compounds present certain problems. It is an intermediate temperature, "sulfur-activated" cobalt-molybdenum catalyst that is completely tolerant of not only sulfur, but also of other likely impurities in the gasifier raw gas stream. It is operable over a range of 400° to 800°F (204°-427°C) (4, 6). Its primary advantage is described below.

Acid Gas Removal

The natural gas and naphtha reforming processes yield, after the carbon monoxide shift conversion step, a high-temperature gaseous mixture consisting of hydrogen, nitrogen, water vapor, carbon dioxide, residual methane, carbon monoxide, and certain inerts, principally argon, from the air fed at the secondary reformer.

The partial oxidation process yields, after particulate removal by water scrubbing and possibly electrostatic precipitation, but before shift conversion, a high-temperature gaseous mixture of hydrogen, carbon monoxide, carbon dioxide, methane, hydrogen sulfide, carbonyl sulfide, condensable organic vapors, ammonia, and water vapor. The methane and condensable vapors are generally present only in a relatively low temperature (<1300°F, 704°C) coal gasification process such as the Lurgi. Most processes operate at high temperature (>1800°F, 982°C) to avoid formation of these impurities.

It is absolutely necessary that in either process, the sulfur compounds, the carbon oxides, and the condensable organics be reduced to a few parts per million in the 3:1 mol ratio hydrogen:nitrogen synthesis gas going to the catalytic ammonia synthesis converter (Ammonia Synthesis Conversion section). Methane and argon are not poisons to the synthesis catalyst, but do cause purge losses that are necessary to prevent buildup in the synthesis loop.

In the partial oxidation process, it is necessary that at least the sulfur compounds be removed before shift conversion unless the new "sulfur-activated" shift catalyst is used (Carbon Monoxide Conversion section), in which case the acid gas removal step can follow shift conversion.

It is beyond the scope of this text to cover the innumerable interactions of the many variables involved in the numerous commercially available processes. Only the basic information is given here. The literature abounds in detailed descriptions of the individual processes (1, 2, 4, 6).

Basically, the impurities in the crude synthesis gas are removed by scrubbing the entire volume of gas, after it has been cooled by heat exchange to less than 150°F (66°C). It is scrubbed with aqueous solutions of chemical absorbents such as monoethanolamine or potassium carbonate, or with certain organic liquids such as methanol and the dimethyl ether of polyethylene glycol, to physically absorb the acid gases, leaving the syngas nearly free of the impurities. Little hydrogen or nitrogen is absorbed by these media. The scrubbing may be accomplished in either packed or plate towers; the saturated absorbents are regenerated (desorbed) by heating and/or flashing the scrub loop to lower pressure.

In partial oxidation processes, the scrubbing is generally done in two stages, one prior to shift conversion, primarily for sulfur removal (but including some CO_2), and the other stage after shift conversion, primarily to recover relatively pure carbon dioxide for urea synthesis. If the sulfur-activated shift catalyst is used, the two stages of acid gas removal may follow shift conversion, but two stages are still required. The first is operated under conditions of temperature and pressure that preferentially remove virtually all the sulfur as H_2S, along with some CO_2, while the second removes virtually all the remaining CO_2, again to be recovered for urea synthesis.

In the gas and naphtha reforming processes, it is seldom that more than one stage of acid gas (CO_2) removal is required since no other impurities capable of being removed by these systems are normally present.

The physical absorbent liquids have become the dominant type in both gas reforming and partial oxidation processes in recent years because (1) they are considerably more flexible, i.e., preferential absorption of H_2S in the first stage before or after shift conversion, leaving pure CO_2 adequate for urea synthesis for second-stage recovery and (2) significantly less energy is required for regenerating the absorbent (1, 2, 4, 6).

Final Synthesis Gas Purification

In spite of the often complex and generally effective processes for removal of syngas impurities (preceding section), residual impurities always remain in the syngas. These must be removed or transformed to compounds not poisonous to the ammonia synthesis catalyst.

In the gas reforming process, the only residual poisons are the carbon oxides. In the majority of cases, these are transformed to methane in a methanation catalytic converter. The cold syngas is reheated by heat exchanges to about 500°F (260°C) and passed through a packed tower containing an alumina-supported nickel oxide catalyst. Both the carbon-monoxide and -dioxide react with the hydrogen present to form methane and water:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

The procedure is simple and effective; however, its disadvantage is apparent. Valuable hydrogen is consumed and purging requirements in the synthesis loop are increased. Nevertheless, this is the most economically viable mode of operation for the gas reforming process (1).

Partial oxidation processes, which require both oxygen and high-purity nitrogen for syngas makeup, have the advantage in at least final syngas purification. The cold gas from the acid-gas removal system is simply scrubbed in a plate tower with liquid nitrogen at such temperature that part of the liquid nitrogen boils off at the proper rate to yield the desired $H_2:N_2$ syngas mol ratio while the remaining liquid thoroughly removes essentially all impurities including water vapor. Little or no purging is required in the ammonia synthesis loop following nitrogen wash (2). However, the procedure is not economically viable for gas reforming plants, unless, fortuitously, an air separation plant is required for oxygen in another part of an industrial complex.

Ammonia Synthesis Conversion

There is little doubt that the greatest research and development effort toward establishing a viable synthetic ammonia process was expended on the synthesis step itself. Obviously, had this not been the case, beginning with the more than 10 years and 20,000 tests of Haber and Bosch, the synthetic ammonia industry may never have risen to its present status.

It is beyond the scope of this text to explore the vast amount of data developed over the years that deal with the complex thermodynamics and chemical kinetics of the apparently simple catalytic, exothermic reaction.

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_3(1) + 32.1 \text{ kcal}$$

Needless to say, many hundreds of man-years and hundreds of millions of dollars have gone into the optimization of the continuous, single-train process with capacities of up to 1,500 tons per day.

Basically, the synthesis loop consists of the main compressor section, the catalytic converter, the recirculating loop condenser, and the recirculating compressor. The purified synthesis gas pressure is raised in the main compressor from the 400-500 lb/in^2g (2.8-3.4 x 10^6 Pa) in the syngas preparation section to the "optimum" synthesis pressure of about 2,200-3,500 lb/in^2g (15.2-24.1 x 10^6 Pa), or in some cases up to 5,000 lb/in^2g (34.5 x 10^6 Pa). The main compressor, generally a multistage, electrically driven, reciprocating piston type in plants of up to 500 ton-per-day capacity, or a multistage centrifugal compressor in larger plants, is equipped with interstage water-cooled heat exchangers to maintain the gas temperature within the design limitations.

Following compression, the syngas is fed to the single catalytic converter where the reaction is carried out at about 800°F (427°C) (1, 2). Although converter design varies considerably, the potassium-alumina promoted iron oxide catalyst is generally arranged in several baskets in the vertical converter and the feed gas is divided into several streams, one to the top and the remainder to the spaces between catalyst baskets. This is to maintain a relatively even temperature profile along the height of the converter (2).

The catalytic reaction of the hydrogen and nitrogen takes place in the converter, but does not approach completion. In a compromise between chemical kinetics, thermodynamic equilibrium, and metallurgical and design considerations, the conversion per pass is only about 20%-25%. Obviously, the unconverted syngas must be recycled by means of the recirculating compressor (which may be one or two stages in the main compressor, or may be driven by the main compressor drive turbine or motor) after separation by water cooling or refrigerative cooling and condensation of the ammonia that is formed in each pass. Thus the volume of recirculated gas is about 4 to 5 times that of the fresh makeup syngas feed, the latter being equivalent to the design production rate of the plant. The recirculation compressor is designed to compress the large volume of recycle gas only a few hundred pounds pressure greater than its inlet pressure to overcome the pressure drop in the synthesis section.

The presence of the inert impurities (methane, argon, perhaps helium) in the syngas, mentioned previously in the acid gas and synthesis sections, present a problem in the conversion loop. Since they cannot be condensed as is the ammonia product, they build up in concentration in the loop to the point where they interfere with the synthesis reaction. To avoid this, a continuous stream of the recycled syngas is "purged" from the recycle loop at a point after separation of the product ammonia. This "purge-gas" flow is generally adjusted to maintain a concentration of 10%-12% inerts in the loop. This may amount to about 0.5 volume percent of the total flow to the converter, or about 2 volume percent of the makeup feed (2). The purge gas, consisting of methane, hydrogen, nitrogen, argon, and ammonia may be used directly as a fuel in the reformer or may be separated into its components by cryogenic and/or molecular sieve procedures for recycle to the process. As previously mentioned, in partial oxidation processes, the availability of liquid nitrogen wash generally makes deliberate purging unnecessary in that what little impurities do bleed through the nitrogen wash are dissolved and removed in the ammonia product (1).

In the past, the liquid product was stored at autogenous pressure and ambient temperature (i.e., 165 lb/in^2g and 90°F or 1.1 x 10^6 Pa and 32°C) in pressure storage vessels. Current practice is to use ammonia in a refrigeration unit

to chill the liquid product to about -28°F (-33°C), where its vapor pressure is essentially zero pounds per square inch gage, for storage at atmospheric pressure. Continuous bleed-off, recompression, and condensation of a small amount of the tank's vapor phase is required to ensure the low temperature storage stability (4).

Energy Requirements

Ammonia synthesis from hydrogen and nitrogen is an energy intensive process; however, most of the energy consumed is in the gas preparation (hydrogen) section.

As indicated in the Chemistry section, the theoretical energy required in the basic methane steam reforming process is 19.7 x 10^6 Btu per ton of synthetic liquid ammonia. This serves as a basis for determining the thermal efficiencies of all ammonia (hydrogen) processes. Comparative energy requirements for processes utilizing hydrogen produced from the various feedstocks are given in table 13.

It should be recognized that the above data are approximate and, in the cases of the hydrocarbon and coal processing, are relative to the present industry average. Many of the innovations (recent developments section) that permit significant reductions in energy consumption in gas and naphtha plants could be applied to the partial oxidation processes as well, thus also increasing their thermal efficiencies appreciably.

It should also be recognized that the significant increases in thermal efficiency of the gas reforming plants indicated above can be achieved only with a significant increase in capital investment of those plants for energy recovery systems.

Table 13. Comparative energy requirements for processes using hydrogen (2, 4, 7, 8)

Process (feedstock)	Energy consumption Btu/ton x 10^6	Thermal efficiency, %
Natural gas[a]	41.2	48
Natural gas[b]	29.0	68
Natural gas[c]	26.0	76
Naphtha[d]	43.2	46
Fuel oil[d]	45.9	43
Coal[d]		
Existing low pressure	45.0	44
Future high pressure	40.5	49
Electrolysis of water (plus air separation plant)		
Existing[e]	97.0	20
Potential[e]	38.0	52

[a]U.S. industry average, The Fertilizer Institute, 1979.
[b]New Canadian plant, Pullman-Kellogg design, 1981.
[c]Potential third generation design.
[d]Relative to footnote a, industry average.
[e]Based on practical 10,000 Btu per kWh.

Recent Developments in Technology

The drastically increasing costs of the various conventional feedstocks, naphtha, fuel oil, and natural gas, have spurred a vast amount of activity aimed at reducing the overall unit consumption of feedstock (energy) in ammonia synthesis. This activity has had two directions: (1) significant reduction in unit feedstock requirements, primarily for natural gas, and (2) the development of new partial oxidation technology for gasification of coal, an alternate abundant, lower cost feedstock in the United States and many other countries. Since either approach would require several volumes if detailed, only the basic technological principles will be listed here (6, 7, 9, 10, 11).

1. Potential improvements in gas/naphtha reforming technology.
   a. Combustion air preheat in reformer—common only in large plants erected in last few years. Retrofit will become common. Estimated savings, 0.7 x 10^6 Btu per ton.
   b. Process air and gas feed preheat—again, in use only in new plants. Estimated savings, 0.6 x 10^6 Btu per ton.
   c. Generation of superheated steam by heat exchange. Estimated savings, 1.0 x 10^6 Btu per ton.
   d. Use of physical absorbents in acid gas removal system; now in use only in newer plants. Estimated savings, about 2 to 4 x 10^6 Btu per ton.
   e. Fine-tune existing acid gas removal systems, using latest operating indices devised by developers. Estimated savings, about 2 x 10^6 Btu per ton.
   f. Substitute scrubbing for final syngas purification to minimize methanation losses, or selectively oxidize CO to CO_2 with a bleed stream of air from main air compressor. Estimated savings, 0.8 x 10^6 Btu per ton.
   g. Substitute improved centrifugal compressors for reciprocating compressors in 300-500 ton-per-day units. Possible savings, 1.0 x 10^6 Btu per ton.
   h. Substitute gas turbines for steam turbines as prime drivers. Estimated savings, 1.0 x 10^6 Btu per ton.
   i. Recover values (H_2 and CH_4) from purge gas by cryogenic, semipermeable membrane, or absorbent systems. Estimated savings, 0.5 x 10^6 Btu per ton.
   j. Redesign of synthesis converter to reduce pressure drop and increase level of indirect steam generation in converter. Estimated savings, 1.6 x 10^6 Btu per ton.

In addition to these individual unit process improvements, there are several somewhat radical departures

from conventional practices that can lead to significant energy savings. In one for which data are available, a portion of the fuel gas is used to power gas turbine-driven compressors, with turbine waste heat being used to preheat the gas feedstock and combustion and process air. The acid gas removal system is operated at up to 1,500 lb/in^{2}g (10.3 x 10^6 Pa) (vs conventional 500 lb/in^{2}g, 3.4 x 10^6 Pa) which results in very high purity syngas, low purge losses, and low acid gas sorbent regeneration energy. The process is reported to consume only 29 x 10^6 Btu per ton of ammonia and to have a lower capital investment than conventional plants (9).

Recently, an engineering design firm released some details of a design that incorporates many of the unit operations changes listed above and for which is claimed an energy consumption of only 26 million Btu per ton (10).

2. Potential improvements in partial oxidation technology.

It is obvious that some of the potential improvements listed above for the hydrocarbon reforming processes might be incorporated in the unit operations downstream of the gasification unit in the partial oxidation process. Many have been in existing partial oxidation processes, both with residual fuel oil and coal.

Out of the tremendous amount of literature that has been generated concerning the production of synthesis gas (H_2 + CO) from coal, the single most important fact emerging is that most research and development effort seems to have been directed toward medium- to high-pressure gasifier operation as opposed to numerous existing processes operating at near-atmospheric pressure (6). Although much of this work is aimed at fuel usage (low to intermediate Btu gas or pipeline quality gas by methanation), much consideration has been given to ammonia production as well.

In the latter case, coal gasification even at minimum ammonia synthesis pressures (2,000-2,500 lb/in^{2}g, 13.8-17.2 x 10^6 Pa) has been considered and may be attempted in second or third generation processes. Generally, however, most designs for ammonia production are limited to about the same pressure range of current reformer operation, i.e., about 500 lb/in^{2}g (3.4 x 10^6 Pa). In "synthetic" fuel processes, present mechanical and metallurgical considerations have limited most gasifier development to about 1,000 lb/in^{2}g (6.9 x 10^6 Pa) (6).

The energy saving to be gained by gasifier operation at elevated pressure is obvious. The energy of compression of only the small volume of combustion oxygen is a fraction of the energy of compression of the very large volume of departiculized raw synthesis gas as practiced in present technology. The trade-off for high-pressure operation is in the mechanical difficulties involved in injecting the coal feed and discharging the residual ash or slag. Generally this is accomplished through time-cycle feed and discharge lock hoppers. In at least one process, however, coal feed is in the form of a heavy aqueous slurry that is injected by high-pressure reciprocating pumps. The TVA gasifier is of this type and one troublesome lock-hopper operation is eliminated (6).

Gasification temperature has long been the subject of intense study. Low raw gas temperature (1,200°F, 649°C) requires less oxygen per unit of syngas, but produces a considerable amount of by-products (phenols, ammonia, methane, oils, and condensable organic vapors) that most syngas producers, particularly ammonia producers, prefer to avoid. As a result, nearly all second generation processes (as well as many first generation processes) operate at high gas temperatures (1,800°-2,600°F, 982°-1,427°C) so that only the principle syngas constituents, H_2 and CO (after acid gas removal), are produced (6). All other gases or vapors are cracked at this temperature. The trade-off is the somewhat higher oxygen requirement and the more severe effects on the gasifier components.

Another area of intense study has been in the determination of the effects of coal ash-formation, agglomeration and slagging characteristics on mechanical "ash" discharge and gasifier bed (either fixed, stirred, fluidized, or entrained) performance, on degree of coal conversion, and on overall thermal efficiencies (6). The effect on mechanical operation and therefore on plant reliability may be the overriding factor in gasification economics. While discussion of such a complex subject is beyond the scope of this text, it can be said that out of the many being studied, those few high-pressure gasification-process designs that can solve—and, in time will solve—the problem of mechanical reliability will certainly bring the cost of coal-based ammonia down to meet the rising cost of gas-based ammonia in the years ahead. It may be unfortunate that the recent concurrent surplus of world oil supplies and changes in national policies have seriously reduced activities in the general field of synthetic fuels from coal. It remains to be seen when operational reliability of some few designs can be established. TVA is continuing limited operation of the demonstration-scale Texaco entrained bed, water-quench gasifier system at Muscle Shoals, and is still pursuing requests for funding of a much larger unit for methanol production.

Some Department of Energy contractual work and some private sector work still continues. Also, at least

one company, Eastman Chemical Products, recently constructed a dual Texaco gasifier-based chemical complex in Kingsport, Tennessee (12). The unit has a capacity of up to 1,800 tons of coal per day. The plant is designed to produce acetic anhydride from captive CO and methanol and imported acetic acid. While NH_3 will not be produced, such a unit could produce up to 1,400 tons per day. However, in actual operation one gasifier will be on standby. No doubt, experience gained by the operation of TVA Texaco unit at Muscle Shoals was useful in the final design and operation of the Eastman units.

AMMONIA PRODUCTION ECONOMICS

In view of the widely varying factors influencing ammonia process economics, this discussion will be limited to estimated plant prices from new (1982) plants in an industrial area on the United States Gulf Coast for the gas- and oil-based plants and in proximity to a coal mining area for the coal-based plant (4, 6, 7, 11). The primary purpose of the data in table 14 is to give an estimate of the relative 1982 prices of ammonia as produced from the four basic feedstocks—natural gas, naphtha, fuel oil, and coal (present technology). It has been assumed that the necessary planning and the construction were begun on time to start up the plants in early 1982. The line item cost data in table 14 are given in sufficient detail to permit the reader to substitute different values that better suit his own situation.

The calculated prices have little relation to current United States or world market prices because of the depression of prices due to current overcapacity, the general slump in the economy, and the fact that many larger, older plants or plants with existing low-cost gas contracts (or subsidized gas as in some foreign areas) can, at the present time, produce and sell at much lower prices than can a new United States Gulf Coast plant. Further, it is naturally assumed in these estimates that the plant owners have erected the plants on the predication that their prices will become competitive in the near term, as the fertilizer demand increases.

While the absolute accuracy of the estimated prices is not great, especially for coal gasification, the relative prices should be reasonably accurate.

The display of two decimal places in the unit costs does not imply an accuracy of this order; it is merely reflective of computer programming. The data show that naphtha, which has greater value as a feedstock for more expensive petroleum products such as gasoline, obviously is priced out of competition for ammonia production. This has proven to be true in many world locations where natural gas is not available. This, then, leaves the partial oxidation processes as the alternatives. If, as predicted in many forecasts, the price of natural gas in the United States reaches $6-$7 per million Btu by 1985 because of continued scarcity and/or decontrol, it is probable that coal, which is likely to escalate far less rapidly, will become an economically viable alternative feedstock. James (11), however, predicts that natural gas will have to reach the $7-$10 per million Btu range before the economic viability of coal-based ammonia becomes a reality. On the other hand, if the second generation gasifiers become less costly, more reliable, and more efficient, as is believed by many, the break-even price of gas may fall in the lower range. Residual fuel oil would appear to be a likely candidate also, but its cost is projected to increase at least as rapidly as that of gas, so, again, coal emerges as the potential ammonia feedstock in the foreseeable future. Retrofit of coal handling and gasification systems to existing reforming synthesis plants should be given careful consideration, particularly for those located in coal mining areas or near navigable rivers whereby coal could be barged in cheaply.

WASTE DISPOSAL PROBLEMS

The natural gas and naphtha steam reforming processes present few problems in waste disposal. In fact, about the only requirement for efficient cleanup is in the condensate from the syngas cooler prior to the acid gas removal step. Small amounts of ammonia are formed in the reformers because of the elevated pressure at which they operate. This ammonia condenses, along with water, in the syngas cooler. It may be removed by steam stripping to allow recycle of the condensate to a waste-heat boiler. The stripped ammonia may be recovered in an aqua-ammonia product (1).

Some leakage occurs in all ammonia synthesis plants—leakage of syngas (CO, H_2, N_2), as well as ammonia, but adequate maintenance of compressor and valve packings can maintain this leakage at acceptable environmental levels.

The partial oxidation processes, particularly that of coal, present formidable, but controllable, total environmental pollution control problems—air, water, and land (solids). A significant portion of the capital investment is required to provide for the control of emissions of all types. The problems are complex and details are beyond the scope of this text. The following items are but brief descriptions of the salient areas of pollution control (1, 6).

Coal Receiving and Preparation

Fugitive dust and water runoff from handling stockpiles must be controlled. Dust can be controlled by sprinkling. Pile runoff water must be directed to holding pool, monitored for contaminants, and discharged or directed to the

Table 14. Estimated ammonia plant prices (1982) using four basic feedstocks

Plant capacities 1,150 ton/day or 380,000 ton/yr @ 330 days/year	Steam reforming				Partial oxidation			
	Natural gas		Naphtha		Residual fuel oil		Coal	
Plant investment (PI)	$ 95,750,000		$105,000,000		$120,150,000		$195,400,000	
Working capital (WC)[a]	12,400,000		26,700,000		10,800,000		11,780,000	
Total capital investment (TC)	108,150,000		131,700,000		130,950,000		207,180,000	
Feedstock costs, $/normal unit	3.60/SCF		322/ton		$168/ton		$30/ton	
$/MM Btu (LHV)	3.91		9.05		4.57		1.46	
Production costs	Units/ton	$/ton NH_3	Units/ton	$/ton NH_3	Units/ton	$/ton NH_3	Units/ton	$/ton NH_3
Direct								
Feedstock, MM Btu	16.0	62.56	16.9	152.95	26.9	122.94	33.1	48.33
Catalysts & chemicals, lb	1.0	1.60	1.0	1.70	1.0	0.90	1.0	0.90
Direct labor man-hr @ $13	0.16	2.09	0.16	2.09	0.20	2.64	0.41	5.39
Maintenance 3.5% PI	–	7.22	–	7.92	–	9.06	–	14.74
Supervision, 15% labor	–	0.31	–	0.31	–	0.40	–	0.81
Electricity, kWh @ 0.042	16	0.67	16	0.67	Internal	0	Internal	0
Cooling water, M-gal @ $0.14	2.4	0.35	2.5	0.36	2.7	0.38	3.8	0.54
Boiler feed water (makeup), M-gal @ $1.30	0.1	0.13	0.1	0.13	0.1	0.13	0.1	0.13
Fuel (same as feedstock), MM Btu	11.0	43.01	11.6	104.98	7.6	16.95	11.9	17.37
Analyses, 10% labor	–	0.21	–	0.21	–	0.26	–	0.54
Supplies, 20% maintenance	–	1.44	–	1.58	–	1.81	–	2.95
Plant overhead, 100% labor	–	2.09	–	2.09	–	2.64	–	5.39
Product loss, 2% above subtotal	–	2.43	–	5.50	–	3.16	–	1.94
Indirect								
Depreciation (15-year), 6.7% PI	–	16.59		18.20	–	20.82		33.85
Insurance & taxes, 2.5% PI	–	6.30		6.91	–	7.90		12.86
Interest on debt[b]	–	13.46		17.53	–	17.30		24.62
Return on investment, 25% PI	–	62.99		69.08		79.05		128.55
Credit (Sulfur where applicable)	–	0		0		-3.54		-7.80
Subtotal, plant price		223.45		392.52		282.81		291.10
General sales & administration		14.00		14.00		14.00		14.00
Ex-plant price		237.45		406.52		296.81		305.10

[a]Working capital = value of 30-day raw material supply + 2-month product inventory at production cost.
[b]Rate = 16% on one-half average capital investment over life of plant.

wastewater treatment plant, as necessary. If dry grinding is practiced, the entire pulverizer-dust transport system must be exhausted to fugitive dust recovery equipment for recycle.

Gasifier

The gasifier produces solid, aqueous, and gaseous contaminants. The latter are removed from the syngas stream in the gas purification system. The slag quench water and particulate removal scrub water are discharged from the gasification section. After settling, a portion is recycled to the section. The remainder is treated biologically and chemically in a large wastewater treatment plant so that the net water discharge from the plant battery limits meets all State and Federal pollution abatement requirements. The slag and quench water associated with it are transported to a slag-disposal area, the runoff from which must also be directed to the wastewater treatment plant if contaminated.

Gas Purification System

The gas purification system in a coal-based plant is much larger and more complex than that of a steam reforming plant. The water-scrubbed raw synthesis gas contains, in addition to H_2, CO_2 (about 3 times the amount in gas reforming), and CO, contaminants such as H_2S, COS, and NO_x from "high" temperature gasifier and additional methane, tars, phenols, oils, and ammonia from "low" temperature gasifiers. As a result, the gas purification system can include a COS catalytic hydrolysis converter (to H_2S); a complex condensate (tars, oils, phenols, ammonia, etc.) recovery and separation system; a multistage, preferential acid gas removal train, either after or before and after CO shift conversion, that removes sulfur compounds as well as some CO_2 for feed to a sulfur recovery system in the first stage; a second and possibly third stage that removes the remainder of the CO_2 and some sulfur, then further desulfurizes that CO_2 that is designated for urea production; and finally a liquid nitrogen wash that scrubs out all but a few parts per million of any residual contaminants in the synthesis gas. The net gaseous and liquid emissions from these complex systems must meet water standards for all of the condensables and air standards for H_2S and SO_2, CO, CH_4, and NO_x.

Synthesis Section

Once past the extremely complex purification systems above, pollution abatement is minor and entirely similar to that for reforming plants.

As one might suspect, the cost of the complex gas purification and pollution abatement systems mentioned briefly above is quite high. It approaches 50% of the total cost of the plant, excluding the condensables recovery system in a "low" temperature gasification train (6).

ANNUAL PRODUCTION OF ANHYDROUS AMMONIA

The fertilizer use of anhydrous ammonia is discussed in chapter 1 and later in this chapter. However, it should be mentioned that a significant proportion of the total anhydrous ammonia produced is consumed in industrial production of materials other than nitrogen fertilizers. Table 15 illustrates the growth of both usages, as well as plant capacity, since 1970 in the United States.

It will be noted first that production capacity reached a zenith in 1978 at 22 million tons per year, then declined about 1 million tons as older, less efficient plants were shut down. It is expected that this trend will continue for several years. Second, fertilizer usage has increased fairly steadily over the past 11 years (9 million to 15 million tons per year), while industrial usage has remained fairly constant over the years.

The fertilizer usage of ammonia is fairly well known. In addition to the use of about 40% of the total fertilizer ammonia applied directly to crops, the remainder is consumed in the production of well-known nitrogen fertilizers such as ammonium nitrate and urea, both as solids and liquids; some synthetic ammonium sulfate; and various ammonium phosphates, also as both solids and liquids.

The industrial uses of anhydrous ammonia are less well known. It is used in the production of over 80 inorganic compounds, some 400 organic amino or nitro compounds, and hundreds of indols, pyridines, quimolines, and nucleic compounds. It is used in tonnage quantities in such industrial fields as explosives, synthetic fibers and plastics, pulp paper, metallurgy, refrigeration, synthetic rubber, water treatment, detergents, textiles, and dyes, as well as supplemental nitrogen animal feeds (13).

World production capacity for anhydrous ammonia, excluding the United States, is estimated to be about 110 million tons per year (1981). Production is believed to be about 70% of capacity, or 77 million tons, of which about 65 million tons is used in agriculture (14).

Table 15. Anhydrous ammonia production and capacity in the U.S. (5)

Year	Plant capacity 10^6 tons/year	Annual production, millions short tons		
		Total	Fertilizer	Industrial
1970	16.9	13.8	9.1	4.7
1975	18.4	16.4	10.4	4.0
1978	22.0	16.9	12.1	4.8
1981	20.9	19.0	14.8	4.2

As indicated in the production and use sections, continued improvements in ammonia production and transportation facilities, such as ammonia pipeline systems, large regional atmospheric storage tanks, refrigerated barges and ships, and jumbo tank cars have made anhydrous ammonia the most economical source of nitrogen delivered to the farm.

There are now two long pipeline systems in the United States for transporting ammonia from the producing plants to the major consuming area. The Mid American Pipeline Company (MAPCO) system extends from northern Texas into Kansas, Nebraska, Minnesota, and terminates in Iowa. The Gulf Central Pipeline pumps ammonia from the Mississippi Valley area, extending through Louisiana, Arkansas, Missouri, Iowa, and Nebraska, with a branch line into Illinois and Indiana. The MAPCO pipeline is about 850 miles (1,367 km) in length and has a capacity above 1,300 tons per day. The Gulf Central Pipeline is about 2,000 miles (3,219 km) long and can pump over 3,000 tons per day. Anhydrous ammonia is transported through the pipelines as a liquid. Usually the ammonia going into a pipeline is warmed to the approximate soil temperature surrounding the pipeline buried 3 to 4 feet (1 meter) below the surface.

Branch pipelines terminate at facilities that store anhydrous ammonia in large atmospheric storage tanks with capacities ranging from 6,000 to 30,000 tons. Liquid ammonia in the pipeline is under pressure, and when the ammonia flows into a flash tank, the pressure is reduced to atmospheric. A portion of the ammonia evaporates and the negative heat of evaporation reduces the temperature of the liquid ammonia to near -33°F (-36.1°C) before it is pumped into atmospheric refrigerated storage at branch terminals. The ammonia vapor is liquified by compression then water cooled and returned into the flash tank. Similar systems for refrigerated ammonia storage are used on barges and on oceangoing ships (4). It is especially important that, with the advent of atmospheric ammonia storage, ammonia be heated prior to loading into transport equipment to avoid thermal shock, which can weaken the metal in the transport tank.

One railway tank car equipment company is experimenting with a tank car fabricated from metal that will resist thermal shock. However, test results with this tank car are not yet available. In addition to refrigerated storage terminals, facilities are available along the pipeline route to load the warm ammonia into trucks and railcars for shipment.

Most major nitrogen-consuming areas are reached by either pipeline or barge transportation. In addition, railcars are readily available that have pressure tanks for containing 24 to 73 tons of anhydrous ammonia. It is a practice to have "unit train" shipments of ammonia with as many as 100 cars shipped directly from the producing plants to the consuming area. Because of these excellent transportation facilities, it is possible to deliver anhydrous ammonia to dealers for retail sales at a relatively low cost.

ANHYDROUS AMMONIA RETAIL OPERATION

Usually most anhydrous ammonia retail dealers have pressure-type storage tanks varying in size from 12,000 gallons (45,425 l) to 50,000 gallons (189,270 l). Liquid ammonia is transferred from a railroad tank car or a truck transport tank into the dealer storage tank with an ammonia compressor or a positive displacement pump. The ammonia compressor is the most frequently used method. Transfer is accomplished by removing vapor from the vapor space in storage tank and pumping these vapors into the tank being unloaded. The removal of vapors from the storage tank reduces the temperature of the liquid ammonia at the liquid-vapor interface and, therefore, the pressure exerted by the liquid ammonia is reduced. The compressed ammonia vapors are heated by the compressor and the hot vapors are injected into the vapor space of the transporting tank. The vapor compressor has produced a pressure differential between the transporting tank and the storage tank which allows the liquid ammonia to be easily transferred from the transport tank into the storage tank. Reducing the vapor pressure of the ammonia vapor remaining in the transport tank to about 45 lb/in^{2}g (31 x 10^4 Pa), as discussed later, will result in a loss of only 0.5% by weight of the original ammonia load.

The vapor compressor or the liquid-ammonia pump used for transfer should be labeled for ammonia service. This assures that the pump working pressure and pump seals will be suitable. If a positive displacement pump is used for ammonia transfer, the pumping system can produce a high pressure and, therefore, the positive displacement pump must be equipped with a pressure regulated bypass valve and a discharge pipe to return liquid ammonia into the tank being emptied.

Railroad tank cars are equipped with dip tubes for liquid withdrawal and one vapor return line. The connection for fittings and the valves are located beneath the dome cover. These tank cars require a vapor transfer pump for unloading. Transport trucks with a bottom unloading valve can unload anhydrous ammonia using either the vapor transfer pump or a positive displacement pump. Some general information published in numerous articles concerning unloading anhydrous ammonia are as follows:

1. An adequate supply of clean water should be available, either as an emergency eyewash and shower or an open tank that a person can be submerged in.

2. Brakes should be set at the unloading rack and wheel chocks used to assure nonmovement of the transport tank.
3. The hose should be inspected for defects and any kink in the hose straightened. The hose subject to ammonia transfer pressure should be designed for a minimum working pressure of 350 lb/in^{2}g (241 x 10^4 Pa) and a minimum rupture pressure of 1,750 lb/in^{2}g (1,206 x 10^4 Pa). The hose assembly must be capable of withstanding a test pressure of 500 lb/in^{2}g (345 x 10^4 Pa).
4. The operator should wear a gas mask equipped with an ammonia canister, protective gloves, boots, and suit made of rubber or other materials impervious to anhydrous ammonia while making or breaking connections. The wearing of a gas mask should be considered necessary, especially when working on top of a railroad tank car.
5. The liquid ammonia valves should be opened slowly to check for leaks around the fittings, to assure that the bleed valves are closed, and to keep excess flow valves from closing.
6. The liquid valves should be opened completely and then the vapor line valve should be opened on the transport tank.
7. The valve at the compressor should be set so that vapors are pumped from storage into the transport tank. (Different procedures are followed if liquid pumps are used.)
8. The vapor valve on the storage tank should be opened slowly and the system pressure allowed to equalize and then the liquid valve opened slowly to fill the ammonia storage tank.
9. The compressor should be started and operated until the liquid transfer is complete as indicated by an inline flow indicator.
10. To remove vapor from the tank, the liquid valves should be closed and the vapor valve position reversed so that vapor is pumped from the transport tank. The vapor pressure in the tank should be reduced to about 45 lb/in^{2}g (31 x 10^4 Pa).

Truck transports that haul anhydrous ammonia are usually equipped for liquid unloading through valves in the bottom of the tank. The transport is usually unloaded using a positive displacement pump located at the storage terminal or a truck mounted pump powered by a take-off shaft.

The general unloading procedure is essentially the same as for unloading railcars. The terminals that handle anhydrous ammonia truck transports are usually adjacent to frequently traveled roadways and, for the safety of the operator and road traffic, the ammonia mask and other protective equipment should be worn while making connections and starting the ammonia flow so that corrective measures can be taken rapidly if connection leaks or hose rupture occurs during the initial transfer.

Additional procedures for transport truck unloading follow:

1. Connect the liquid hose between the storage and transport tank and then the vapor hose connection.
2. Open the liquid and vapor valves on the storage tank and the block valve upstream from the pressure bypass valve which is usually near, or built into, the pump. (Note: This valve should always remain open unless the pump is being serviced.)
3. Slowly open the liquid valve on the transport tank and read gauge pressures on the transport and storage tank.
   a. If the transport tank pressure is higher, allow the pressure to force the anhydrous ammonia into the storage tank.
   b. When the pressures are nearly equalized, open the vapor valve on the transport and start the transfer pump.
   c. If the pressure is higher in the storage tank than in the transport tank, open the vapor valve on the transport and allow the pressure to equalize before the transfer pump is started.
4. An inline flow indicator will help determine when the transport is empty. Some operators look for a flexing of the liquid unloading hose.

During the entire unloading procedure the operator should:

1. Continue to wear protective gear. The gas mask could be exchanged for tight-fitting goggles and a face shield.
2. Never leave the transfer operation unattended.
3. Never fill a tank to more than 85% of capacity.
4. Always open the bleed valve to relieve the pressure between the connection before disconnecting the hose.
5. Always use hose and fittings designed and approved for ammonia and never tamper with pressure relief valves or other fittings.

Loading Nurse Tanks

The general safety precautions listed for rail tank cars and transport trucks should be followed. On seeming level ground, unchocked nurse tanks have rolled from loading areas.

To fill a nurse tank using a compressor, the liquid hose from the storage tank should be connected to the liquid fill valve and the vapor hose connected and the valves opened so that vapors are removed from the nurse tank and pumped into the storage tank. The compressor continually reduces pressure in the nurse tank and the ammonia fills to the proper level.

If a liquid pump is used, the pump forces liquid ammonia into the nurse tank, and the vapors are vented through the vapor hose and returned into the storage tank.

Anhydrous ammonia should be transported, stored, and handled in accordance with Federal, State, and local regulations. For more detailed instructions see the "Agricultural Anhydrous Ammonia Operators Manual," The Fertilizer Institute's "Operational Safety Manual for Anhydrous Ammonia," and American National Standard Institute's "Safety Requirements for the Storage and Handling of Anhydrous Ammonia."

USE OF ANHYDROUS AMMONIA IN AGRICULTURE

HISTORY AND EVOLUTION

The use of anhydrous ammonia in agriculture began in California in 1932. In the 50 years that have elapsed, a tremendous effort has been invested in bringing ammonia to its present level of acceptance. Despite this acceptance, questions are frequently asked. "Why was anhydrous ammonia considered for use as a fertilizer when the popular solid nitrogen compound, ammonium sulfate, was readily available?" This question can be answered by briefly reviewing developments that demonstrated the feasibility of its use and the development of equipment and techniques for application.

To gain an understanding of the development of anhydrous ammonia for agricultural use it is necessary to look beyond 1932 to the mid-1920s. At that time commercial fertilizers were just beginning to be used in southern California and mechanical devices for their application were not well developed. In the citrus groves, particularly, sodium and calcium nitrate or ammonium sulfate were being used at 5 or more pounds per tree and in most cases were being spread by hand. This was a tedious and time-consuming operation.

In 1928 two brothers, Eugene and John Prizer (15), concerned with this labor problem on large citrus groves, built an applicator that would dissolve soluble fertilizers and introduced them into irrigation water. One of the principal products used at that time was ammonium sulfate produced by reacting ammonia with sulfuric acid. The price paid for the acid was extremely high, even during the depression period. In considering ways to reduce overall costs, Shell Chemical Company engineers proposed the direct use of ammonia gas to eliminate the need for the acid. It was thought that it might be possible to introduce ammonia into the water of irrigated areas in California. The water, being spread in the normal process of irrigation, would distribute the fertilizer uniformly over the field. The principal problem was thought to be one of proving whether water treated with ammonia would be acceptable for growing crops.

Dr. Ludwig Rosenstein, at that time chief chemist of Shell Chemical Company, approached Dr. D. R. Hoagland of the University of California to discuss the possibility of applying anhydrous ammonia in irrigation water. Dr. Hoagland seemed optimistic and suggested to Dr. Rosenstein that he contact Dr. D. D. Waynick at the Association Laboratory to undertake experimental work on such a project. Dr. Waynick had established the Association Laboratory at Anaheim, California, to offer citrus growers advice on irrigation, fertilization, and pest control. Dr. Rosenstein made the necessary arrangements with Dr. Waynick in 1932 to do experimental work on the use of anhydrous ammonia in irrigation water (15).

The first experimental applications of anhydrous ammonia were made on citrus groves in southern California. Although the experiments were designed to measure crop response to the fertilizer, they were also planned so that data on many facets of the application procedure could be collected. This early work showed that the concentration of ammonia in water was a critical factor in avoiding ammonia losses and having even distribution throughout the field. The length of irrigation run and the type of soil were found to be critical factors. While furrow irrigation was the normal procedure in citrus and row crop areas of California, there were many areas where flood or contour irrigation was practiced, particularly in the deciduous orchard areas of northern California, or on preplant irrigations for grain and cotton. Studies with flood irrigation revealed that ammonia distribution with this method of irrigation was also quite uniform. Concurrent with studies on distribution of ammonia, work was also carried out on depth of ammonia penetration into the soil immediately around the furrow. Numerous cross section studies were made of irrigation furrows where inch square samples were drawn from the bottom of the furrow downward as much as 12 in. (30.48 cm) and laterally to the center of the plant beds. These early workers also studied the effectiveness of various application times. Early experiments showed that the use of ammonia in sprinkler systems was unsatisfactory due to high ammonia losses.

These early studies by Drs. Rosenstein, Hoagland, and Waynick and other members of the University of California staff provided the basic information on which the early agricultural anhydrous ammonia industry was based.

One of the first applications of ammonia in a closed system was in early 1934 at the grove of R. M. Simon near Tustin, California. Results were highly undesirable. The water for this grove was extremely hard, very high in calcium and magnesium bicarbonate. The underground waterlines at this orchard were small, 10 in. (25.4 cm) or less in diameter. During the first run it was rediscovered that when ammonia is dissolved in hard water, calcium

carbonate is precipitated. This precipitate would adhere to the sides of the pipeline even in fast moving water and a 10-in. (25.4-cm) line could be plugged, or its carrying capacity drastically reduced over a short period of time.

Although the injection of ammonia into irrigation water was proven feasible in open systems, the sale of anhydrous ammonia expanded slowly during the depression years of the late 1930s. Early in 1939 it became apparent that if a big volume of sales was to be obtained it would be necessary to apply ammonia in places where irrigation was not practiced, or was not practiced at the time of fertilizer application. No one had begun work on the problems inherent in the injection of ammonia until equipment developed by a telephone company was observed laying underground cables in the Sacramento area. The equipment consisted of an oversized subsoiler with a tube down the back of the blade through which the lead sheathed cable was passed. The equipment suggested welding a tube down the back of an ordinary cultivator shank and releasing the ammonia at the depth to which the shank ran.

To test the practicality of such a device, ammonia metering equipment was installed on a killifer furrowing tool and a tube welded down the back of each shank. The first applicator, though crudely assembled, worked satisfactorily. Three hours after the first application, a cross section of the injection area was exposed and soil was removed in 1-in. cubes (2.54-cm) for analysis. Data showed that ammonia was retained in an area roughly 3 in. (7.66 cm) laterally from the point of ammonia release, downward about 2 in. (5.08 cm) and upward along the shank channel, almost 5 in. (12.7 cm). This type of equipment became standard for all early experimental work and the first commercial applications. After commercial applications were begun in 1942 and soils of all degrees of firmness were encountered, a more complete study was initiated on the effect of shank design on the ammonia absorption pattern. Concurrently with the early field studies, laboratory work was begun to study the chemical aspects of anhydrous ammonia injection. Ammonia was applied at various rates for pH and nitrification studies. This work showed that although the pH was initially elevated at the point of injection, it soon returned to normal or slightly below as nitrification began. Nitrification was comparable to that for solid forms of ammonium fertilizers. Experimental work showed that seed germination was inhibited and seedlings were killed if they were placed in close proximity to the point of injection. However, 3 to 4 in. (10.2 cm) away, all seeds germinated and seedlings grew normally, showing nitrogen stimulation soon after they emerged. These early laboratory and field studies also showed that growing plants could be successfully sidedressed with anhydrous ammonia provided that the shanks were run just at the edge of the rooting zone and from 6 to 8 in. (15.2 to 20.3 cm) deep (15). In 1943, Dr. W. B. Andrews, with the Mississippi Agricultural Experiment Station, began field trials with anhydrous ammonia for corn and cotton at many sites in Mississippi. This work, which was supported by the TVA, led to widespread adoption of the use of anhydrous ammonia in Mississippi, the South, and the Midwest (figure 16).

Concurrent with studies to investigate the effects of anhydrous ammonia on soil conditions and plant growth was development of the associated equipment needed for distribution and transport. Metering equipment, tanks, and transportation methods all evolved with increasing interest in anhydrous ammonia for agricultural uses. As the use of anhydrous ammonia spread from area to area, companies became interested in producing trailer-type applicators designed especially for injection. Frequently, the equipment took the form of a folding "wingup" design which allowed movement over highways from field to field without a special permit. Liquid phosphoric acid was made available to agriculture, and applicators were built to dual apply ammonia and phosphoric acid. Today refinements of these early handling and applications systems continue, and the interest in anhydrous ammonia for agricultural purposes continues to increase. Anhydrous ammonia currently represents the most economical form of nitrogen available to the farmer.

ROLE OF AMMONIA AS FERTILIZER

Principal factors that have made nitrogen the key element in world and U.S. fertilizer use are dramatic crop responses, changes in economics of production and distribution, and reasonably good availability of raw material.

Before the advent of synthetic ammonia, sources of nitrogen were few and relatively expensive. The major commercial materials consisted of guano, Chilean nitrate of soda, by-product ammonia, and other sources. These materials were seldom located in areas of consumption; thus handling and transportation increased the cost to the point where the farmer could afford to use very little nitrogen.

The development of the synthetic ammonia industry changed this economic picture. Ammonia was converted to new end products and new methods of handling these materials were developed. Improved ammonia production technology led to cheaper products, and these changes led to an improved competitive relationship between nitrogen and other plant nutrients. The preeminence of nitrogen among the plant nutrients is due to its production at a great number of geographic locations in the world. Nitrogen for ammonia production is readily and cheaply available from air. In the earlier technology of synthetic ammonia production, feedstocks to supply the required hydrogen were limited to refinery and coke oven gas. In the past 30 years,

however, equipment has been designed to produce synthetic ammonia from a number of hydrogen sources. Raw materials now available for synthetic ammonia production include the following: natural gas, crude oil, coal, lignite, naphtha, and electrolytic hydrogen (see production section, this chapter). In recent years, supplies of natural gas and naphtha have become limited and more costly, leading to efforts to develop the technology for the production of ammonia from coal and lignite. These efforts have only been moderately successful thus far, but the development is continuing in an effort to make these products more economically competitive as sources of hydrogen.

Over the past 30 years, there have been many changes in the types of nitrogen fertilizers produced. Specific trends in nitrogen use are shown in table 16. In 1950, approximately equal amounts of N were used in fertilizer mixtures and for direct application but since that time nearly three times as much nitrogen was used in direct application as in mixtures (figure 17).

The major factor leading to the rapid increase in direct application of nitrogen has been the availability of large amounts of nitrogen solutions and anhydrous ammonia plus convenient methods of using these materials in cropping systems. The economics of production and

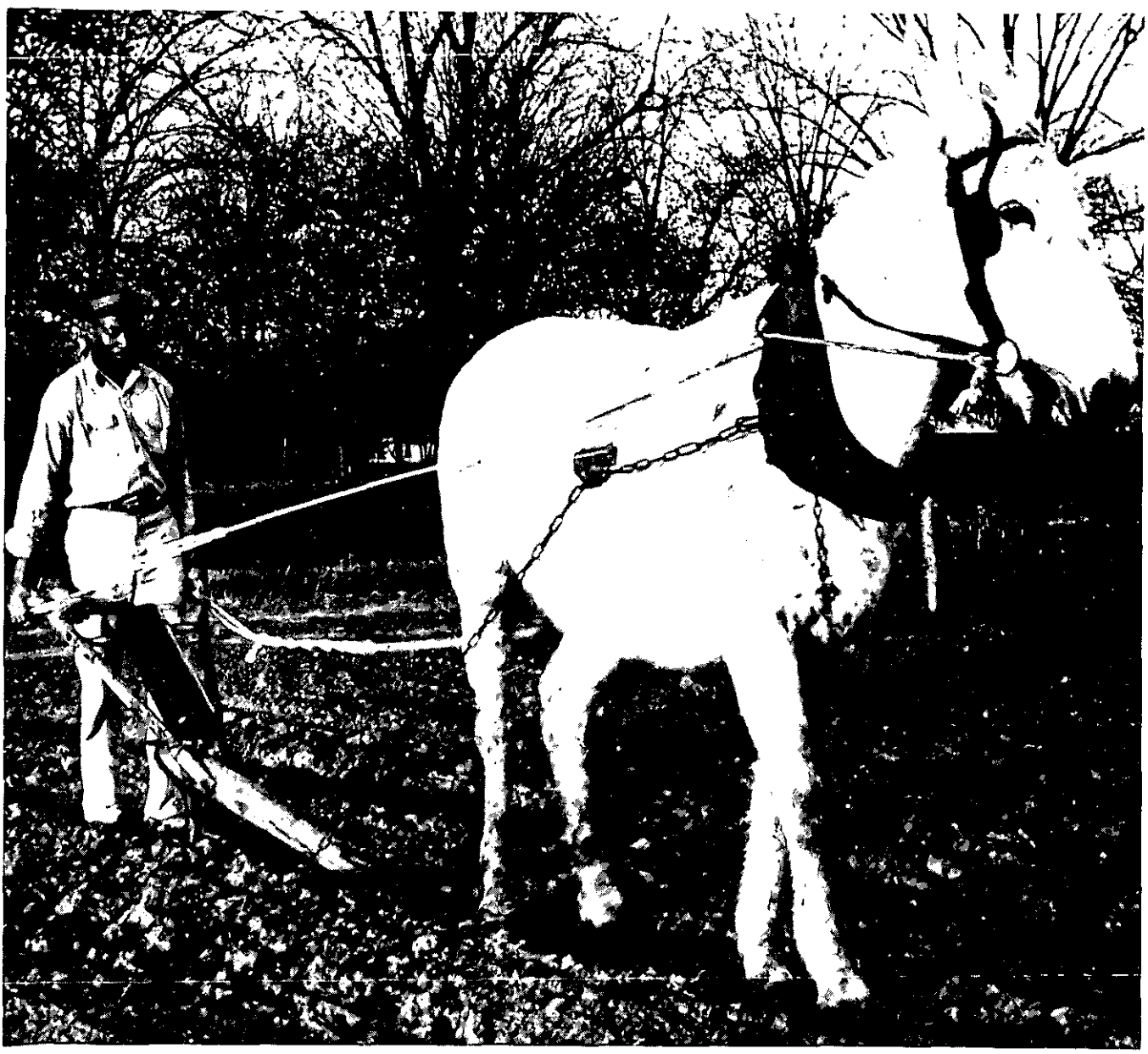

Figure 16. This photo shows how anhydrous ammonia was first used at the Mississippi Delta Branch Experiment Station

distribution favor the use of these intermediate products rather than the higher cost solid and liquid NPK products which require further processing to produce. Figure 18 shows the extent to which the intermediate products have gained favor in the nitrogen marketplace. The economics of production, distribution, and application of liquids and ammonia so highly favor this system it can be expected to increase in relative importance in the future.

APPLYING AMMONIA

Certain characteristics of ammonia make it a popular fertilizer and also one that must be handled and applied with considerable care to avoid hazards inherent in the product and to maximize crop yields. Anhydrous ammonia has a boiling point of -28°F (-33.3°C), and nonrefrigerated storage requires high pressure vessels. At 100°F (37.8°C), the product exhibits a gauge pressure of 197.2 lb/in^2 (135.9 x 10^4 Pa). The product's popularity is due to its high analysis, 82% nitrogen, and the fact that it represents the lowest cost source of nitrogen for the U.S. farmer. One reason for this economic advantage is that the product can be used directly and requires no additional chemical processing which may add to the cost. The second reason is the excellent facilities for transporting and storage of liquid ammonia. Ammonia is readily transported by truck, rail, and barge and now two ammonia pipeline systems exist for transportation from producing areas to major consuming areas in the Midwest. Many large atmospheric storage tanks have been constructed ranging from 5,500 to 45,000 tons in capacity. These tanks are refrigerated at atmospheric pressure by using the ammonia as a refrigerant to maintain it in liquid state at -28°F (-33.3°C) or slightly below.

Injecting Ammonia

Anhydrous ammonia is injected into the soil through tubes mounted on the back of knives or tines at which point liquid ammonia immediately changes to gas. To prevent loss of the gas into the atmosphere, faulty applicator equipment or incomplete closure of the injection channel must be avoided. Figures 19-21 illustrate various

Table 16. Consumption of selected nitrogen direct application materials—United States

Fiscal year	Anhydrous ammonia	Aqua ammonia	Nitrogen solutions	Ammonium nitrate	Urea	Ammonium sulfate
			(short tons of nitrogen)			
1960	581,924	85,380	194,740	415,855	64,596	106,959
1961	666,234	86,489	292,566	446,585	92,448	115,715
1962	767,425	99,783	371,379	468,523	132,804	116,687
1963	1,006,762	116,448	471,392	499,378	165,198	147,121
1964	1,148,071	157,531	526,755	555,320	184,327	148,865
1965	1,281,968	163,933	595,859	547,488	193,713	161,848
1966	1,606,872	200,814	712,445	610,705	211,615	165,797
1967	1,973,596	177,175	784,392	710,503	227,952	174,834
1968	2,457,261	163,047	803,092	786,346	243,359	167,306
1969	2,576,431	143,715	839,925	863,792	264,755	157,042
1970	2,844,058	143,778	969,882	952,861	242,758	160,911
1971	3,254,160	151,321	1,036,498	969,091	273,607	185,386
1972	2,982,274	150,165	1,009,119	1,015,548	357,386	192,205
1973	2,700,704	130,416	1,144,407	1,095,651	432,420	197,088
1974	3,427,672	148,071	1,184,507	1,061,743	467,934	193,025
1975	3,294,794	140,497	1,191,691	941,881	524,183	170,614
1976	4,025,258	146,180	1,620,308	985,555	729,250	219,760
1977	4,040,328	132,204	1,685,028	936,863	855,344	220,226
1978	3,721,289	115,500	1,591,935	820,356	880,753	188,208
1979	4,003,845	98,563	1,723,860	841,272	967,040	157,846
1980	4,499,947	133,219	1,908,917	884,718	946,359	175,566
1981	4,610,005	146,474	2,047,464	986,630	980,054	197,937

Source: USDA, Commercial Fertilizers, Statistical Reporting Service, annual reports.

types of knives and equipment which can be used for the application.

Proper closure of the channel requires the right amount of soil moisture. Overly wet soil does not fill the knife opening properly and water may actually compete with ammonia for adsorption sites on colloidal surfaces. Very dry soil can retain large amounts of ammonia as long as the soil tilth allows sealing of the knife opening. Cloddy soils also present problems in closure.

Depth of placement in most soils ranges from 6 to 9 in. (15.2-22.9 cm) but sandy soils require deeper placement because of their low ammonia retention capacity. Spacing between channels is usually 12-18 in. (30.5-45.7 cm) depending upon the crop. Wider spacings often result in uneven growth.

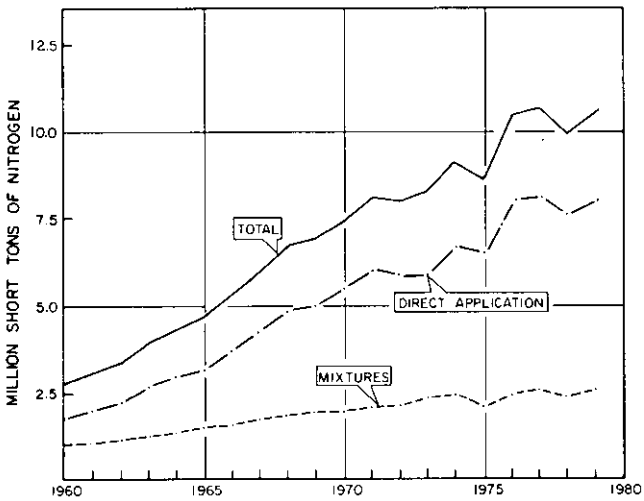

Figure 17. Nitrogen fertilizer consumption (16)

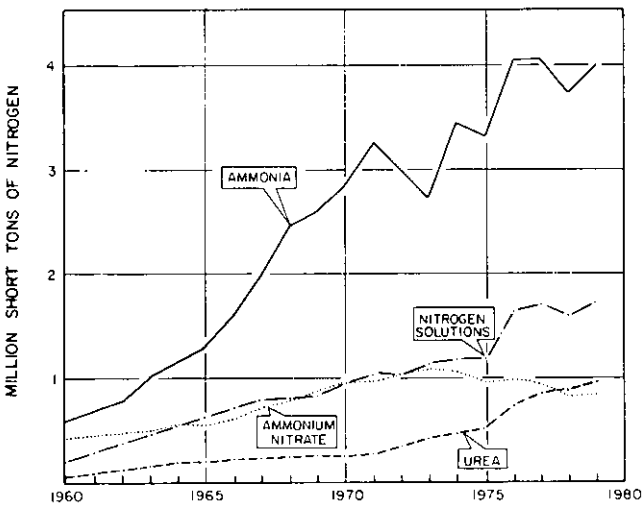

Figure 18. Consumption of nitrogen fertilizer materials (16)

Figure 22 (17) illustrates the effect of soil moisture content and spacing of applicator outlets on ammonia retention in soil. An increase in the moisture content had a pronounced effect on lowering the gaseous loss of ammonia. A point of practical significance is the reduced loss that accompanied the narrower applicator spacing when the same rate of ammonia was applied. Greater losses at wider spacing undoubtedly resulted from greater localized concentration at the point of injection.

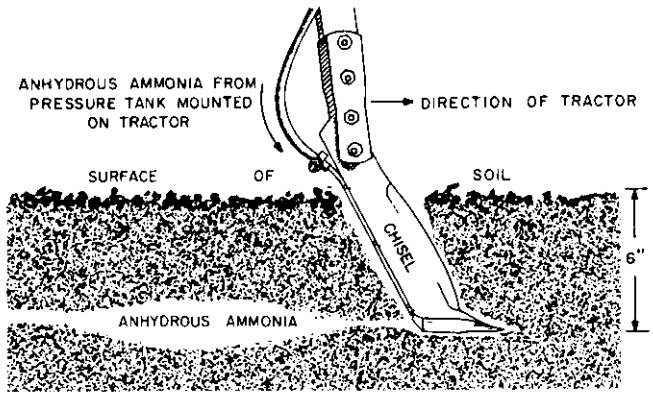

Figure 19. Front swept knife for ammonia application

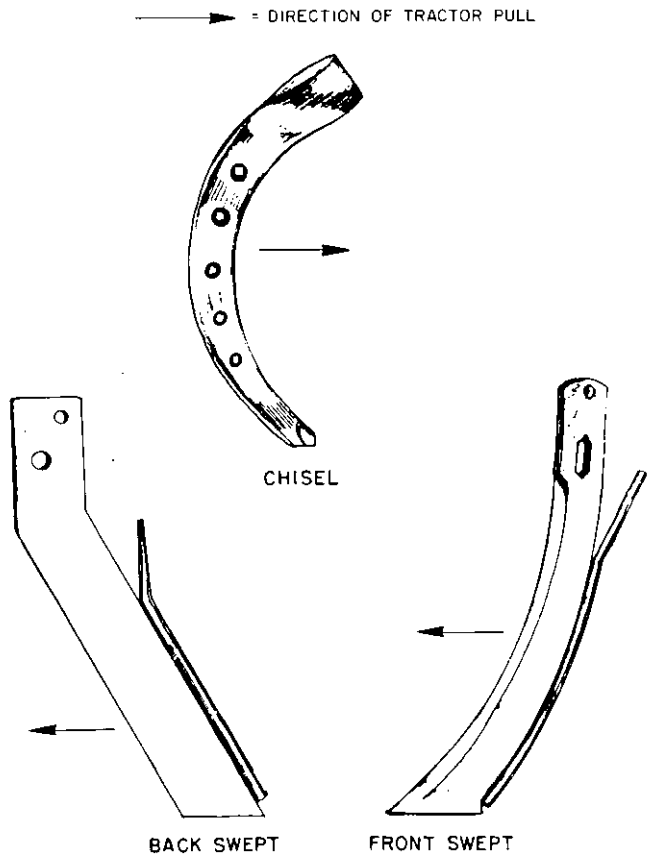

Figure 20. Various type knives for ammonia application

Initially the ammonia is retained in a localized zone about 1 to 3 in. (2.5-7.6 cm) in diameter around the point of injection. The concentration in this limited zone usually is such that the ammonia is toxic to micro-organisms and sterilizes the soil to the point where no nitrates form except around the fringes of the zone. The ammonia or ammonium ions gradually move to less concentrated areas and rapidly change to the nitrate form. A more complete discussion of the factors involved in the retention of ammonia in the soil and the interactions with chemical constituents of the soil follows later in the chapter.

A possible disadvantage to the use of anhydrous ammonia is the power requirement necessary to place the material in the soil at a depth where losses are avoided. The increase in popularity of nitrogen solutions and aqua ammonia is partially due to the application of these materials at shallower depths, thus reducing energy requirements and fuel costs. There has been an effort to decrease application costs of ammonia through the use of large tractors so that an applicator with wider swath widths can be used. This increases the number of acres that can be treated in a day which results in lower labor and equipment costs per acre of applied nitrogen. Another way to decrease application costs is to use equipment that applies ammonia during other tillage operations. Figure 23 shows a sketch of a V-blade used in wheat growing areas where anhydrous ammonia is applied during tillage operations which follow wheat harvest. It is the practice in those areas to pass the V-blade about 3 to 4 in. (10.2 cm) beneath the soil. This helps to kill weeds, tills the soil, and leaves a protective stubble mulch on the surface to prevent wind and water erosion. Usually 50 to 80 lb/acre (56 to 90 kg/ha) of ammonia can be applied without noticeable losses of ammonia.

Application of Ammonia in Irrigation Water

Application of plant nutrients through irrigation water has several possible advantages. Among them are (1) nutrients may be applied when crop or soil conditions would pro-

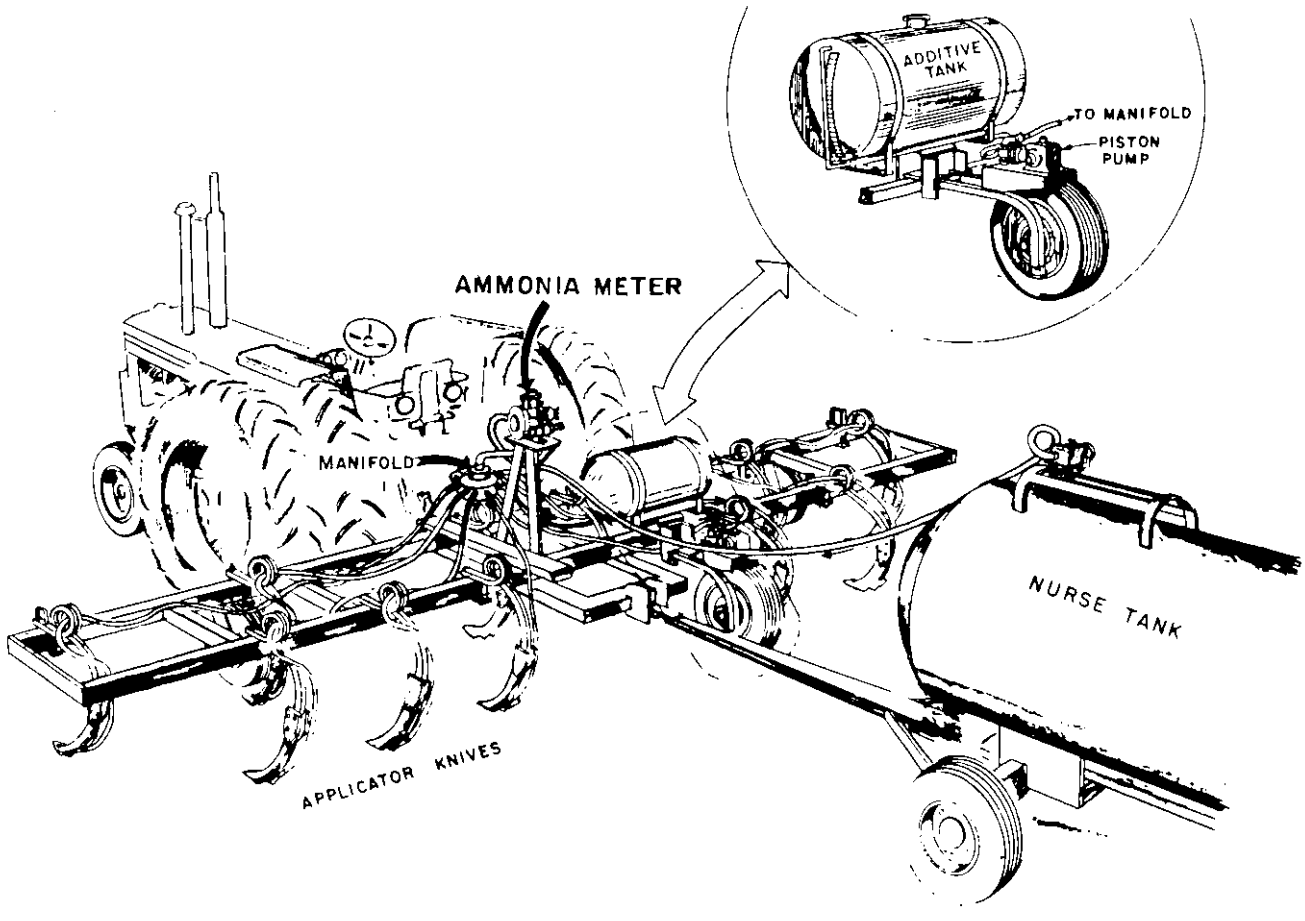

Figure 21. Tractor drawn ammonia application equipment

hibit fertilization by other conventional means, (2) nutrient supply can be regulated to coincide with nutrient demand by the growing crop, (3) less labor and equipment are required for application, and (4) soil compaction by heavy application equipment is eliminated. Like any practice, the application of ammonia in irrigation water has some limitations which must be recognized in adapting it to practical operations.

The objective must be to place the N where the crop can make use of it efficiently. The ultimate measure of success will be crop response when ammonia application in irrigation water is combined with other practices in a complete crop production program and is evaluated against alternate choices. Discussion that follows considers several important factors that must be monitored closely if the application of ammonia through irrigation water is to be successful and incorporated into other cultural practices.

Volatilization–Chapman (18) found the concentration of ammonia added to irrigation waters could decrease as much as 50% between the head and the lower end of the furrow. This decrease may be due to fixation of the ammonia by the soil or volatilization; however, the latter is believed to be the larger factor. The quantity of anhydrous ammonia in water should not exceed 110 ppm and in some highly alkaline water should not exceed 40-50 ppm. It is recommended that ammonia be applied in irrigation water when air temperatures are 40°F (10°C) or less. Ammonia losses by volatilization are usually negligible up to 72°F (22.2°C). Studies show that very significant losses can and do occur at temperatures over 100°F (37.8°C) unless the concentration of ammonia is kept low (40 to 50 ppm). Due to the high vapor pressure of ammonia it should not be used in sprinkler systems.

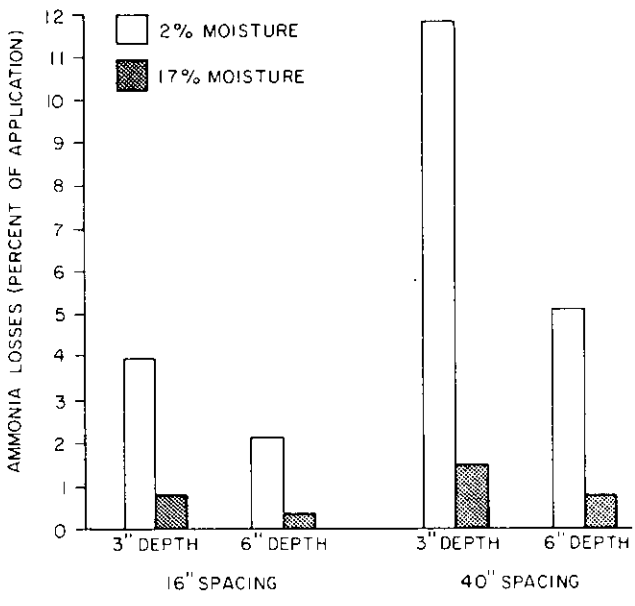

Figure 22. Effect of soil moisture content and applicator spacing on ammonia retention in the soil

Distribution–Where furrow or flood irrigation is practiced, more water percolates into the soil at the head of the furrow or flood basin than at the tail. Likewise, more ammonia would be expected to be absorbed at the head of the run. To offset this, ammonia is sometimes withheld during the first part of the irrigation period, thus avoiding part of the accumulation at the head of the furrow or basin.

Soil textures, slop of land, crops to be grown, and many other factors help determine the length of water runs. The shorter the run the more uniform the ammonia application although it may be more economical from a labor standpoint to run water 1/4 mile (0.4 km) or further. More efficient use of ammonia will result by limiting runs to 1/8 mile (0.2 km) or less. Extremely long runs, which require a long time to apply water, increase the effects of deep and irregular wetting (especially on coarse, porous soils). Since ammonia is adsorbed by soil surfaces, losses by leaching on medium and heavy textured soil are not significant.

Placement–Because ammonia is held in the top 2 or 3 in. (5.1 to 7.6 cm) of soil when applied in irrigation water, it is essentially a surface placement. For row crops, the surface placement may result in N being placed above the major root zone and perhaps in soil that is too dry for efficient root feeding during at least part of the period between irrigations. Between irrigations, much of the ammonia may be converted to nitrate which would move into the root zone with the next irrigation. In this case, any delay in N reaching the crop could be avoided by applying ammonia one irrigation earlier.

Surface placement of ammonia may also stimulate weed growth, thus contributing to the problems of weed control.

Carbonate Precipitate–Many waters used for irrigation contain large amounts of dissolved calcium and sometimes

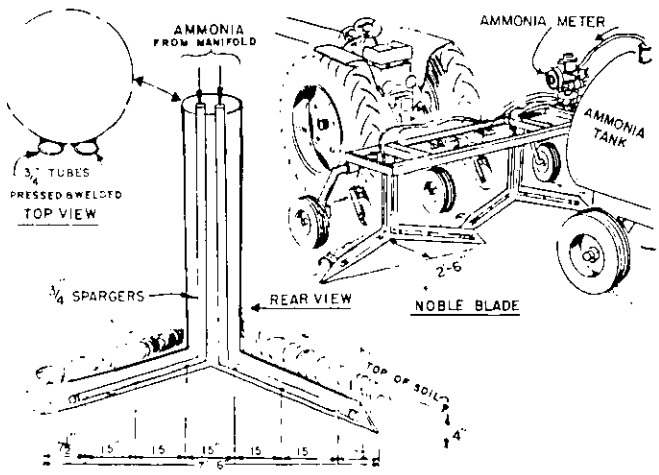

Figure 23. V-blade ammonia applicator

magnesium. When ammonia is added to these waters the pH is increased, bicarbonate is converted to carbonate, and a precipitate of calcium carbonate forms. In closed systems, this precipitate can cause serious problems—clogging lines, valves, gates, siphons, etc. When water is carried in an open ditch this deposit is evident as a white precipitate. Loss of dissolved calcium also can have a deleterious effect on water quality if the water contains significant levels of sodium. Sodium compounds which are more soluble than calcium compounds at high pH levels remain in the water. This results in a higher sodium to calcium ratio in irrigation water which reduces percolation rates and restricts downward movement of the water and dissolved ammonia.

In certain areas of the Southwest, sulfuric acid is available to growers and can be used to acidulate the irrigation water prior to incorporation of ammonia. The result is a lowering of pH, thus eliminating the precipitation of calcium carbonate from the water. Sodium buildup in the soil is reduced and infiltration rates are improved since calcium remains in the irrigation water.

Obviously the use of anhydrous ammonia in irrigation water has several important advantages. However, use of this practice must be tempered with caution based on a complete knowledge of how ammonia reacts with water and soil, if its maximum effectiveness is to be obtained. The agronomic effectiveness of ammonia applied in water appears to be equal to other forms of soluble nitrogen when precautions are taken as outlined above.

Cotton growers in irrigated areas have found water run ammonia is an effective means of supplementing the nitrogen supply during the growing season. The data in table 17 from Hopkins (19) show a slight delay in nitrogen uptake from ammonia compared to a nitrogen solution containing 68% of the N as nitrate. This delay in uptake may suggest the need for modifying the timing of ammonia application, but should present no problem where N content of the petioles is being monitored and need can be anticipated a few days in advance. This method of fertilization permits growers to apply fertilizer to a crop which is at the stage where entering the field with mechanical devices for fertilization may be impossible.

Table 17. Nitrate-nitrogen content of cotton petioles after N applied in irrigation water (19)

Days after application	NO_3-N in petioles, N source		
	Untreated	CAN[a]	NH_3
		ppm	
0	750	800	750
1	400	1,150	480
3	400	1,100	500
6	500	1,000	800
11	500	1,000	1,000
15	500	900	1,100
22	400	900	1,050
30	250	780	900

[a]Calcium-ammonium nitrate solution containing 11.6% NO_3-N and 5.4% NH_4-N.

AMMONIA RETENTION AND ADSORPTION IN SOILS

Following NH_3 injection, essentially all the ammonia is retained by the soil unless improper application techniques are used. High NH_3 concentrations and high pH may be found within the retention zone. Immediately after ammonia application, concentrations ranging from 1,000 to 2,500 ppm N have been reported to occur in a horizontal, cylindrically shaped zone with a diameter of 1.2 to 2.4 in. (3 to 6 cm) (17). Concentrations approaching 1,000 ppm may persist in this zone for a period of several weeks. Through gaseous diffusion and diffusion in solution, the NH_3 distributes radially outwards from the line of injection. According to available data, the ultimate diameter of the localized zone generally does not exceed 3.9 to 4.7 in. (10 to 12 cm) with knife application. This means that at usual field application rates and with a knife spacing of 39.4 in. (100 cm), a maximum of 20% of the plow layer will be influenced by NH_3 (20, 21). Distribution patterns may be considerably different with other implements such as a V-blade (22).

The volume of the retention zone mainly depends on the rate of NH_3 application, row spacing, moisture content, buffering capacity, texture, and nitrification capacity of the soil. The initial distribution pattern is controlled to a large extent by the moisture content of the soil because NH_3 is highly soluble in water and NH_3 diffuses slowly in the aqueous phase as compared to the gaseous phase. Soil moisture functions largely as a temporary repository of NH_3 from which it is subject to slow movement by mass flow with water or by gaseous diffusion away from the zone of high NH_3 concentration (23). The ammonia gas immediately following injection is converted to ammonium hydroxide and ammonium ions which in turn are absorbed by the soil clays and organic matter.

Under field conditions, soil moisture content may have an indirect effect on the soil's capacity to retain applied ammonia by affecting sealing of the injection channel (23). Hanawalt reported that a high enough moisture level was more important in this respect than a high cation exchange capacity (CEC), exchange acidity, and clay and organic matter contents (24).

In a study using 76 soil samples from 20 different soil profiles of the Pacific Northwest, Young concluded that

total NH_3 retention could be described by the following relationship (25).

ppm NH_3-N = 147 + 596 (% organic C) + 43.4 (% clay)

The equation indicates the importance of the organic fraction on NH_3 retention by soils. The highly pH dependent CEC of soil organic matter was largely responsible for this property.

Nitrogen applied to soil as anhydrous NH_3 is subject to adsorption by the organic and mineral fractions of the soil and may be dissolved in soil water. When applied to moist soil and at proper depth, sorption is nearly complete and rather limited movement occurs at the point of placement.

A number of physical and chemical reactions are responsible for NH_3 retention. They range from weak physical sorption by H-bonding to irreversible incorporation of NH_3 into soil organic matter. Physically adsorbed NH_3 is in a dynamic equilibrium with the gaseous phase and is subject to movement by diffusion. Physical absorption only occurs when there is a positive pressure of NH_3 in the soil atmosphere. As soon as NH_3 pressure decreases, equilibrium is shifted and some of the physically adsorbed NH_3 returns to the gaseous phase.

The chemisorbed NH_3 is strongly bound to specific adsorption sites on soil colloids and little migration will occur within the soil. The basic mechanism for chemical binding of NH_3 consists of acquisition of a proton by the NH_3 to form NH_4^+, which is subsequently bound to exchange sites on clay and humus particles. Ammonia may also react irreversibly with organic matter with formation of various NH_3-organic matter complexes. These complexes are characterized by high chemical stability and high resistance to microbial decomposition.

The size and kind of minerals in soils affect the amount of ammonia which may be adsorbed. Generally, the amount of adsorption is proportional to the surface area of the adsorbent, thus a sandy soil has a lower specific surface (surface area per unit weight) than a clay soil and its capacity for adsorption of ammonia is consequently lower. A general observation has been that losses of ammonia after application of anhydrous ammonia are more likely on sandy than on heavy soil. Even in sandy soils the clay fraction is usually the most important mineral portion with respect to adsorbing properties. A relatively small percentage of clay may completely dominate the chemical and physical properties of a sandy soil. In addition to the amount of clay, the kind of clay present is a major factor affecting adsorption. Clay minerals such as kaolinite have only external surface on the order of 2.4×10^4 to 4.9×10^4 ft^2/lb (5 to 10 m^2/g), while expanding clay minerals such as montmorillonite and vermiculite have internal surface as well as total surface areas of the order of 3.9×10^6 ft^2/lb (800 m^2/g). The expanding clay minerals thus have a greater capacity for ammonia adsorption than those with only external surface area.

Mechanisms of Ammonia Absorption on Minerals

The reaction which results in the greatest stability of ammonia on mineral surfaces is its conversion to the ammonium form. The formation of the NH_4^+ proceeds when NH_3 reacts with protons (H^+). Thus an acid soil or minerals having exchangeable hydrogen ions on the CEC may provide the necessary protons for NH_4^+ formation.

$$H^+ (clay^-) + NH_3 \rightarrow NH_4^+ (clay^-)$$

These exchangeable hydrogen ions are associated with negative charges within the clay lattice arising from isomorphous substitution of trivalent aluminum for tetravalent silicon in the tetrahedral layers and divalent ions such as MG^{2+} and FE^{2+} for Al^{3+} in the octahedral layers of 2:1 type clay minerals. The ammonia may react also with protons arising from hydroxyl groups associated with silicon on the edges of clay minerals or in amorphous material in the soil.

While in the ammonium form, the N cannot be lost to the atmosphere nor can it be easily leached out of the soil by water. The ammonium form (NH_4^+) has a positive electrical charge and is thus attracted by the negative electrical charge on soil mineral surfaces. It enters into ordinary cation exchange reactions in the same manner as metal cations on the exchange complex such as K, Ca, and Mg. Exchangeable NH_4^+ is available for plant utilization or microbial nitrification. Thus this reaction converts a toxic gaseous compound into a nontoxic relatively immobile nutrient.

In addition to ammonium formation, another adsorption mechanism plays a role in NH_4^+ retention in the soil. This reaction involves coordination between ammonia and exchangeable metal ions on the mineral surfaces, and has a lower energy of reaction than that of NH_4^+ formation (26, 27). The NH_3 molecule has a pair of unshared electrons on the N atom which may be shared with ions capable of accepting these electrons. The resulting bond is called a coordinate bond of "ion-dipole" interaction. The adsorption of ammonia on the cations in the soil system is analogous to the hydration of these ions by water. In fact, the very similar molecules, ammonia and water, compete for coordination positions (28, 29).

The NH_4^+ ion will enter into ion exchange reactions with other cations and be displaced into the soil solution. Under equilibrium conditions, a certain portion of the ammonium ion will exist on the CEC of the soil and a smaller portion in the solution phase depending on the total amount of NH_4^+ ion present, the kind and amount of associated exchangeable cations in the system, and the nature of the mineral providing the cation exchange sites.

Ammonium is very similar to the potassium ion in its chemical reactions, being of similar size and valence; thus its chemical behavior in soils is quite similar (30). When NH_4^+ is on the surface of soil minerals, it is considered to be easily available for either uptake by plants as the NH_4^+ ion or for nitrification by soil micro-organisms. If vermiculite type minerals are present in the soil, it is possible that NH_4^+ may move from a position on the external surface of the mineral to internal exchange sites where it may be rendered relatively unavailable for immediate plant uptake or nitrification (31, 32).

Ammonia-Organic Matter Interactions

Numerous factors affect the relative importance of organic matter and clay in retaining ammonia in soil. Organic matter can play an equal or greater role than clay in stabilizing ammonia in the soil, depending upon the type of soil under consideration.

The immediate effect of injecting anhydrous ammonia into the soil is to create an alkaline reaction in the retention zone. The high alkalinity and the associated high concentration of ammonia cause partial sterilization of the soil including drastic reduction in the number of nitrifying organisms. Nitrification of injected ammonia commences at the periphery of the retention zone and proceeds toward the center. Because *Nitrobacter* which oxidizes nitrite to nitrate is more sensitive to high pH and high ammonia concentration than *Nitrosomonus* which converts ammonium to nitrite, there can be an appreciable accumulation of nitrite; the nitrite may subsequently react chemically with the soil organic fraction to form stable organic nitrogen complexes and nitrogen gases.

The relative importance of inorganic and organic soil components in retaining ammonia depends on the nature of the soil, but in general the organic fraction is more reactive on a weight basis. Mortland (33) investigated the adsorption of ammonia by dry clays and muck and found both H-muck and Ca-muck adsorbed more ammonia than did the clays. Sohn and Peech (34) found that organic soils fixed considerably more ammonia than mineral soils; for the mineral soils, the quantity of ammonia fixed was highest for acid soils containing large amounts of organic matter. The results of Sohn and Peech (34) indicated that at least 50% of the ammonia fixed in their experiment was due to reaction of ammonia with soil organic matter. Burge and Broadbent (35) measured fixation of anhydrous ammonia by dry samples of organic soil ranging from 14% to 43% carbon and found that the quantity of ammonia fixed was linearly related to carbon content. They calculated that under aerobic conditions, 1 molecule of ammonia was fixed for every 29 carbon atoms.

Organic matter in soils exhibits cation retention capacities which are high in relation to those of mineral soils, although it is now established (36) that the ability of these materials to retain monovalent cations is somewhat lower than for polyvalent ones. Ammonia reacts with carboxyl and possibly other acidic groups present in the organic fraction to form salts which might be termed "ammonium humates." In the immediate vicinity of the ammonia injection band, all such groupings are probably saturated with ammonium ions.

At the present time, several plausible mechanisms have been proposed for ammonia fixation reaction by organic matter. These are based on the fact that ammonia fixation proceeds most favorably at high pH values and that autoxidation occurs simultaneously. Mattson and Koutler-Andersson (37) suggest that fixation takes place in the lignin-derived fraction of soil organic matter. The presence of aromatic rings with two or more hydroxyl groups was believed essential. They postulated the formation of amino phenols, which, upon oxidation to more reactive quinone-imino compounds could then form stable condensation products with N incorporated in heterocyclic rings.

The important question with respect to the ammonium fixed in soil organic matter is whether it is available to plants. Research on this subject indicates that the availability is relatively low. In a greenhouse experiment with soil containing fixed ammonia which was tagged, Burge and Broadbent (35) observed that, in one cutting of sudangrass, 4.3% of ammonia was utilized as compared with 1.14% of the untagged native soil N. In the second cutting, only 1.31% of the remaining tagged N was taken up by the plants. This suggests that the availability of at least part of the fixed ammonia may be somewhat better than that of indigenous soil N but less than that of mature crop residues.

In summary it appears that the availability of anhydrous ammonia to plants and the degree to which losses occur by volatilization depend to a considerable extent on the chemical reactions between ammonia and soil organic matter. The relative importance of organic and inorganic soil components in retaining ammonia depends on the nature of the soil, but the organic fraction is more reactive on a weight basis than is the inorganic fraction. Laboratory investigations indicate that as much as one-fourth of the anhydrous ammonia added to soil may be fixed by lignin and lignin-like substances. Ammoniacal N from sources other than anhydrous ammonia is subject to the same fixation processes.

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Chapter 6

Liquid (Solution) Fertilizers

By Frank P. Achorn and Lawrence C. Faulkner

The term "liquid fertilizer" used in this chapter refers to solution type fertilizers such as aqua ammonia, nonpressure nitrogen solutions, and liquid-mixed fertilizers in which all of the plant nutrients are in solution. About 7 million tons of nonpressure nitrogen solutions and about 3 million tons of liquid-mixed fertilizers were used in 1982 for direct application in the United States. Use of nitrogen solutions is growing at an average rate of about 10% per year and liquid mixtures at a rate of about 3% per year. Reasons for the popularity of solution type fertilizers are:

1. They are easy to transport and handle and usually can be applied at a much faster rate than solid fertilizers.
2. They can be applied more uniformly than solids.
3. They are excellent carriers of pesticides, which sometimes can be added at the farm. Because solution fertilizer-pesticide mixtures can be applied uniformly, excellent pest control can be obtained, and one pass across the field can be eliminated.
4. Unless solubility is exceeded, solutions are excellent carriers of micronutrients; it is possible to accurately place the small amount of required micronutrient at the desired location with efficient fertilizer application.
5. Solutions in most instances have a manufacturing and application cost about the same as solid mixtures.
6. Solutions are especially well adapted to new and special types of application such as application through drip irrigation or sprinkler type irrigation units.
7. Solutions are excellent for accurate placement in the row at locations where they can be used efficiently.

Solutions were originally produced from merchant-grade furnace orthophosphoric acid which contained 54% P_2O_5 and no polyphosphate. A major problem in producing solution mixtures was that plant nutrient concentration had to be relatively low. For example, an 8-24-0 was the popular grade normally produced from merchant-grade furnace orthophosphoric acid. Later the furnace acid process was developed for the production of superphosphoric acid that contained between 75% and 80% P_2O_5 and had a polyphosphate content between 40% and 85%. With the higher polyphosphate content furnace phosphoric acid, it was possible to produce an 11-37-0 liquid grade (figure 24).

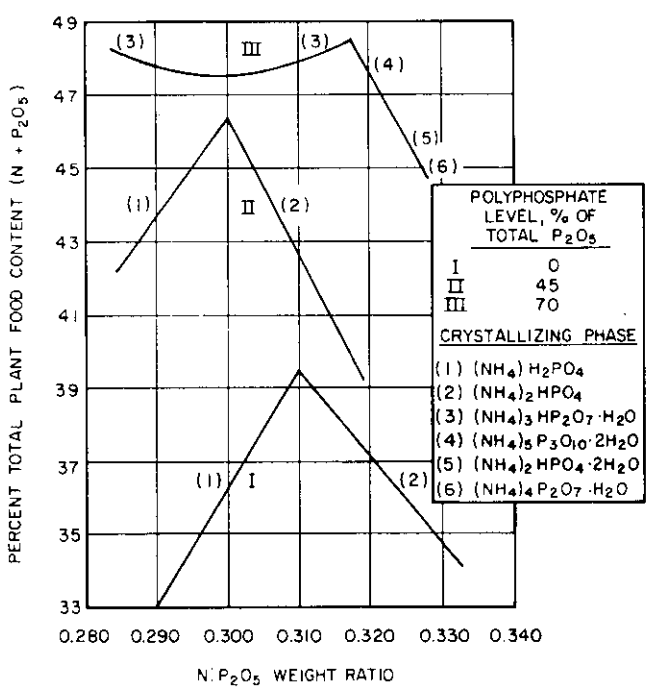

Figure 24. Effect of polyphosphate level and N:P_2O_5 weight ratio on solubility of ammoniated phosphoric acids at 32°F

Also it was possible to dissolve significantly larger quantities of micronutrients in the 11-37-0 ammonium polyphosphate solution. In the late 1960s and early 1970s, it became impractical from the standpoint of cost to produce fertilizers from furnace phosphoric acid for general agriculture. Somewhat earlier TVA had developed a process for the production of superphosphoric acid from wet-process phosphoric acid (1, 2) and at that time also developed processes for the use of wet-process superphosphoric acid to produce 10-34-0 or 11-37-0 liquid fertilizers (3, 4).

Processes for the production of the ammonium polyphosphate solutions from wet-process superphosphoric acid will be described later in this chapter. Although many of the problems encountered with the use of solution type fertilizers have been solved, there continue to be some problems which require additional work. Some are:

1. It is impossible to produce high analysis potash content in solution-type mixtures from usual raw materials.
2. In some instances, it is impossible to dissolve the desired amount of micronutrients in the solution (Fe, Mn, etc.).

The solution type fertilizer business is well established and now represents about 60% of the fluid mixtures consumed in the United States.

AQUA AMMONIA

Aqua ammonia is not nearly as popular in the United States as anhydrous ammonia; but, it is safer to use. Because of the safety factor, it is a more practical material for use in developing countries.

The most popular aqua ammonia solution contains 20% N and exerts no significant vapor pressure at temperatures below 97°F (36°C). Therefore, aqua ammonia of this concentration is stored in covered nonpressure storage tanks usually built to withstand 5 lb/in^{2}g (3.5×10^4 Pa) and equipped with pressure and vacuum safety valves. These valves are set to open at 1.051 and 0.991 times absolute atmospheric pressure.

Aqua ammonia usually is produced in a plant in which anhydrous ammonia, water, and recycled cool aqua ammonia are mixed continuously in a simple pipe mixing chamber. Enough water is added to adjust the specific gravity of the liquid to that of aqua ammonia containing 20% nitrogen or other desired concentrations. A 50-ton tank car of anhydrous ammonia can be converted to 206 tons of aqua ammonia in 5 to 8 hours depending upon the plant's cooling capacity.

Because aqua ammonia has a low vapor pressure, it does not need to be injected as deeply into the soil as does anhydrous ammonia. Most operators have found they do not have excessive ammonia losses if they inject the aqua ammonia about 3 to 5 in. (8 to 13 cm) beneath the surface. Applicators used for applying aqua ammonia are similar to those for anhydrous ammonia because they have injection knives. Since these knives penetrate about one-half the depth of anhydrous ammonia knives, much less power and energy is required to pull them. Also, aqua ammonia can be applied at a much faster rate. It can be applied during such field operations as plowing and disking without high ammonia loss.

Some companies apply aqua or anhydrous ammonia through ditch irrigation systems. This is done at very low concentrations and during early spring when the temperature of irrigation water is low. Enough ammonia is added to produce a slight ammonia odor in the irrigation water. Possibly this technique may help developing countries with application.

LIQUID SOLUTION FERTILIZERS

Nitrogen

One of the most popular liquid materials for direct application in the United States is nonpressure nitrogen solution (28-0-0 to 32-0-0). Use of these solutions is increasing faster than is anhydrous ammonia. During 1982 about 7 million tons of these solutions was used in the United States. The most frequently mentioned reasons for the increased popularity of nitrogen solutions are usually the same as for liquid mixtures. In addition to the advantages mentioned for liquid mixtures, the reasons most dealers and farmers prefer to handle these solutions instead of anhydrous ammonia are:

1. Nitrogen solutions are safer to handle, store, transport, and apply.
2. Storage and transport equipment costs are less for nonpressure nitrogen solutions.
3. Application speed is much higher for nonpressure nitrogen solutions which results in lower application costs.

Nitrogen solutions usually are produced from urea, ammonium nitrate, and water. They contain a corrosion inhibitor and can be stored and used in mild steel (carbon steel) equipment. Solutions sold in the United States have three concentrations: 28%, 30%, and 32% N. Their salt-out temperatures vary directly with their plant nutrient concentrations. Some of the physical and chemical characteristics of the three nonpressure solutions are shown in table 18. The inhibiting agent most often used in these solutions is a small quantity of anhydrous ammonia; usually about 10 lb of ammonia/ton (5 kg of NH_3/ton) of product is added to adjust the pH of the solution to 7.5. Another effective inhibiting agent is ammonium phosphate. Only a small quantity of ammonium phosphate (0.05% to 0.2%

P_2O_5) is required to inhibit the solution. This phosphate material reacts with the mild steel tank to form a corrosion inhibiting iron phosphate film.

Nonpressure Nitrogen Production

Two types of production processes are used—batch and continuous. Both are fairly simple; in each process concentrated urea and ammonium nitrate solutions are measured, mixed, and then cooled. In the batch process, solutions are weighed in a mix tank and the corrosion inhibitor is weighed separately and added to the mix tank. Finished product is cooled after it is mixed. The continuous process is similar except the urea solution, ammonium nitrate solution, water, and corrosion inhibitor are metered and fed continuously to a mixing chamber similar to the simple baffled mixer shown in figure 25. Material from the mixing chamber is cooled and pumped to storage.

Table 18. Physical and chemical characteristics of three nonpressure solutions (5)

Grade, % N	28	30	32
Composition, % by weight			
Ammonium nitrate	40.1	42.2	44.3
Urea	30.0	32.7	35.4
Water	29.9	25.1	20.3
Specific gravity, 60°F (16°C)	1.283	1.303	1.32
Salt-out temperature, °F (°C)	-1 (-18)	+14 (-10)	28 (-2)

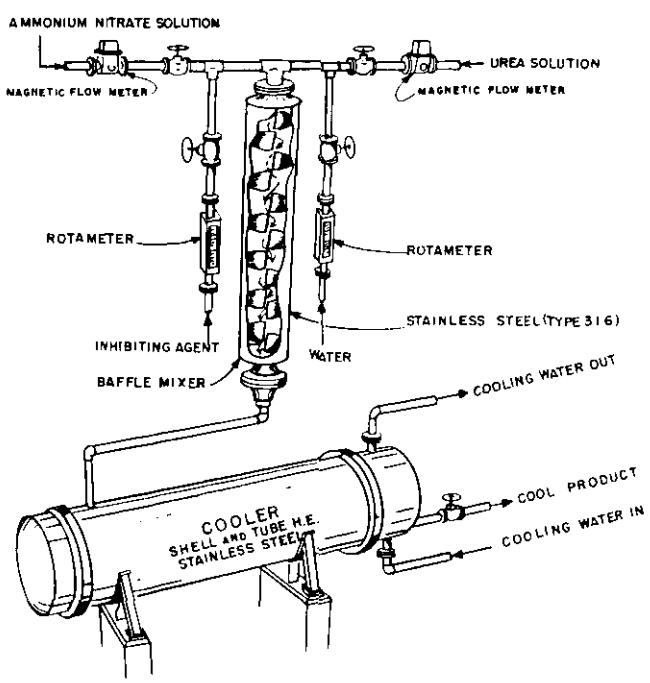

Figure 25. TVA continuous urea-ammonium nitrate solution plant

Recently in the United States there has been some interest in producing nitrogen solution from prilled urea and ammonium nitrate. When using a batch mix tank to produce solution from these solid materials, hot water is required to speed dissolution of the materials. Usually enough heat is supplied so that all solids will be dissolved at the end of the 30-minute mixing time. About 50 lb/ton (25 kg/ton) of saturated steam is required for a reasonable mixing time. This process is more expensive than the solution process; however, special pricing policies can make it desirable to produce a solution from solid materials. Also, it may be practical to use this procedure in some developing countries where solid materials are available.

Recently, one ammonia pipeline company, which also has a river terminal close to the pipeline, decided that it was economical to produce hot ammonium nitrate solution from ammonia at the pipeline and mix it with prilled urea received by barge. A similar procedure may be advisable for countries receiving anhydrous ammonia and prilled urea by ship. At the point of delivery, anhydrous ammonia could be converted to nitric acid and then to hot ammonium nitrate solution. This ammonium nitrate solution could then be mixed with the prilled urea to produce the nonpressure urea-ammonium nitrate solution.

Solution Fertilizer Mixtures

As mentioned earlier, the use of orthophosphate base solution (8-24-0 from furnace phosphoric acid) is practically nonexistent at the present time. This is because the cost of producing the solutions from furnace-grade phosphoric acid is too high as compared to producing them from the more economical wet-process orthophosphoric acid. In addition to these disadvantages, previous experience shows that mixtures produced from orthophosphate base solutions usually contain considerably less plant nutrient than those produced from ammonium polyphosphate solutions.

There still remains a slight amount of furnace superphosphoric acid (76% P_2O_5 and 50% polyphosphate) used in the fluid fertilizer industry. However, most of this is used to produce specialty type fertilizers by mixing the furnace phosphoric acid with potassium hydroxide, ammonia, and urea solution. When this is done, mixing is usually accomplished in a batch mix tank that is equipped with an aqua or anhydrous ammonia sparger. Material is passed from this tank to a pipe-type heat exchanger. Cooling is accomplished by passing water across the tubes and liquid through the tubes.

Most of the solution mixtures are produced by regional fertilizer plants which use wet-process superphosphoric acid and the new TVA pipe reactor process to produce ammonium polyphosphate base solution of grade 10-34-0 or 11-37-0 (3).

The superphosphoric acid is produced by concentrating merchant-grade orthophosphoric acid (54% P_2O_5) to superphosphoric acid in a vacuum or atmospheric concentrator. The superphosphoric acid usually contains about 68% to 70% total P_2O_5 of which 20% to 35% is present as polyphosphate. Physical and chemical characteristics of a typical superphosphoric acid are shown in the following tabulation:

Chemical analysis, % by weight	
Total P_2O_5	70.0
Polyphosphate, % of total P_2O_5	30.0
Sulfate (SO_4)	3.8
Aluminum (Al_2O_3)	1.1
Iron (Fe_2O_3)	1.0
Magnesium (MgO)	0.4
Fluorine (F)	0.27
Solids (insol. in CH_3OH)	0.15
Solids (insol. in H_2O)	0.01
Specific gravity, 75°F (24°C)	1.96
Viscosity, centipoises, 126°F (52°C)	400

Nearly all the polyphosphoric acid in wet-process superphosphoric acid is in pyrophosphate form; the remaining P_2O_5 is present as orthophosphoric acid. Conversion to superphosphoric acid increases the cost, but long shipping distances generate freight savings that reduce or eliminate this disadvantage.

More than 130 U.S. plants use the TVA pipe reactor process to produce an estimated 1.5 million tons of 10-34-0 or 11-37-0 grade product per year. Other countries such as Belgium, France, and the USSR also use this TVA process to produce an ammonium polyphosphate solution. Two typical plants are shown in figure 26. The plant on the left has a combination mix tank-cooler design. The upper part of the tank consists of a section filled with plastic "Pall Ring" packing. Liquid is recirculated to this section while air is drawn through the section to partially cool the liquid. Liquid from the bottom of the tank is passed through a heat exchanger where it is further cooled before being pumped to storage. Anhydrous ammonia is passed through this same heat exchanger, vaporized, then passed into the tee section of the pipe reactor. Superphosphoric acid is pumped by a positive displacement pump to this same tee section, where the acid and gaseous ammonia react to form a hot melt at 600°F (316°C). Usually some ammonia is added to the recirculation line to adjust the pH of the liquid to 6 for production of the 10-34-0 grade. The water content is controlled by adding water to the recirculation line.

The plant on the right uses a separate mix tank and an evaporative cooler. The mix tank is used for mixing hot melt from the pipe reactor with recirculating liquid. By having a separate mix tank it is possible to maintain a high liquid temperature (180°F [82°C]), which enhances mixing of the melt in the liquid and also provides an excellent means of evaporating and superheating the anhydrous ammonia used in the pipe reactor. Data indicate that plants with the separate mix tank usually produce an ammonium polyphosphate liquid of slightly higher polyphosphate content than those with the combination mix tank-cooler. Probably one reason this occurs is because of the high temperature of the ammonia used in the pipe reactor. Ammonia not added to the pipe reactor is usually added as liquid ammonia to the mix tank. Usually about 60% of the ammonia is added to the pipe reactor and 40% to the mix tank. This tank is equipped with a small scrubber in which cooled 10-34-0 grade product is used to scrub exit gases from the mix tank.

Both plants have efficient, inexpensive evaporative coolers. Very few contaminants are lost from either of the plants. There is a considerable loss of water as steam and water vapor.

Physical and chemical characteristics of a typical ammonium polyphosphate solution of grade 10-34-0 made by this process are tabulated below:

Chemical analysis, % by weight	
Nitrogen	10
P_2O_5	34
Polyphosphate, % of total P_2O_5	65-70
Viscosity, centipoises, 80°F (27°C)	75
Specific gravity, 80°F (27°C)	1.400
Salt-out temperature, °F (°C)	<32 (<0)

A considerable amount of the 10-34-0 grade solution is used for direct application in the Wheat Belt and other areas in which potassium is not deficient. Most of the ammonium polyphosphate solutions of grade 10-34-0 or 11-37-0 are used in small mix plants to produce NPK mixtures. A typical plant is shown in figure 27. Ammonium polyphosphate solution is mixed with nitrogen solutions containing 28% to 32% N (urea-ammonium nitrate solutions) and sometimes also potash to produce such clear liquid grades as 7-21-7, 8-8-8, and 21-7-0.

Sometimes the liquid mix plant produces a potash base solution such as a 2-6-12 or 4-11-11 grade and transports it to a satellite station where it is mixed with nitrogen solution and 10-34-0 grade ammonium polyphosphate solution to produce NPK mixtures. At the satellite station each liquid is metered and mixed in the farmer's nurse tank.

Urea-Phosphate Route

Production of satisfactory liquid fertilizers from wet-process acid normally requires the use of superphosphoric acid, with ammoniation in a pipe reactor, to ensure a polyphosphate level sufficient to sequester the impurities. Even with this procedure, however, results often are less than

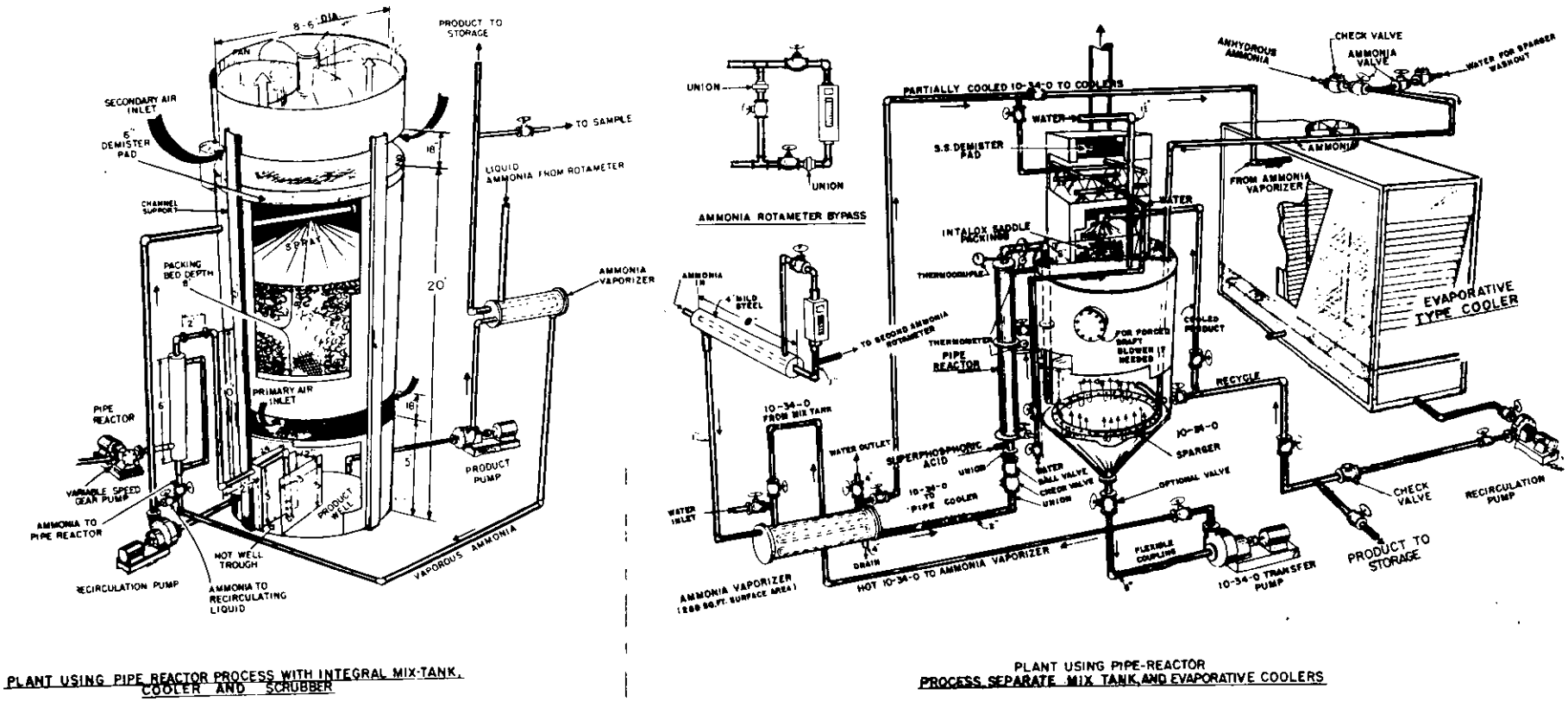

Figure 26. Typical pipe-reactor plants for production of ammonium polyphosphate solution

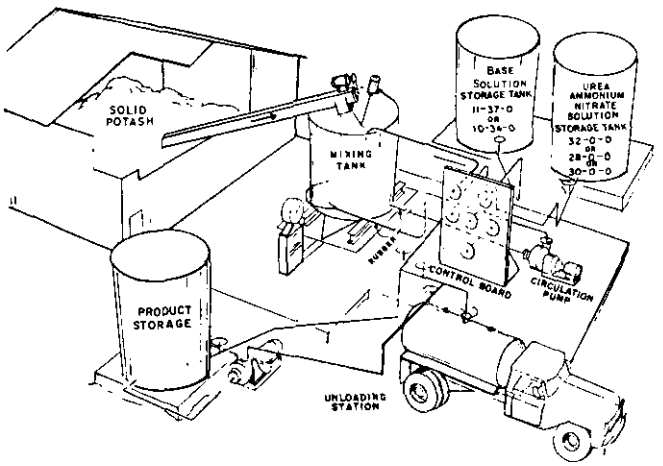

Figure 27. Liquid fertilizer mix plant

desirable. For example, if the superphosphoric acid is derived from black acid, the product liquid will be black unless specially clarified. Also, if the starting acid has relatively high impurity content, the product liquid will have limited storage stability. In view of these problems, TVA has for several years been investigating methods for either partially purifying wet-process acid or using other methods to produce satisfactory liquids from impure acid. One of these methods consists of using crystalline urea phosphate [$(NH_2)_2CO{\cdot}H_3PO_4$] as an intermediate.

In the first part of the process, the crystalline urea phosphate intermediate is produced from merchant-grade (54% P_2O_5) wet-process phosphoric acid and urea in a two-stage crystallization process. The crystalline urea phosphate is of 17-44-0 grade and contains only 15% to 20% of the objectionable impurities (iron, aluminum, magnesium, and fluorine) originally contained in the feed wet-process acid. Most of the impurities leave the process in a by-product side stream of mother liquor that can be utilized satisfactorily for other purposes, such as production of solid or suspension fertilizers. About 20% of the phosphate feed accompanies the impurities in this by-product stream.

In the second part of the process, the crystalline urea phosphate is melted at 210°F (99°C) in one reactor by a combination of direct ammoniation and external steam heat. The melt then overflows to a second reactor which operates at about 300°F (149°C) using external steam heat for conversion of orthophosphate to polyphosphate to produce about 50% polyphosphate level melt. This melt is then dissolved in water and ammoniated to a pH of 6.2 to produce a 50% polyphosphate light amber-colored liquid of 14-29-0 analysis.

Potential uses of the 14-29-0 base solution include its use in three-component liquids. Examples of these three-component liquids that do not salt out down to 32°F (0°C) are 7-14-7, 5-10-10, and 10-20-5. These grades are made by the addition of KCl and water. The 8-8-8 grade is made by the addition of KCl, water, and urea ammonium nitrate solution.

Micronutrients in Solutions

The need for micronutrients in the United States is increasing and the reasons for this increase are:

1. Most cropped land is managed more intensively.
2. The shift to high-analysis fertilizers has reduced the amount of micronutrients formerly applied as impurities in low-analysis fertilizers.
3. Better methods for identification of deficiencies are now available.
4. New crop varieties have a higher nutrient requirement.

Deficiencies of one or more micronutrients are reported in most States. In some areas, there is little or no immediate need for the application of micronutrients, but in other areas yields of some crops are substantially reduced without the addition of micronutrients.

Correction of micronutrient deficiencies is made by soil or foliar applications. Soil applications of inorganic iron sources are usually ineffective; one or more foliar spray applications may be required for severe iron chlorosis in certain crops. Boron, copper, zinc, manganese, and molybdenum are usually applied to the soil. However, molybdenum is required in such small quantities that it is often dusted on seeds. A survey conducted by TVA field representatives who have fertilizer development programs in 41 States indicates that most of the micronutrients now being used are applied with a starter or broadcast fertilizer.

Since only small amounts of each micronutrient are usually required, their application together with primary nutrient fertilizers is one of the most practical methods for applying micronutrients to crops. It is difficult to obtain the uniform distribution and application of a relatively small quantity of a required micronutrient by means of a solid fertilizer mixture. On the other hand, the application of micronutrients with fluid fertilizers appears to be the most convenient method of uniformly applying small quantities of micronutrients over a large area. TVA has been conducting research to determine the reactions of various micronutrient sources and evaluate their agronomic effectiveness. Some sources form insoluble reaction products which are unavailable to plants. Other micronutrient sources may cause caking of dry fertilizers, or they will not dissolve in liquid fertilizers. While certain sources of micronutrients may be applied with solids or fluids to result in products of good physical properties, these sources may not be effective for plant growth. Tests have been conducted at

TVA and other institutions to determine which combinations are agronomically effective. Results of these tests have been published and reprints are available (6, 7, 8, 9, 10, 11, 12).

Questions that often arise concerning the addition of micronutrients to fluid fertilizers are:

1. What are some of the sources of micronutrients?
2. How much of each micronutrient can be added to liquids without crystals forming?
3. What mixing procedure should be used in dissolving the micronutrient into the fluid mixture?

Sources of Micronutrients

Table 19 shows some of the inorganic sources of micronutrients that are now available. It shows the micronutrient content as percentage by weight of the element in each source.

Table 20 is a tabulation of some of the chelated micronutrient sources. The industry was surveyed and a list was made of the chelated sources available; however, these sources have increased in number and at such a rapid rate that some of the newer sources of chelated micronutrients may have been missed. The cost of the micronutrient element in most chelates is several times more than the cost of the element in the inorganic sources. However, most manufacturers of the chelates report that those sources are about 5 to 10 times more effective than the inorganic sources. University personnel have reported that chelated micronutrients are as much as five times more effective than inorganic sources of micronutrients (13, 14, 15, 16).

The solubility of the inorganic sources of micronutrients in clear liquid fertilizers varies considerably. Boron as borax is soluble in large enough quantities in liquid mixed fertilizer to meet most agronomic needs. However, only a small quantity of copper and manganese can be dissolved in orthophosphate solutions. Larger quantities of micronutrients can be dissolved in ammonium polyphosphate solutions such as 11-37-0 and 10-34-0 than can be dissolved in orthophosphate solutions such as 8-24-0. Laboratory tests were made to determine the approximate amounts of micronutrient materials that can be dissolved at room temperature in 11-37-0 made from electric-furnace phosphoric acid (17, 18). For comparison, similar tests were made with 8-24-0 base solution produced from orthophosphoric acid. The amounts of micronutrients that dissolved after 24 hours of agitation (laboratory wrist-type shaker) are shown in table 21. Also shown are the estimated values for 10-34-0 solution of average purity that is produced from wet-process superphosphoric acid.

Most of the values for 10-34-0 are based on average data from several different companies that use 10-34-0 made from different wet-process superphosphoric acids. The average result indicates that the quantity of micronutrients that can be dissolved in this type of 10-34-0 is 75% of the quantity that can be expected since part of the polyphosphates in this type of 10-34-0 is required to sequester (essentially dissolve) the impurities (Fe, Al, etc.) introduced by the wet-process phosphoric acid.

These tests indicate that larger quantities of inorganic micronutrients can be dissolved in ammonium polyphos-

Table 19. Summary of micronutrient content of various inorganic micronutrient sources

Material	Micronutrient content, wt. % of element
Sources of boron	
Sodium tetraborate pentahydrate ($Na_2B_4O_7 \cdot 5H_2O$)	14.7
Borax ($Na_2B_4O_7 \cdot 10H_2O$)	11.2
Sodium tetraborate pentaborate	20.5
Sources of copper	
Cupric sulfate monohydrate ($CuSO_4 \cdot H_2O$)	35.1
Cupric sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$)	25.5
Cuprous oxide (Cu_2O)	86.1
Cupric oxide (CuO)	79.8
Sources of iron	
Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$)	20.1
Ferric sulfate nonahydrate [$Fe_2(SO_4)_3 \cdot 9H_2O$]	20.4
Sources of manganese	
Manganous sulfate monohydrate ($MnSO_4 \cdot H_2O$)	24.7
Manganous carbonate ($MnCO_3$)	46
Manganous-manganic oxide (Mn_3O_4)	69.0
Sources of molybdenum	
Sodium molybdate (Na_2MoO_4)	46.6
Sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$)	39.6
Sources of zinc	
Zinc carbonate ($ZnCO_3$)	56
Calcined zinc concentrate (impure ZnO)	74
Zinc oxide (ZnO)	80.3
Zinc sulfate monohydrate ($ZnSO_4 \cdot H_2O$)	36

Table 20. Micronutrient content of some organic micronutrient sources

Material	Micronutrient content, wt. % of element
Sources of copper	
Sequestrene Na_2Cu copper chelate	13.0
Hamp-Ene 9% copper chelate	9.0
Danitra copper chelate	7.5
Rayplex Cu	6.7
Sources of iron	
Sequestrene Na Fe iron chelate	12.0
Sequestrene 138Fe iron chelate	6.0
Sequestrene 330Fe iron chelate	10.0
Hamp-Ene 14% iron chelate	14.0
Danitra iron chelate	10.5
Rayplex Fe	9.6
Sources of manganese	
Sequestrene Na_2Mn manganese chelate	12.0
Hamp-01 9% manganese chelate	9.0
Danitra manganese chelate	10.0
Rayplex manganese	8.5
Sources of zinc	
Sequestrene Na_2Zn zinc chelate	14.2
Hamp-Ene 14.5% zinc chelate	14.5
Danitra zinc chelate	10.5
Rayplex zinc	10.0
Multiple sources of micronutrients	
Chelated nutramin (Mn, Fe, Zn, Cu, B, and Mo)	
Key-El (Zn, Mg, Cu, and Fe)	
Multiplex (Zn, Mn, Fe, Cu, and S)	

phate solutions than in orthophosphate solutions. For example, 60 times as much zinc as zinc oxide can be dissolved in 11-37-0 ammonium polyphosphate solution as in 8-24-0 orthophosphate solution. Other tests indicate that little magnesium can be dissolved satisfactorily in either ammonium polyphosphate solution or orthophosphate solution. Therefore, the addition of compounds that contain magnesium to clear liquid fertilizers should be avoided.

Most plant operators want to know how much of an inorganic micronutrient can be dissolved in mixtures produced from 11-37-0 or 10-34-0. It would be difficult to determine this for all cases. Plant and small-scale tests indicate that in most instances it can be calculated by the use of the quantity of 11-37-0 or 10-34-0 in the formulation and the quantity of the micronutrient compound that can be dissolved in the 11-37-0 or 10-34-0 base solution. For example, the amount of zinc as zinc oxide that can be dissolved in a 7-21-7 produced from 11-37-0, 32-0-0 potash, and water is calculated as follows:

1. The quantity of 11-37-0 used to produce a ton of 7-21-7 grade is calculated to be 1,135 pounds.
2. This 11-37-0 will dissolve up to 3% zinc as zinc oxide.
3. The amount of zinc oxide that can be dissolved in a 7-21-7 grade is then calculated by the following formula:

$$\frac{1{,}135 \times 0.03 \times 100}{2{,}000} = 1.7\%\ \text{Zn}$$

A similar procedure can be used in determining the amount of inorganic micronutrients that can be dissolved in mixtures produced from 10-34-0 made from wet-process superphosphoric acid.

Some plant operators want to include more than one micronutrient in a liquid mixture. An empirical type of procedure has also been developed for the use of several micronutrients in mixtures produced from 11-37-0. This procedure is as follows:

1. Never exceed the maximum amount of each individual micronutrient which can be dissolved in 11-37-0 or 10-34-0.
2. The sum of all the micronutrients added should not exceed 3% of the amount of 11-37-0 used in the mixture.

In most instances, this procedure for the addition of several micronutrients to mixtures produced from 11-37-0 has worked well. It should also work satisfactorily for mixtures produced from 10-34-0. An example of its use is as follows:

Assume that an 8-8-8-XZn-XB-XMn is to be produced. It is assumed the Zn:B ratio is 3, and the Zn:Mn ratio is 10.

1. First determine the maximum quantity of the three micronutrients that can be dissolved in 11-37-0. Care should be taken to avoid exceeding the maximum amount of each individual micronutrient that can be dissolved. Also the sum of Zn, B, and Mn should not exceed 3%. Calculations show that when the micronutrients are dissolved in 11-37-0, the resulting grade is a 10-34-0-2.0Zn-0.7B-0.2Mn.
2. About 471 pounds of 10-34-0-2.0Zn-0.7B-0.2Mn would be required to produce the 8-8-8 liquid. Therefore, the Zn content of the 8-8-8 would be calculated as follows:

$$\frac{471 \times 0.02 \times 100}{2{,}000} = 0.47\%\ \text{Zn}$$

The boron content would be calculated as follows:

$$\frac{471 \times 0.007 \times 100}{2{,}000} = 0.17\%\ \text{B}$$

The manganese content would be calculated as follows:

$$\frac{471 \times 0.002 \times 100}{2{,}000} = 0.05\%\ \text{Mn}$$

Table 21. Solubility of micronutrients, 24-hour agitation

Material added	% by weight of element (Zn, Cu, Fe, Mn, B, Mo) In 11-37-0 base solution	In 10-34-0[a] base solution	In 8-24-0 base solution
Zinc oxide	3.0	2.25	0.05
Zinc sulfate	2.0	1.30	0.05
Zinc carbonate [$Zn(CO_3)_2$]	3.0	2.25	0.05
Cupric oxide (CuO)	0.7	0.53	0.03
Copper sulfate ($CuSO_4 \cdot 5H_2O$)	1.5	0.14	0.13
Ferric sulfate [$Fe_2(SO_4)_3 \cdot 9H_2O$]	1.0	0.80	0.08
Manganous-manganic oxide (Mn_3O_4)	0.2	0.15	0.02
Sodium molybdate ($Na_2MoO_3 \cdot 2H_2O$)	0.5	0.38	0.50[b]
Borax ($Na_2B_4O_7 \cdot 10H_2O$)	0.9	0.90	0.90

[a]Made from wet-process superphosphoric acid.
[b]Largest amount tested.

3. Therefore, the clear liquid 1:1:1 ratio with Zn, B, and Mn would be an 8-8-8-0.47Zn-0.17B-0.05Mn.

Field storage and laboratory data indicate that this liquid would store well for several days. However, when more than one micronutrient is used in a liquid mixture, the micronutrients sometimes react with each other and cause an increase in the salting-out temperature with the result that crystals form in the mixture. For example, mixtures of 11-37-0, zinc oxide, and manganous-manganic oxide will react to form insoluble compounds. Sometimes these reactions take place over a long period of time, but often they occur in a very short period. Also, crystals often form in liquids containing any micronutrients if the liquid is stored for a prolonged period. For this reason in the TVA field programs, the storage of liquid mixtures that contain micronutrients is not recommended.

In some instances, the inorganic micronutrients are not sufficiently soluble in clear liquid mixtures to meet agronomic requirements where genuine deficiencies exist.

The solubility of chelated micronutrients is usually not a problem. Only one-fifth to one-tenth as much micronutrient element is required as a chelate compared with an inorganic source. Therefore, the amount of chelated metal elements soluble in liquid mixtures produced from 10-34-0 or 11-37-0 is generally sufficient to meet recommended agronomic requirements.

Future Solutions

In recent years, most of the growth in the fluid fertilizer industry has been in the production of suspension fertilizers. However, the solution fertilizer market is still considerably greater than that of suspension fertilizers. The growth of nitrogen solutions has been substantially higher than the growth rate for anhydrous and aqua ammonia, and it is expected that larger quantities of nitrogen solution will be used in the future. The main reason for this increase in popularity is its ease of handling and application. Also it is safer to use the nitrogen solution in preference to anhydrous or aqua ammonia.

Solution mixtures such as 7-21-7 which is a starter fertilizer continue to be popular and as the farmer strives to increase his yields, specialized placement of fluids may become more important. For example, recently Kansas State University determined that there was some beneficial effect of injecting solutions and anhydrous ammonia simultaneously beneath the surface of the ground. With this type operation, a trouble-free solution type fertilizer is required. The use of nitrogen solution and solution mixtures in special applications such as through drip irrigation units and sprinkler irrigation systems is gaining in popularity. In the colder regions of the United States, the use of a starter type fertilizer to promote early growth and crop maturity is probably beneficial to the farmer. Generally, if fluid fertilizer is to be applied by the farmer, it is preferable to use solution instead of suspension fertilizers because of their trouble-free quality. For these and other reasons it is expected that the use of nonpressure nitrogen solutions and solution mixtures will continue at increased levels.

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Chapter 7

Suspension Fertilizers—Production and Use

By J. G. Getsinger, F. P. Achorn, and George Hoffmeister

Suspension fertilizers are characterized as fluid fertilizers containing a suspending agent such as a gelling-type clay. Suspensions usually contain finely divided solids that are held in suspension by the gel. The formulation and manufacture of a suspension need to be controlled carefully so that the gel is strong enough to support the solids without their settling but weak enough to allow the suspension to be easily agitated, poured, or pumped.

Suspension fertilizers apparently had their origin in the late 1950s (1, 2, 3). Because of the need for including potassium in fluid fertilizers beyond the limit of the solubility of potassium, growth of suspensions accelerated (4). Fluid fertilizers containing nitrogen and phosphate as ammonium polyphosphates have respectably high soluble concentrations of these two plant foods, but potassium salts are less soluble. Therefore, increased need for a suspension was identified. Other advantages of suspensions in comparison with solutions soon became apparent.

A solution is an ideal form of fluid fertilizer for reliable handling, measuring, and applying to the soil. A solution is uniform and homogenous. It has a low viscosity and does not require mixing. It is usually transparent so that any stray foreign material can be easily seen. It does not settle in tanks or clog pipes or nozzles, and can be gravity fed by measurement through a simple orifice. However, solutions have certain characteristics that endow them with disadvantages. Solutions have solubility limits which dictate the concentration and proportion of each of the plant food components. These limits dictate the grade of the solutions. Furthermore, since solubility depends on temperature, the grade must be low enough to withstand the lowest expected temperature without salting out any of the soluble materials. These requirements sometimes make for very low concentrations of fertilizer solutions with resultant high cost of handling, storage, and application.

The relative purity or impurity of the raw materials is one of the most important considerations in obtaining a satisfactory solution. In addition, the choice of the anions and cations in the solution will affect solubility tremendously. The common cations are ammonium and potassium. The usual anions are phosphate, nitrate, chloride, and sulfate. The phosphate anion is complicated by the solubility-boosting attribute of the polyphosphate form of phosphate. When consideration is given to impurities, polyphosphates, salting-out temperatures, and the use of various raw materials, solution fertilizers are seen to be quite complex fertilizer materials.

The development and use of suspensions was motivated by the disadvantages and limitations of solutions outlined above. Some advantages of suspensions are:

1. Less pure and therefore cheaper raw materials can be used in making suspensions.
2. Solubility of materials is not a limiting factor; therefore, the concentrations can be higher and the ratios of plant nutrients are almost unlimited.
3. Additional plant nutrients, such as micronutrients, can be added to suspensions in the quantities or proportions desired without concern for their solubility (5).
4. Furthermore, less costly forms of the micronutrients, such as oxides rather than the more soluble sulfates, can be used in suspensions.
5. Pesticides are more compatible with suspensions than with solutions (6).

Some of the disadvantages of suspensions are:

1. They contain solids which can settle, clog nozzles, and cause stoppages in pipes.
2. They are more viscous than solutions, thus viscosity sometimes becomes a limiting factor in their preparation.
3. Suspensions require periodic agitation during storage.
4. The processes for making suspensions require a clay addition step with the attendant equipment for handling and mixing the clay.

BASIC STUDIES

Measurement of Gel Strength

Since a suspension is a gel and the ability to suspend depends on gel strength, research on suspension fertilizers required some means of measuring gel strength. Therefore, a gelometer was developed at TVA (7) (figure 28).

A torsion wire suspends a bob, and a turntable supports a cup that contains a suspension fertilizer. To make a gel strength measurement, the bob is lowered into the cup and immersed into the sample at a prescribed depth. The cup is rotated by a drive motor at a constant rate, and initially the bob rotates at the same speed as the cup, since there is essentially no force resisting the bob rotation; however, as the cup and bob rotate further, the wire, which is fixed at the top end, is twisted and exerts a torque against the gel. When the torque reaches the point at which the gel is broken, the rate of rotation of the bob decreases. The angle of deflection (amount of rotation) at that point indicates the torque being exerted by the wire. Thus, the torque is a measure of the gel strength and is directly proportional to the diameter and inversely proportional to the length of the torsion wire. The wire is calibrated to measure torque in gram-centimeters, and the gel strength is expressed in these units. Gel strength values determined in this manner can be related to other observations of the quality of the suspensions, and relative gel strengths give an important, fast determination of the suspending characteristics of a particular suspension. Generally, a gel strength of about 1 to 2 gram-centimeters is adequate for most suspensions. It is more difficult to define a gel strength that is too high. Usually the viscosity would be the limiting factor on a suspension; the viscosity and the gel strength increase together.

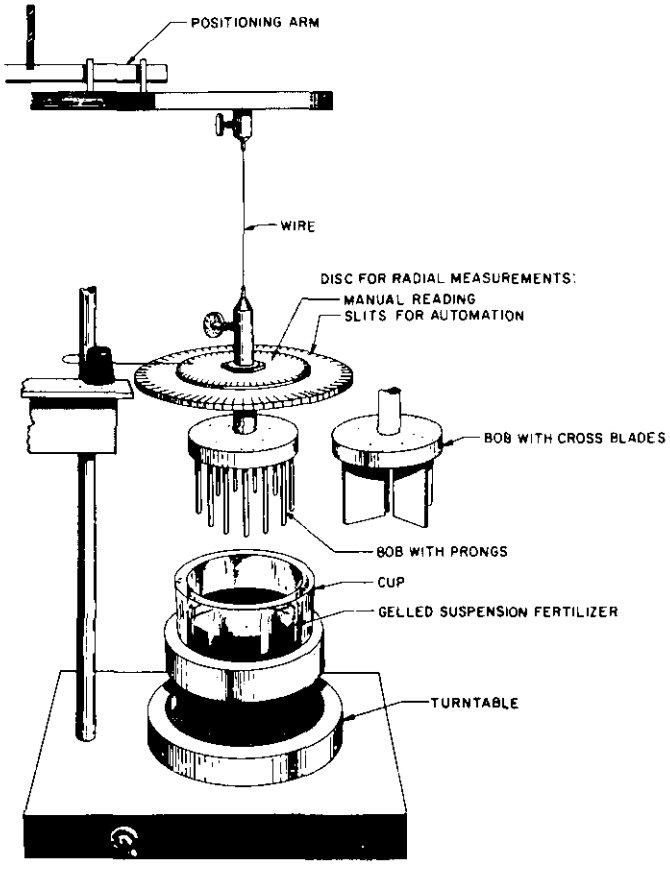

Figure 28. Basic parts of TVA gelometer

Gelling with Attapulgite Clay

Usually, the suspending agent used in suspension fertilizers is attapulgite clay obtained in south Georgia and north Florida (8, 9). Attapulgite is a hydrated magnesium aluminum silicate. The clay is composed of needle-shaped crystals that are so small they can be seen only by great magnification (8). 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 salts present in fluid fertilizers, the individual crystals immediately assume the regular structural orientation of a gel. 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.

Research has shown that only vigorous shear-type agitation of the clay-fertilizer suspension can provide the desired degree of disruption and, hence, the desired gel strength. This type of stirring requires high tip speed of the agitator. One of the most effective shear-type mixers is a centrifugal pump. Tip speeds of impellers of centrifugal pumps usually range from about 50 to 80 feet (15.2-24.4 m) per second. For this purpose, the higher the speed, the better the results. To obtain complete gelling, multiple passes of the suspension through the pump are required.

Therefore, the pump should be large enough to avoid excessive time for gelling. The number of passes required is related to the speed of the impeller—the slower the impeller speed, the more passes needed for complete gelling. The practical range is about 10 to 20 passes. The amount of shear required depends on several factors. For example, if the fluid contains nitrates or polyphosphates, the amount of shear required is increased. Also, if the fluid is a liquid with no solids present, the amount of shear required is higher than it would be for a fluid that contained solids. The action of the solids in increasing the effectiveness of the mixing and the resulting higher gel strength is not understood. However, the presence of solids, such as crystals of urea, ammonium nitrate, or ammonium phosphate, evidently overcomes much of the resistance to gelling imparted by the anions of nitrate and polyphosphate.

The efficiency of gelling dry clay in a fluid can be increased by increasing the clay content in a portion of the fluid during the gelling step and then mixing the concentrated gel with the remainder of the fluid to obtain the desired clay content. For example, for a product with 2% clay, the entire amount of clay could be added to one-fourth the fluid for gelling, giving a clay content during the gelling step of 8%. After gelling, the concentrated gel then would be mixed with the other three-fourths of the fluid to obtain a final product with 2% clay. Gelling of the clay by this procedure allows more efficient use of the agitator which works on a smaller volume of material. It increases the viscosity and, therefore, increases the shearing action of the agitator during the gelling step. It increases the proportion of solids, which increases the gelling action as previously described.

Another method to facilitate gelling of clay in fluid fertilizers is to chemically disperse the clay (10), either in water or in urea or ammonia solutions, before adding the clay to the fluid fertilizer. Clay, however, cannot be dispersed in the presence of fertilizer salts, and when the dispersed clay is added to the fluid fertilizer, the salts cause immediate gelling of the clay. Clay concentrations in a dispersion can be as high as 25% or 30% with viscosities low enough to allow easy handling with good flowability. One of the more effective dispersants is tetrasodium pyrophosphate (TSPP). The amount of this dispersant required for dispersing clay in water is 2.25% of the weight of clay.

Clay also can be pregelled in water without a dispersing agent; however, a clay concentration of about 10% is the limit because of excessive thickness or viscosity of greater concentrations. The use of a dispersing agent lowers the viscosity and, therefore, allows higher clay concentrations in clay dispersions (see Fluid Clay section).

Another characteristic of most suspension fertilizers is that when suspensions are stored without agitation, the gel strength of the suspension increases. The gel can become so strong that the suspension will no longer flow and the suspension will be difficult to remove from storage tanks. To prevent excessive increase in gel strength, the suspension must be periodically sparged or otherwise agitated in the storage tank, as will be discussed later.

Fluid Clay

Since dry clay is difficult to gel in some suspensions, dispersed clay is marketed to improve the gelling of the clay (11). This fluid clay also offers the advantage of nondustiness in handling. TVA has developed a fluid clay containing urea (12). The dispersing agent is TSPP. The urea serves two principal purposes: to lower the freezing point of the liquid phase to about 15°F (-9.4°C) and to reduce the initial viscosity of the product. The clay content is about 25% and the nitrogen content from the urea is about 9%.

The fluid clay has two serious disadvantages. One is that viscosity increases with storage time, particularly in hot weather and without agitation, such as the conditions that occur in a tank car in the summer. The other disadvantage is the higher freight cost as compared with shipping dry clay. Practical countermeasures to these disadvantages might be to produce the fluid clay only in cool weather and near the point of use.

Research has indicated that hydrolysis of the urea and TSPP causes the increase in viscosity. The formation of ammonium carbonate and orthophosphate, both gelling agents, partially gels the concentrated clay and causes thickening. Leaving urea out of the formulation during hot weather probably would be advisable.

Use of Other Suspending Agents

Sepiolite clay (13, 14), which is mined in Nevada, is similar to attapulgite in crystalline structure but contains only about one-tenth of the amount of aluminum typically found in attapulgite. Sepiolite is a hydrated magnesium silicate. It forms a gel in suspensions in the same manner as attapulgite. Sepiolite is more reactive than attapulgite with the slightly acidic liquid phase of fertilizer suspensions and this reaction weakens the gel with time.

Bentonite is a clay found in Wyoming and neighboring States (15). It is primarily a hydrated aluminum silicate, but its swelling and gelling characteristics when wetted with water come from the small amount of sodium it contains. Bentonite cannot be gelled when it is added dry to a concentrated fertilizer ionic solution. Bentonite must be gelled in water or nonionic solution before it is added to the suspension. A clay content of 10% in water is about the maximum that can be readily handled.

PRODUCTION OF SUSPENSIONS

Phosphate Base Suspensions

One of the earliest phosphate base fluids for suspensions was 10-34-0 ammonium polyphosphate solution (16). The solution was used together with potassium chloride to make NPK suspensions; clay was added as a suspending agent. TVA developed the concept of a phosphate base suspension containing its own clay. At first, a suspension of this type with a grade of 12-40-0 was made from ammonium polyphosphate (APP) solution made from electric-furnace phosphoric acid (17). Later the grade was increased to 13-41-0, and the suspension contained crystals of diammonium phosphate (DAP) (18). Then a phosphate base suspension made from a mixture of electric-furnace and wet-process phosphoric acid was produced. The grade of this material was 13-39-0 (19).

Ammonium Orthophosphate Base Suspension, 13-38-0— More recently, a process was developed for making a base suspension entirely from wet-process phosphoric acid and ammonia (20). A flow diagram of the process is shown in figure 29. The feed acid is merchant-grade with 54% P_2O_5, but it can be as low in concentration as 40% P_2O_5. The product has a grade of 13-38-0 and contains 1.5% clay.

Phosphoric acid and gaseous ammonia are fed to a first-stage reactor. The heat of reaction causes the contents to boil. Water is added to the first-stage reactor as necessary to hold the boiling point at about 230°F (110°C). The degree of ammoniation is controlled by measuring the pH of samples of the contents diluted with about four parts of water to one part of material and holding the pH at about 5.4. The reactants overflow to the second-stage reactor where more ammonia is added. Also, a slight amount of water is added in this reactor to adjust the concentration. The temperature in this second-stage reactor is held at about 200°F (93°C) by recycling a cooled stream of material back to the second stage as necessary. The pH of the material in this stage (sample diluted 4 to 1 with water) is held at about 6.5. The effluent from the second stage is pumped to an evaporative cooler where the product is cooled with air to about 125°F (52°C). Effluent from the cooler flows by gravity to a third-stage reactor where additional ammonia is added. Cooling is provided in the third stage to hold the temperature at about 120°F (49°C). Material flows from the third stage to a clay-mix tank where attapulgite clay is added and gelled with a recirculation pump. The mixture is further cooled with cooling water to about 115°F (46°C). The pH of the product (measured after 4 to 1 dilution with water) is kept at about 7.1. The product is then pumped to storage.

The purpose of the three-stage ammoniation is to make a concentrated suspension with satisfactory physical properties. The relatively high temperature and low pH conditions in the first stage promote the precipitation of the impurities, principally iron and aluminum, in a form

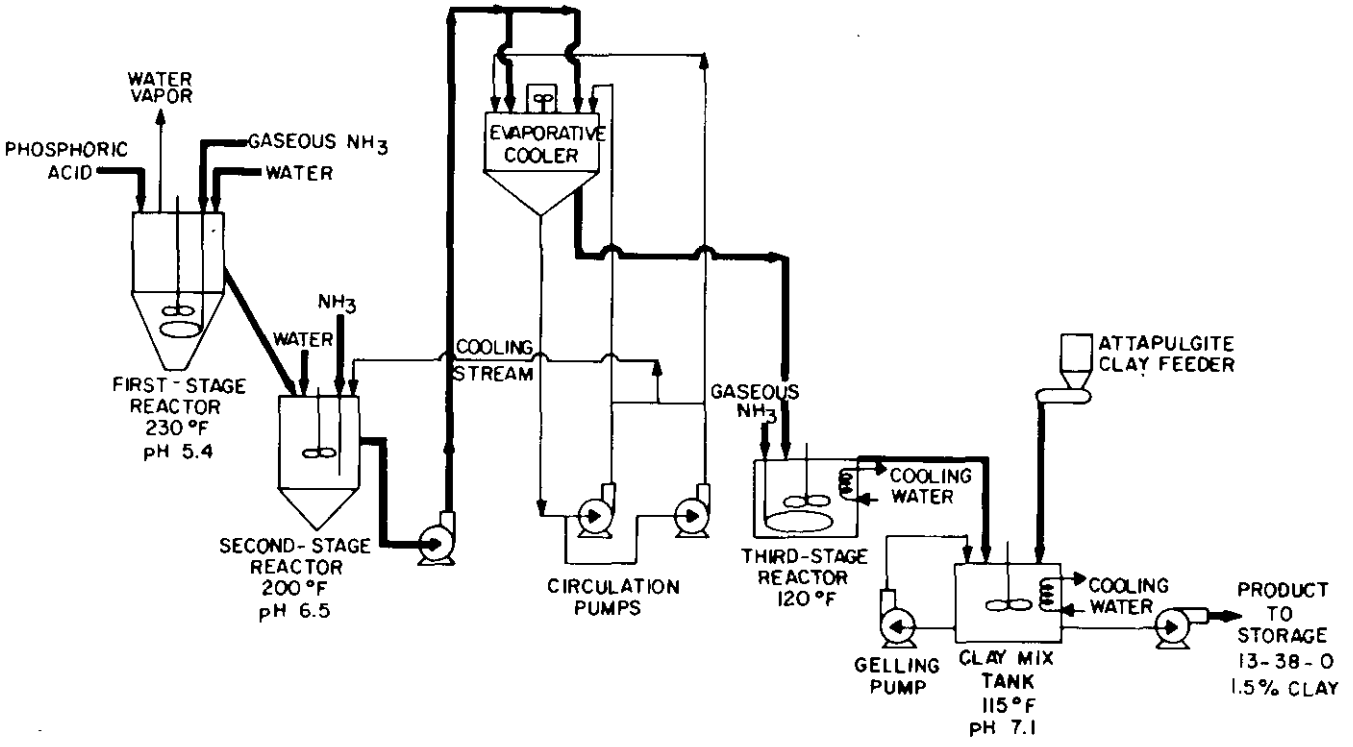

Figure 29. Production of 13-38-0 ammonium orthophosphate suspension fertilizer

that is crystalline rather than amorphous so that the final product viscosity will be lower. The temperature is lowered in the second stage so that the ammonia loss will be minimized. In the third stage, the monoammonium phosphate (MAP) crystals are converted to DAP. The DAP crystals are small enough and have a shape that inhibits their settling.

In preliminary operation of this plant without a third ammoniation step, the product (11-39-0) contained crystals as MAP, and these rodlike crystals settled excessively in railway tank cars during transport. Further research and development work on the process, including a test developed to simulate vibration received by the products in a railway tank car, was necessary to develop the modification involving the third-stage formation of DAP.

The product is higher in concentration than 10-34-0 base solution and, therefore, can be stored and shipped at costs below those for 10-34-0. The cost of production of 40% to 54% acid, which is suitable for feed to this process, is less than that of superphosphoric acid required for the production of 10-34-0. Furthermore, less energy is required for production of the acids of lower concentration. The 13-38-0 suspension carries its own clay, which is useful for blending with other materials for making suspensions without having to add clay at the mixer-dealer level.

The primary problem with 13-38-0 suspension is that it solidifies at about 15° to 20°F (-9.4° to -6.7°C). Thickening at low temperatures can be reduced satisfactorily by diluting with water in the storage tank to 36% P_2O_5. Also, the solidification temperature can be lowered to about -5°F (-51°C) by adding some ammonium polyphosphate solution to provide about 12% of the P_2O_5 as polyphosphate. The addition of a small amount of sulfate (4%) also lowers the solidification temperature.

About 200,000 tons of satisfactory 13-38-0 material has been shipped by TVA and used mostly in the southeastern States.

Polyphosphate Base Suspension, 9-32-0—A process employing a pipe reactor was developed at TVA for producing APP suspension from merchant-grade wet-process phosphoric acid, ammonia, and suspending clay (21). The objectives in this process were threefold: (1) that the product would contain polyphosphate so that it would withstand cold-weather storage and handle satisfactorily, (2) that the product would be made from merchant-grade phosphoric acid rather than superphosphoric acid, and (3) that existing pipe-reactor plants producing 10-34-0 solution fertilizer from superphosphoric acid could be modified to produce 9-32-0 suspension in most of the same equipment. The process as developed is shown in figure 30.

The melt dissolution tank and the evaporative cooler are usually present in most 10-34-0 solution plants. The equipment for heating the acid and ammonia and for adding clay would need to be provided. The key feature of this process is to provide a suspension containing about 25% of the P_2O_5 as polyphosphate without outside heating of the feed acid or the ammonia. The feed materials are heated by

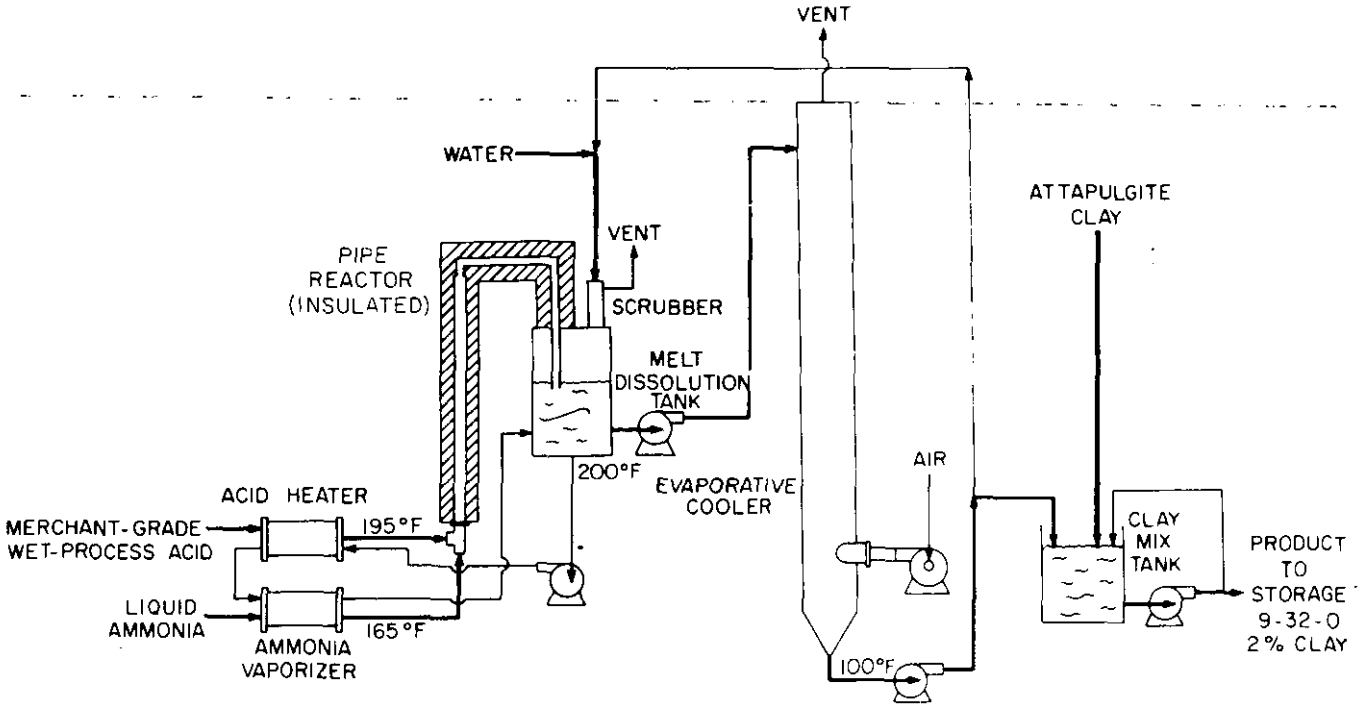

Figure 30. Production of 9-32-0 ammonium polyphosphate suspension fertilizer from merchant-grade wet-process phosphoric acid

heat exchangers where hot solution from the dissolution tank is the heating medium. All of the heat comes from the reaction of phosphoric acid and ammonia. The melt dissolution tank is kept at about 200°F (93°C) by recycling a cool stream from the evaporative cooler. The acid reaches a temperature slightly below 200°F (93°C), and the ammonia a temperature of about 165°F (74°C). Hot solution is pumped from the melt dissolution tank to a packed tower evaporative cooler, where it is cooled to about 100°F (38°C). Part of the cool stream is recycled to the melt dissolution tank to maintain the temperature at about 200°F (93°C). This is about the highest temperature that can be maintained without significant loss of ammonia and without excessive hydrolysis of polyphosphate during the time the material is held in the dissolution tank. The temperature of the solution is desired to be as high as is feasible in order to provide a maximum amount of heat for the acid and ammonia.

Cool solution from the evaporative cooler is pumped to the clay mixing tank where dry attapulgite clay is added to give a clay content of about 2%. A recirculation pump is used for gelling the clay in the solution. The product with a grade of about 9-32-0 is then pumped to storage.

The primary use of this product is as a substitute for the more expensive 10-34-0 APP solution. The 9-32-0 suspension can be used for direct application to the soil or for blending with other materials to make mixed suspensions.

A further modification of this process envisages the use of sulfuric acid together with the phosphoric acid to supply additional heat in the pipe to increase the melt temperature and increase the polyphosphate formation. When phosphoric acid alone is used, the amount of polyphosphate formed is sharply affected by the amount of water in the phosphoric acid; therefore, the use of sulfuric acid in conjunction with phosphoric acid would compensate for acids with higher water content. This modification is under pilot-plant study now.

Suspensions from Solid Phosphates—In some areas, freight rates for fluid fertilizers are higher than for solid fertilizers. The distance of shipping of fluid fertilizer is limited by economics (22). Therefore, many mixer-dealers use solid fertilizers, such as MAP, for producing their own phosphate base suspension (23). The usual procedure is to use a batch fertilizer mixer. The water of formulation is first added to the mixer and then ammonia is started. The MAP is fed to the mixer and ammoniation is conducted as rapidly as possible to elevate the temperature of the material. The combination of reaction with the ammonia and the heat of ammoniation rapidly dissolves MAP in the water. A grade of about 10-30-0 is produced by this means. Usually, urea-ammonium nitrate (UAN) solution, potassium chloride, and clay are added to complete the desired fertilizer mixture. However, a phosphate base can be made by adding and gelling the clay and sending the 10-30-0 to storage. The phosphate base made in this manner does not have very good storage characteristics in cold weather.

A polyphosphate content of about 10% of the P_2O_5 in the solid increases its solubility, shortens the ammoniation time, and improves the storage characteristics of the base suspension greatly (24). Also, the grade of the resulting base suspension can be increased satisfactorily to about 11-33-0 or 12-36-0, depending upon the amount of impurities in the phosphate and the proportion of the P_2O_5 present as polyphosphate. A process is under development that allows the production of polyphosphate in excess of 10% in the solid product by use of a pipe reactor discharging into a granulating drum. This product is expected to be superior to MAP for use in making suspensions.

Nitrogen Base Suspensions

When nitrogen base solution is mixed with a phosphate base suspension, the clay content is diluted and extra clay is needed for adequate suspending action. The gelling of clay in UAN solution to produce a nitrogen base suspension is a very difficult operation. The strong gelling action of ammonium nitrate interferes with the shearing action of the agitator required for separating the particles of dry clay. A nitrogen base suspension carrying its own well-gelled clay for blending with phosphate suspensions was needed. Therefore, TVA has developed processes for producing nitrogen suspensions.

Urea-Ammonium Nitrate Suspension (31% Nitrogen)—A flow diagram of a process for producing a UAN suspension containing 31% nitrogen is shown in figure 31 (25).

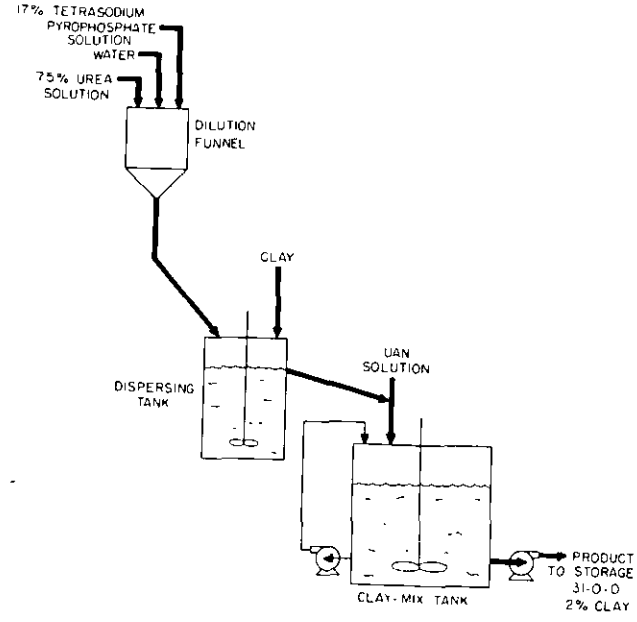

Figure 31. Production of urea-ammonium nitrate suspension fertilizer (31% N)

Attapulgite clay is dispersed in urea solution by the use of a dispersing agent, TSPP. This dispersing step is a necessary prerequisite to effective gelling of the clay in the UAN solution. Urea solution is used in the dispersing step, and the clay content is made as high as possible (30%) to reduce the water content to the lowest possible level. By minimizing the water content, the concentration of UAN solution (32% nitrogen) will be diluted as little as possible when the clay is added. The concentrated clay dispersion is fed to a mixing tank together with UAN solution for the gelling step. Gelling is accomplished with a centrifugal pump. About five passes through the pump on the average are required to gel this concentrated dispersion in UAN solution. Using this system, the product suspension with 2% clay has a nitrogen content of 31%.

Higher Grade Urea-Ammonium Nitrate Suspension (36% Nitrogen)—The development of a process for producing a 36% nitrogen suspension with 1.5% clay from urea and ammonium nitrate is underway. Such a product would lower the freight and handling costs and allow storage of more plant food in the same storage tanks. The process would require concentrated urea solution (87%) and ammonium nitrate solution (88%) as feed for the process. A product containing about 55% urea, 31% ammonium nitrate, and 13% water has a viscosity of about 750 cP at 32°F (0°C). The solidification temperature is about -15°F (-26°C). These characteristics would allow this product to be stored and handled at extremely cold temperatures.

A flow diagram of the process is shown in figure 32. The concentrated feed materials are mixed and sent to a water-cooled heat exchanger where the material is cooled to about 135°F (57°C) which is above the saturation temperature of about 110°F (43°C). This temperature limit is to prevent fouling of the heat exchanger by crystalline urea. The solution is pumped to a clay-mix tank where predispersed clay is added. Then the slurry is pumped to a spray cooling tower where air is used to cool the material to cause rapid nucleation of urea crystals so that small crystals will be formed. The cooling is by combination of evaporation and exchange of sensible heat. Very small urea crystals of a few hundred micrometers in size are desired to prevent growth of crystals to excessive size during storage.

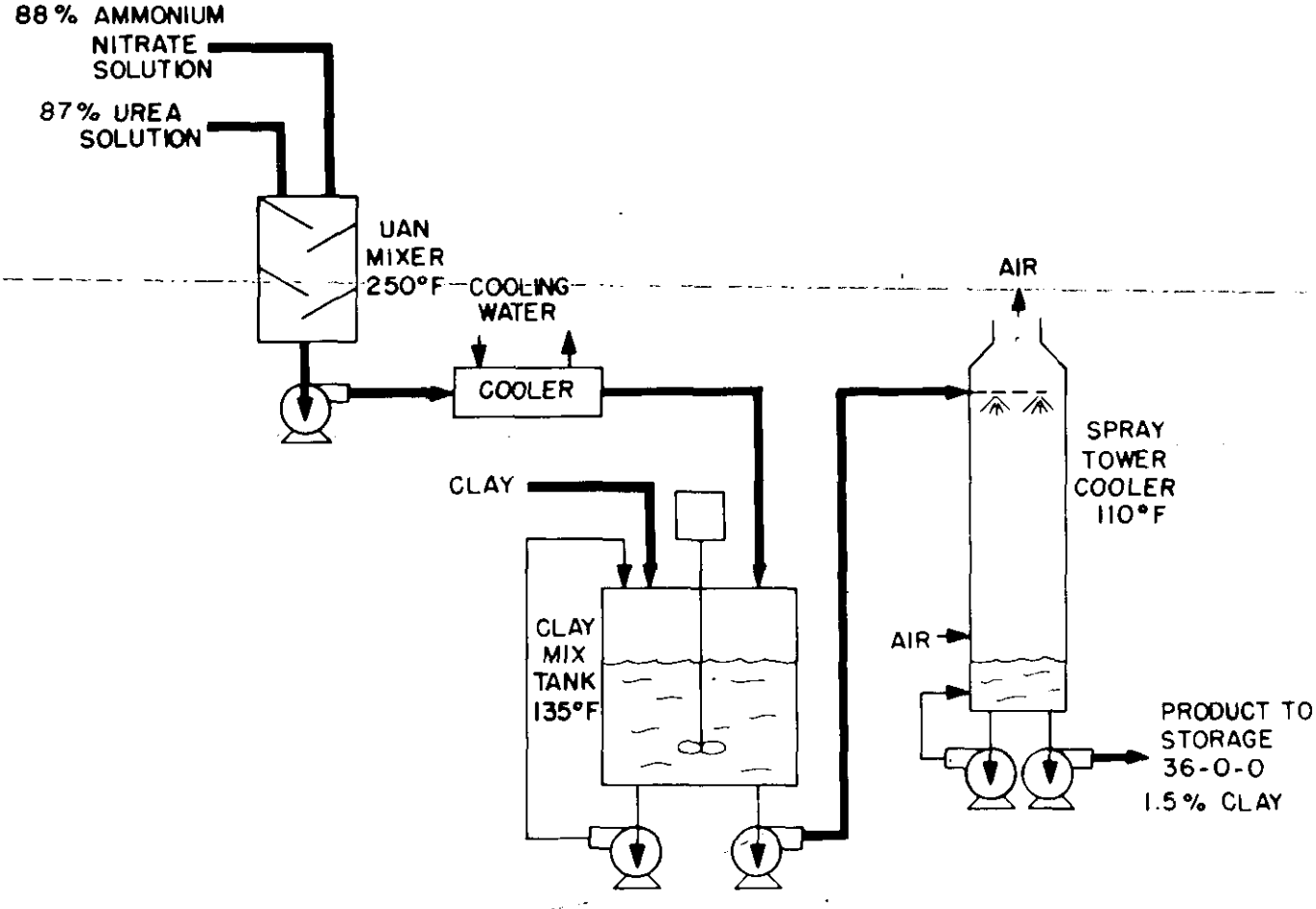

Figure 32.—Production of urea-ammonium nitrate suspension fertilizer (36% N)

Urea-Ammonium Sulfate Suspension—Some soils are deficient in sulfur, and fertilizers containing sulfur are needed for those soils. Since the application of nitrogen can cause sulfur stress in some crops on soils low in sulfur, combining sulfur with nitrogen in fertilizer appears to be desirable. Therefore, TVA developed a process for producing a urea-ammonium sulfate (UAS) base suspension from urea solution, sulfuric acid, and ammonia (26). A flow diagram of the process is shown in figure 33.

Urea solution, sulfuric acid, and ammonia are fed to a reactor. The heat of reaction of the sulfuric acid and ammonia causes the reactor to boil at about 240°F (116°C). The pH is maintained at about 6.3. Water is added to replace water evaporated during the reaction step. Dilute, spent, or by-product sulfuric acid may be used, or concentrated acid is also satisfactory. The reaction product overflows to a surge tank from which it is pumped to a water-cooled heat exchanger. Here it is cooled to about 135°F (57°C) which is just above its saturation temperature. This temperature limit is necessary to prevent fouling of the heat exchanger. From the cooler, the solution goes to a clay-mixing step where 2% clay is added and then to an evaporative spray cooling tower. The product is 29-0-0-5S. It has excellent cold-weather storage and handling properties. Its viscosity at 32°F (0°C) is about 1,200 centipoises and the solidification temperature is about -15°F (-26°C).

The product can be used for direct application to replace nitrogen solutions where sulfur is needed. Also, it can be used in mixed suspensions to provide nitrogen and sulfur where sulfur is desired.

Potash Base Suspensions

Since potassium chloride is the most economical form of potassium, it is the material commonly used for furnishing potassium in suspension fertilizers. Solution-grade potash is usually used. This material is -20 mesh in particle size and contains 62% K_2O.

Potassium chloride is received in the mixing plants as solid material and, in many instances, is batch-mixed with the phosphate and nitrogen materials to give a complete three-component mixed fertilizer. However, a potash base suspension with a grade of 4-14-28 or 4-12-24 can be made by mixing solution-grade potassium chloride in a phosphate base suspension, such as 13-38-0, or a phosphate base solution such as 10-34-0 with the addition of attapulgite clay. The necessary water is added to complete the formulation. Agitation of the mixture, after addition of the potassium

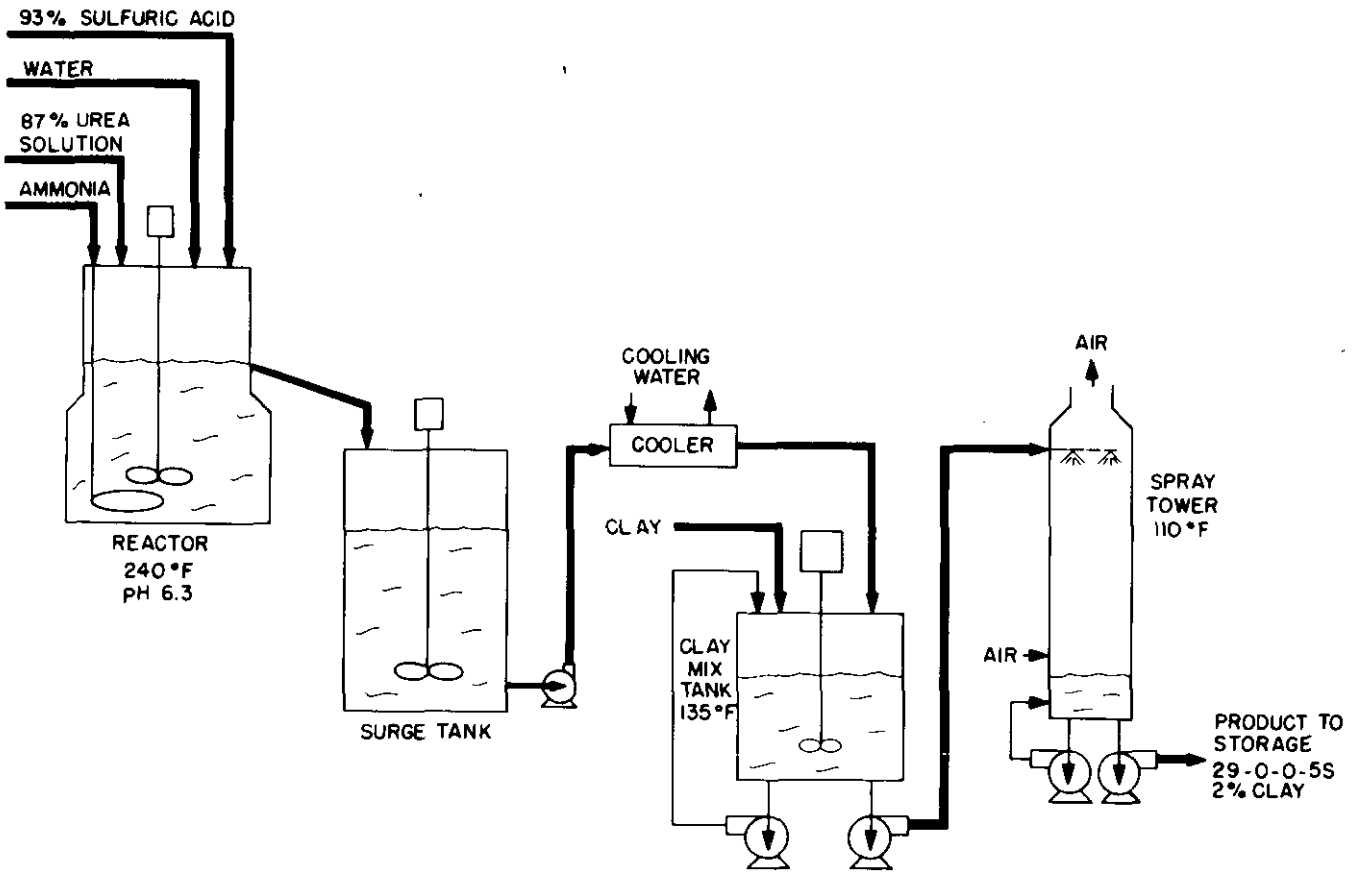

Figure 33. Production of urea-ammonium sulfate suspension (29-0-0-5S)

chloride for 10 to 15 minutes, is required in order to form a stable suspension. The reason for this required agitation time is not understood but is believed to be associated with the chemical reactions that occur between potassium chloride and the other components.

The advantages of making a potash base suspension are: (1) the potash can be mixed with the other components during slack times when the necessary time of agitation for adding the potash can be most conveniently expended; (2) the potash base suspension can be blended with nitrogen and phosphate base suspensions with simple, low-powered mixing equipment to obtain plant nutrients in any desired ratios without having to add and gel clay; and (3) the saving of the time that would be required for mixing each batch during the busy application season.

A potash base suspension is the only feasible fluid base for potash since the solubility of potassium salts is so low.

Fluid Lime

Many crop growing areas have low pH soils that must be adjusted for optimum crop response. For years this pH adjustment has been accomplished by spreading dry ground limestone. Most agriculturalists recommend that all particles in the limestone should be less than 20-mesh in size (0.328 in.) and that at least 60% should be smaller than 100-mesh (0.0058 in.). This is a relatively small size and there is significant dust generation as it is applied. Generally, most agriculturalists agree that the finer the limestone grind the quicker the pH adjustment can be made in the soil. Therefore, it would be desirable to have the particle sizes less than 100-mesh in size. However, because of the fineness of this grind and the dust loss of limestone as it is applied, it is impractical to apply such finely ground limestone in the dry form. In the 1960s, TVA demonstrated that it was possible to produce a suspension which contained 50% limestone, and that this suspension could be easily applied through flooding type nozzles (27). The concept was accepted in the 1970s and at this time a significant number of companies offered fluid limestone to their customers. Since then, the use of fluid limestone has been gaining in popularity.

Most fluid fertilizer manufacturers are interested in fluid limestone as opposed to application of solid limestone because they have suitable applicators for the application of this type of suspension and additional dry type applicators are not required. Also, some farmers are particularly interested in obtaining very rapid pH adjustments of the soils on which they plan to grow a crop. Usually these are farmers that are using rented land or land which they plan to farm for only one season. TVA application demonstrations show the following advantages for limestone suspension (28):

1. There is no dust during handling or spreading.
2. Very finely ground limestone can be used which promotes rapid reaction in the soil.
3. Suspension fertilizer manufacturers with equipment for broadcasting suspension fertilizers can use the same equipment to apply limestone thereby eliminating the need for extra dry spreading equipment.

A sketch of a typical plant that is used to produce fluid limestone as well as suspension mixtures is shown in figure 34. This plant does an excellent job of producing suspensions in 5- to 10-ton batches. Finely ground limestone is stored and added to the mix tank in batches. In other plants conventional solids handling equipment such as bucket elevators, conveyor belts, drag chains, and augers are used to convey the powdered limestone. None of these plants are capable of efficiently handling finely ground limestone; therefore, the companies resorted to the design shown in figure 34 which uses a pneumatic handling system for transporting and handling this powdered material. Some companies transfer the limestone from dry storage tanks to the mix tank through conveyors as shown in figure 34. Others mount an eductor at the discharge of the dry storage tank and add the limestone to a recirculating fluid line of the mix tank. Fluid passing through the eductor causes a negative pressure to develop in the intake of the eductor so that the powdered limestone can be drawn into the fluid.

The formula for producing a 10-ton batch of 50% limestone mixture is shown below.

Materials[a]	Lb/batch
Water	9,600
Attapulgite clay[b]	400
Limestone	10,000
Total	20,000

[a] Usual order of addition.
[b] Five to 10 lb of UAN solution added aids in gelling the clay.

The usual procedure is to add water to the mixer, add and mix the clay, add the limestone, then agitate the mixture until the limestone is thoroughly suspended in the fluid. Plant and small-scale tests have shown that attapulgite clay must be properly gelled to provide enough suspending strength to keep the limestone from settling in storage. Sometimes the operators add 2 to 5 pounds (0.9 to 2.7 kg) of ammonium nitrate per ton of limestone after the clay is dispersed in water to help gel the clay. Ammonium nitrate is usually added as solution that contains 18% N or UAN solution that contains 32% N. Some of the operators also have found it advisable to add about 5 to 10 pounds (2.7 to 4.5 kg) of dispersant such as TSPP to the water

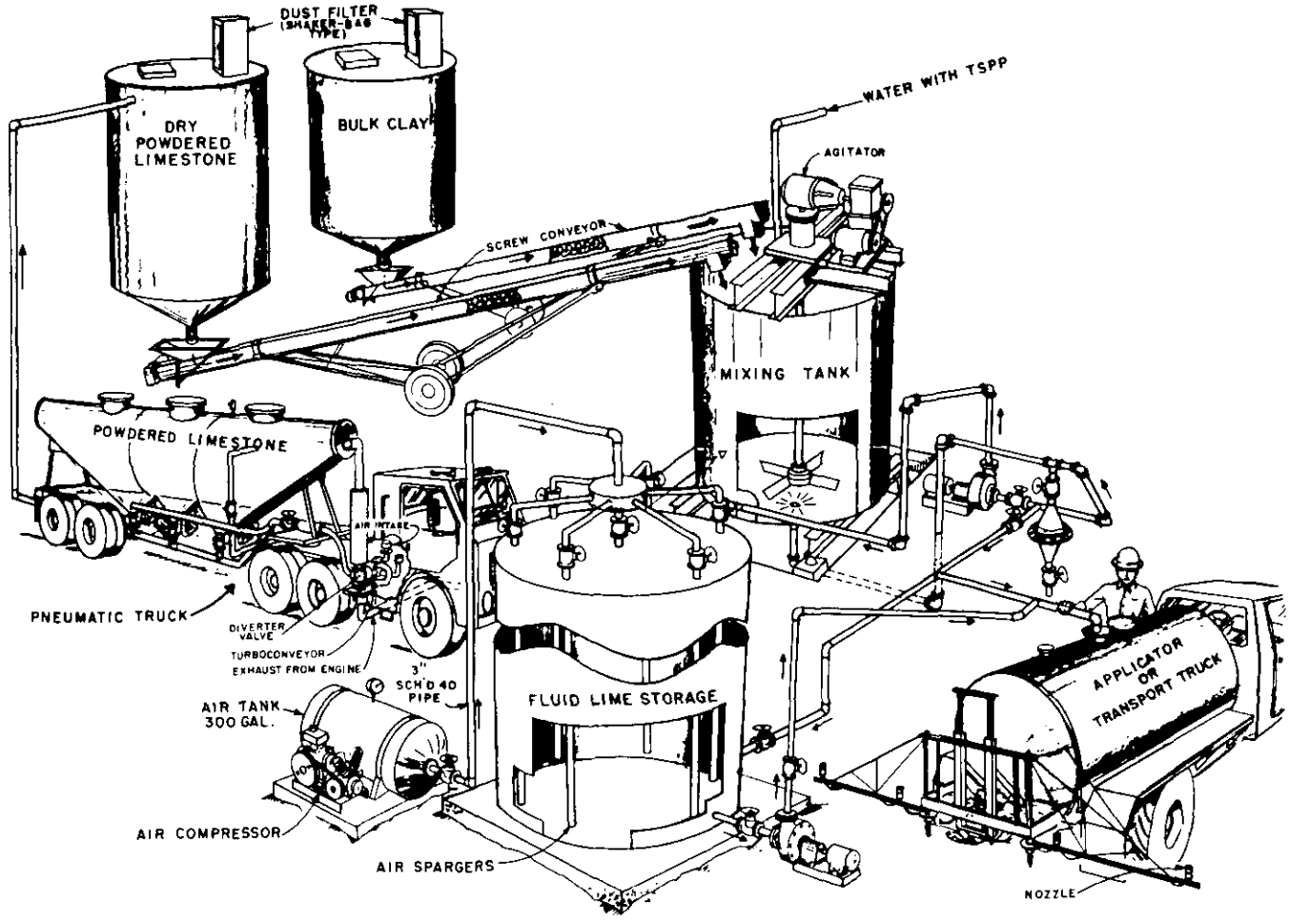

Figure 34. Mix plant for fluid limestone

prior to adding the gelling clay. With these methods, suspensions of 50% or higher limestone content can be produced.

Most dry agricultural limestone has too large a particle size to produce suspensions that will not settle rapidly. This is because in many instances conventional agricultural limestone contains a significant amount of +10 mesh material which cannot be satisfactorily suspended in the fluid. For this reason a standard limestone will not make a good suspension. The limestone must be ground so that all of the particles are -35 mesh and most have a particle size that will pass through a 100-mesh screen. Many quarries now have the grinding capability to supply limestone of this particle size; however, it is usually at a higher price than standard agricultural limestone. For this reason, many dealers are investigating the possibility of using by-product limestones and other by-product materials. They have had excellent results in using limestone dust from air filters that have been installed in dust removal systems at the quarries. Others have attempted to use by-product calcium oxide from cement kilns and have had moderate success in the use of this material. One problem in using calcium oxide is that it reacts with the water to create some heat which causes the lime suspension to become thick; therefore, dilute lime suspensions must be produced. However, some are experimenting with the addition of wetting agents such as lignosulfonate and molasses to suspensions made from "kiln dust."

Based on these experiences, most of the dealers have found it advisable to produce limestone suspensions from finely ground limestone. Some are mixing the suspension with a phosphate base suspension and applying it soon after it is made. Tests have shown that when this is done immediate application is necessary to avoid reversion of the P_2O_5 in the suspension mixture. Others have found that they can readily mix the finely ground limestone with UAN solution and a gelling clay to produce a suspension that contains 14%-15% nitrogen and 50% limestone. These types of nitrogen-limestone suspensions are gaining in popularity since they can help to eliminate some passes of the applicator across the field.

"Fluid lime" generally is applied through conventional fluid application equipment that is used to apply suspension fertilizers. The only change required is the use of larger nozzles to pass the limestone. Usually flooding type nozzles are used.

Phosphate Rock Suspension

The techniques used to produce limestone suspensions can be applied also to making suspensions of finely ground phosphate rock. There is abundant evidence (29) that rock phosphates from some deposits, when finely ground, are very effective sources of phosphorus for low-pH soils. In past years, there was an appreciable amount of fertilization carried out in the Midwest by dry application of finely ground rock; however, the practice now has given way to use of soluble phosphates. Likewise, no use of phosphate rock suspension presently is known. In 1976, TVA reported (30) a study on preparation of phosphate rock suspensions. Advantages recognized for the suspension form of rock were the absence of dust in handling; the possibility of using a finer, more agronomically effective grind of rock; and more uniform application to the field. The TVA tests were made largely with North Carolina phosphate, a rock that is among the more effective for direct application. Grinds of 67% and 87% through 325 mesh were tested.

With simple, high-shear mixing of rock with water, allowable viscosity was not exceeded with rock contents up to about 70% with the coarser rock and 65% with the finer one; corresponding P_2O_5 contents were 21% and 19%. Use of about 0.6% TSPP dispersant increased maximum rock contents to 78% and 70% (23% and 21% P_2O_5). However, none of these suspensions made without use of suspending clay had good storage properties; in unagitated storage those made with the coarser grind settled excessively in 1 to 2 hours and those made with the finer grind did so in 1 to 2 days.

Rock suspensions with much better storage properties were made with use of a small proportion of attapulgite suspending clay; however, both proportion of rock and proportion of clay were limited by the imparted viscosity. Suspension of 18% P_2O_5 content (60% rock) with good storage properties was made by the following procedure: (1) mix rock (87% - 325 mesh) with water, 0.5% attapulgite suspending clay, and 0.3% TSPP dispersant, and (2) add 1% ammonium nitrate as a gelling agent during further mixing. Because of the use of dispersant, only moderate mixing action was required. The resultant suspension stored well, without agitation, for at least 1 month.

Micronutrients in Suspensions

Suspensions provide a means of incorporating large quantities of micronutrients into fluid fertilizers (31). There is no problem with solubility such as is inherent in clear liquids, and the incorporation can be accomplished usually by merely adding appropriate amounts of micronutrients to the suspension mixture while it is being made. Experiments show that grades such as 10-34-0-6Zn and 5-15-30-3Zn can be produced from APP solution (11-37-0 from furnace grade superphosphoric acid), potash, zinc oxide, and clay. This is far more zinc than can be dissolved in a clear liquid and would be enough to meet agronomic requirements. The viscosities of freshly prepared 10-34-0-6Zn and 5-15-30-3Zn were 225 and 679 centipoises, respectively, at 70°F (21°C). This is well below the maximum of about 1,000 centipoises at 70°F (21°C) that can be applied satisfactorily.

Viscosity increases as the amount of micronutrient material is increased and as storage time is lengthened. Table 22 shows the viscosities of three 5-15-30 mixtures (contain 1% clay, P_2O_5 source APP solution 11-37-0) made with three different levels of zinc supplied as oxide of high purity (80.3% Zn).

These data show that as zinc content of the 5-15-30 is increased from 2% to 4%, viscosity of the mixture increases from 459 to 835 centipoises. If the zinc content should be increased still further, the viscosity of the mixture probably would exceed 1,200 centipoises. These data show also that viscosities of the suspensions increase with storage time. However, in some instances periodic agitation of the suspension will reduce and prevent this increase in viscosity. When the 5-15-30-3Zn suspension was agitated by air, its viscosity decreased and did not increase with storage time. The data indicate that the 5-15-30-3Zn should have excellent storage characteristics, provided it is agitated periodically. This suspension should be a popular mixture in a satellite station as a source of both potash and zinc. In these stations it could be mixed in a nurse tank with 10-34-0 or 11-37-0 and 32-0-0 liquids to produce various NPK solution-type mixtures that contain zinc. Mixed with a base suspension and 32-0-0, it could be used also to produce other suspensions.

The tabulation below shows the approximate quantities of each micronutrient material that can be incorporated individually into a 15-15-15 suspension mixture (about 1.0% clay and 70% polyphosphate) without adversely affecting the physical properties of the suspension.

0.35% B as sodium borate
1.20% Cu as copper sulfate
1.20% Fe as iron sulfate
0.34% Mn as manganese sulfate
2.50% Zn as zinc sulfate

The 15-15-15 grade suspension used was produced from 12-40-0 APP suspension (P_2O_5 from furnace phosphoric acid), UAN solution (32-0-0 solution grade), potash (0-0-62), and attapulgite suspending clay. These quantities of micro-

nutrients are sufficient to supply most crop requirements.

Several micronutrients added together as a micronutrient package may or may not cause viscosity problems. The data shown in table 23 are from bench-scale tests.

These data show that the addition of several micronutrients as the source materials shown in table 23 did not have adverse effects on the 15-15-15 suspension. However, plant data show that when manganous-manganic oxide was used in combination with zinc oxide, flowers of sulfur, borax, APP base suspension, 32-0-0, and potash to produce a 16-8-16-1.72S-0.85Zn-0.84Mn-0.09B, the suspension became too viscous to pump after about 1 hour of storage, even though immediately after the suspension was produced, its initial viscosity was only 310 centipoises at 70°F (21°C). Therefore, in the production of suspensions containing several micronutrients, care should be taken to select micronutrient source materials that will not react with each other and form excessively viscous suspensions. It is advisable not to store suspensions that contain several micronutrients unless storage already has been tested and proven satisfactory.

Probably the most convenient way to add micronutrients (usual size 100% -20 mesh) to a mix tank is through an injector similar to the one shown in figure 35. Also those

Table 22. Viscosities of 5-15-30-XZn mixtures[a]

	Centipoises at 70°F (21°C)			
Grade	Freshly prepared	One-day storage[b]	One-week storage[c]	Two-week storage[c]
5-15-30-2Zn	459	966	838	798
5-15-30-3Zn	679	1,436	1,290	1,234
5-15-30-4Zn	835	Too thick to be measured or agitated by air sparging	–	–

[a]5-15-30 made with 11-37-0 (furnace grade P_2O_5), solution-grade potash, and ammonia; clay content 1%.
[b]Material not agitated prior to viscosity measurement.
[c]Viscosity taken after agitation by air sparging.

Table 23. Addition of mixture of micronutrients to 15-15-15 suspension

	Apparent viscosity, Centipoises	
Mixture added	Fresh product	One-day aging
0.1% B as sodium borate ($Na_2B_{4\,0\,7}\cdot 5H_2O$, 14.3% B)		
0.2% Cu as copper sulfate ($CuSO_4\cdot 5H_2O$)		
0.6% Fe as iron sulfate ($Fe_2SO_4\cdot 9H_2O$)	200	470
0.6% Mn as manganese sulfate ($MnSO_4\cdot XH_2O$)		
0.3% Zn as zinc sulfate ($ZnSO_4$, 36% Zn)		

plants that have excellent agitation seem to be able to dissolve micronutrients in clear liquids or to disperse them in suspensions with relative ease. The mixing procedure that usually works best is as follows: add water and clay to mix tank first, disperse the clay in the water by mixing, and then add the UAN solution. Start circulating this mixture through the injector. Then add the micronutrients through the injector into the recirculating fluid. Next the phosphate base solution (10-34-0 or 11-37-0, etc.) is added. The potash is added last in the mixing sequence.

This same mixing procedure works well in plants that do not have injectors, except the preweighed micronutrients are poured from the open bag over the top of the tank while the water-clay-nitrogen solution mixture is recirculated in the mix tank. Care should be taken to avoid dumping the micronutrients in large batches. They should be sprinkled into the tank at a reasonable rate. If this is done, the formation of large balls of micronutrients can be prevented and the micronutrients can be easily dissolved or dispersed in the fluid.

The above information relates to the use of micronutrients with phosphate suspensions that were produced from furnace phosphoric acid. Actually, good results can also be obtained when wet-process phosphoric acid is used as a source of phosphate for the manufacture of the phosphate suspension. However, when the wet-process acid source is used, no more than about 80% of the micronutrient values shown above should be added and, in addition, the total plant nutrient content may have to be lowered by about 10%.

STORAGE OF SUSPENSIONS

Storage Vessels

It is recommended that suspensions be stored in vertical, mild steel or plastic tanks equipped for air sparging (32). A tank size of about 12 feet diameter by about 20 feet tall (16,000 gallons) is very satisfactory. Thickness of the metal should be about 1/4 in. Life of a steel tank can be extended by coating the inside with a material such as an epoxy-base paint.

The tanks may have flat or cone bottoms. Although cone bottom tanks are more expensive than flat bottom, it is easier to resuspend materials that settle in the cone of the tank. When suspensions are not of good quality, solids sometimes settle and collect on the bottom at the outside walls of a flat bottom tank and cannot be resuspended with air sparging. The problem can be avoided with cone bottom tanks.

The foundation for a storage tank should be about 2 feet deep and made of 1/4-in. crushed rock or gravel. The gravel should be well compacted. Concrete may be used

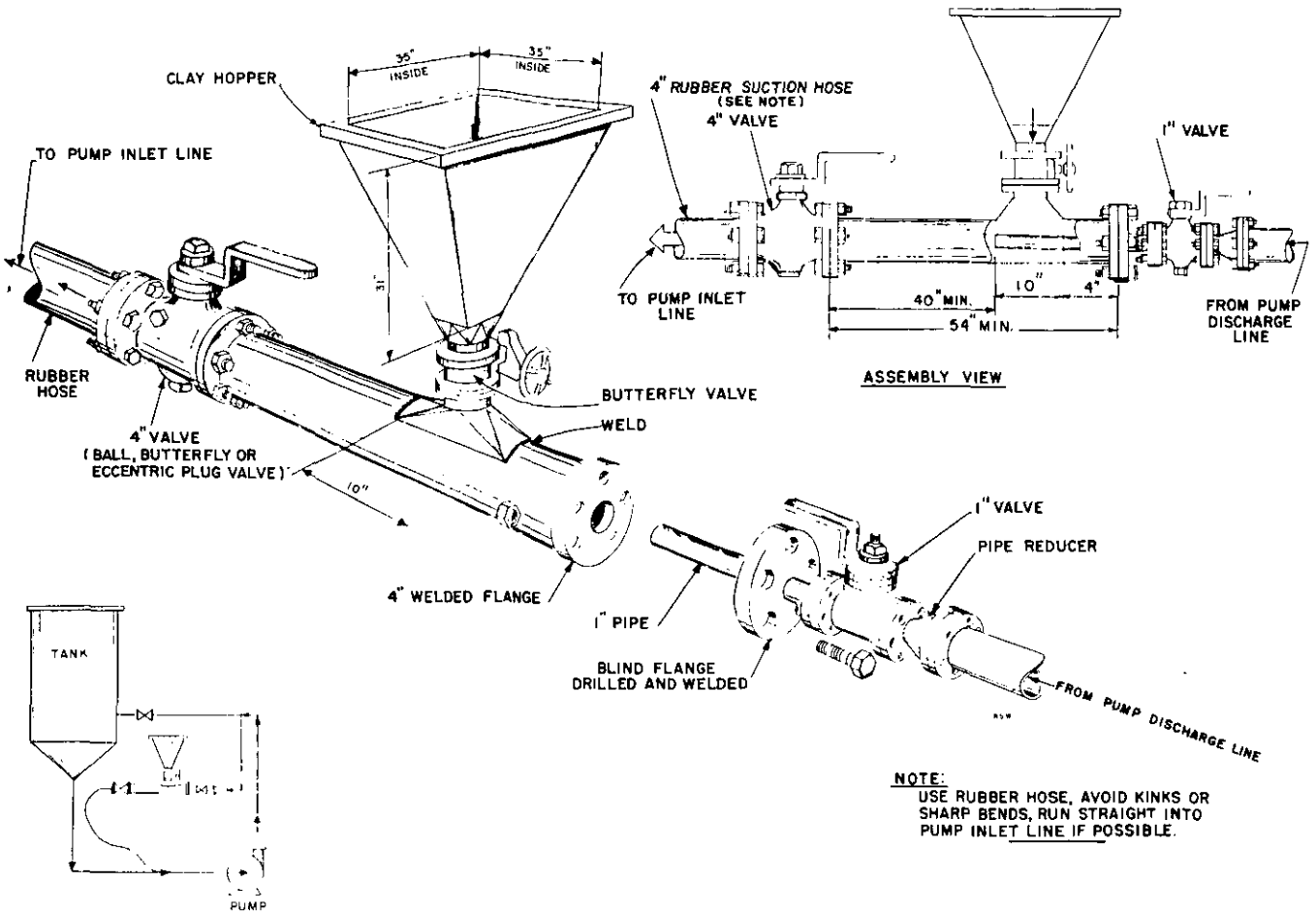

Figure 35. Micronutrient and clay injector for fluids

also. The flat bottom of a steel tank should be coated on the outside with asphalt or epoxy resin paint before it is placed on the foundation. The location should be well drained so that the tank bottom does not ever stand in water.

If a separate centrifugal pump is to be used for transferring the suspension into and out of storage, the pump should have a 5-in. inlet and a 4-in. outlet and be equipped with a 30-hp motor. A more powerful motor may be required if pumping is against a high head, such as a long run of pipe or an exceptionally high elevation. The transfer lines should be 4-in. pipe; the pipe may be black iron or PVC schedule 80 plastic. The plastic pipes should be equipped with expansion joints and should be well supported (see chapter 10).

Sparging

Recommended design for air sparging for flat bottom tanks is shown in figure 36. A sparging system for a cone bottom tank is shown in figure 37. An air compressor powered by a 3-hp electric motor or gasoline engine is adequate. The air reservoir (300-gallon tank) is pressurized to 100 to 125 pounds per square in. Then the control valve for regulating the air discharge is opened wide to allow all the air to discharge through the tank to give the suspension a rolling type mix. The reservoir is recharged then to sparge the next tank. The reservoir may be connected to as many tanks as desired and one tank at the time is sparged.

The primary purposes of sparging air are to prevent the gel in the suspension from becoming too strong, to control syneresis (formation of clear liquid layer on top of the suspension), and to prevent growth of large crystals in the suspension.

For the purpose of controlling gel strength and syneresis, sparging each tank once or twice a week is adequate. "Sparging" means discharging the air from the fully charged reservoir once into the tank.

To prevent excessive crystal growth, other factors have to be considered. Crystal growth in suspensions occurs mainly as a result of cooling the suspension. As the temperature decreases, the amount of salt in the solution phase decreases by crystallizing on the surfaces of the existing crystals. If cooling is uniform throughout the tank, growth

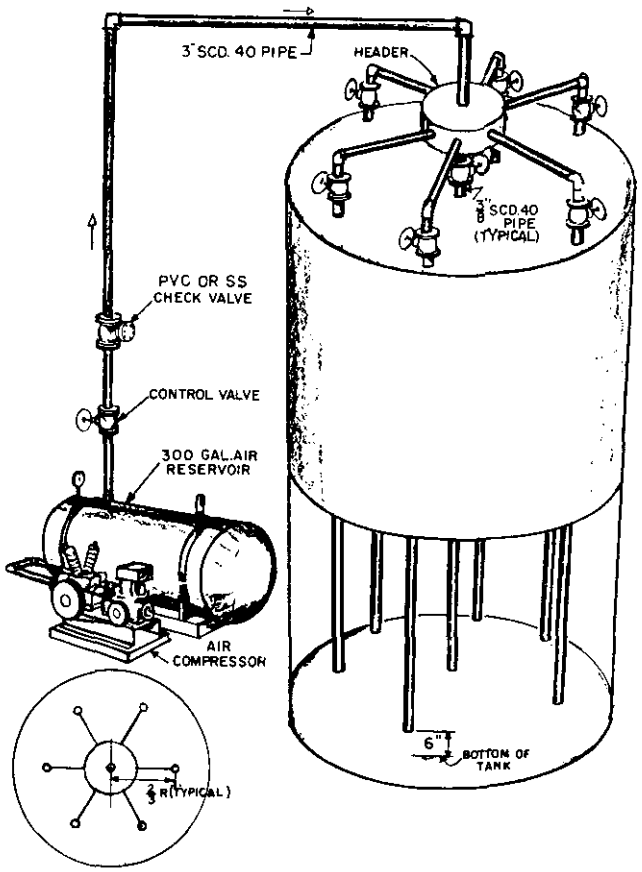

Figure 36. Pipe sparging system for suspensions

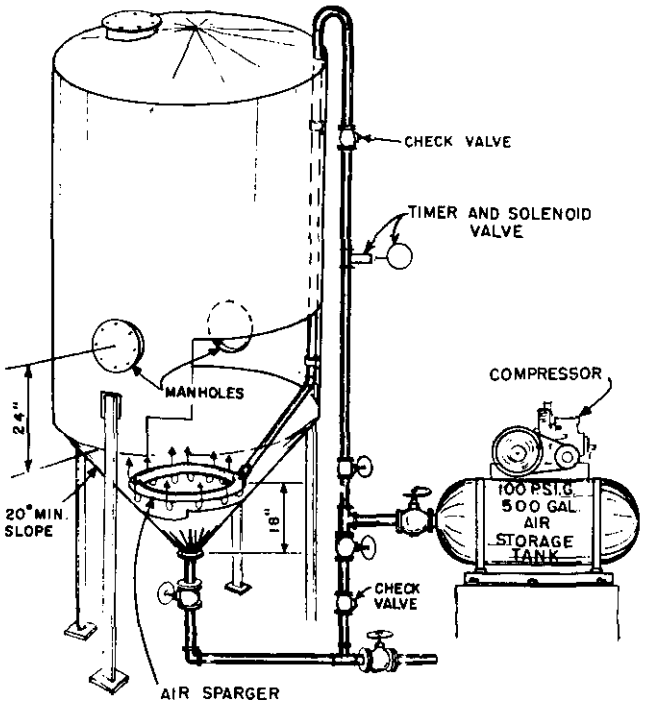

Figure 37. Cone bottom suspension storage tank with air sparger system

of all crystals will be uniform and none of the crystals will grow excessively. However, if the cooling is not uniform, such as getting colder next to the tank wall, the crystals in the colder part of the suspension will grow excessively. They will be fed by the warmer, more concentrated solution phase by diffusion of salt through the liquid to the colder more dilute solution. By this means, selective crystal growth occurs and excessively large crystals may form next to the cold tank wall. The remedy is to sparge the tank frequently when the suspension is cooling. When the air temperature drops in the fall and winter, the suspension should be sparged once or twice daily until the temperature of the suspension is about the same as the temperature of the outside air. This frequent sparging will cause the temperature throughout the tank to be uniform while cooling and will prevent excessive growth of crystals. When the daily average air temperature is about the same as the temperature of the suspension and remains about constant or rises, the routine schedule of sparging once or twice a week may be resumed.

The suspension always should be sparged immediately before it is withdrawn from the tank. Sparging will make the suspension more fluid and should correct any syneresis (mix in any clear liquid layer) that may have occurred.

During winter, in those regions where temperatures are frequently below 0°F (-18°C), a suspension sometimes becomes frozen to a solid mass. However, when the outside temperature subsequently remains above 40°F (4.4°C) for a period of about a week the suspension will become fluid and can be sparged.

TRANSPORTATION OF SUSPENSIONS

One of the drawbacks of liquid mixed fertilizers is low analysis. With the new high-speed applicators which apply fluid fertilizer at a rate of more than 1 acre per minute, it is very difficult to keep the applicator charged and moving. Part of this problem can be solved by using high analysis suspensions so that more plant nutrients per load can be delivered to the applicator. However, there are some problems in transporting suspensions that do not exist with solutions.

The main difficulty is that road vibrations within the transport tank cause the gel structure of many suspensions to weaken enough to allow crystals to settle. This difficulty usually can be circumvented by recirculation of suspension through a sparger while in transport. Figure 38 is a diagram of a transport truck for suspension fertilizers equipped with an agitation sparger. This transport is equipped with a recirculating pump driven by a hydraulic motor. The pump

is a centrifugal type and usually has a discharge diameter of 3 in. Piping to the pump and sparger is of 3-in. schedule 40, stainless steel or plastic pipe. The sparger has 1/4-in. holes drilled on 4-in. centers. The liquid recirculating through the sparger sweeps the bottom of the tank and causes the fluid to be agitated.

Some companies prefer cone-bottom trucks with an air unloading system as shown in figure 39. Air is injected

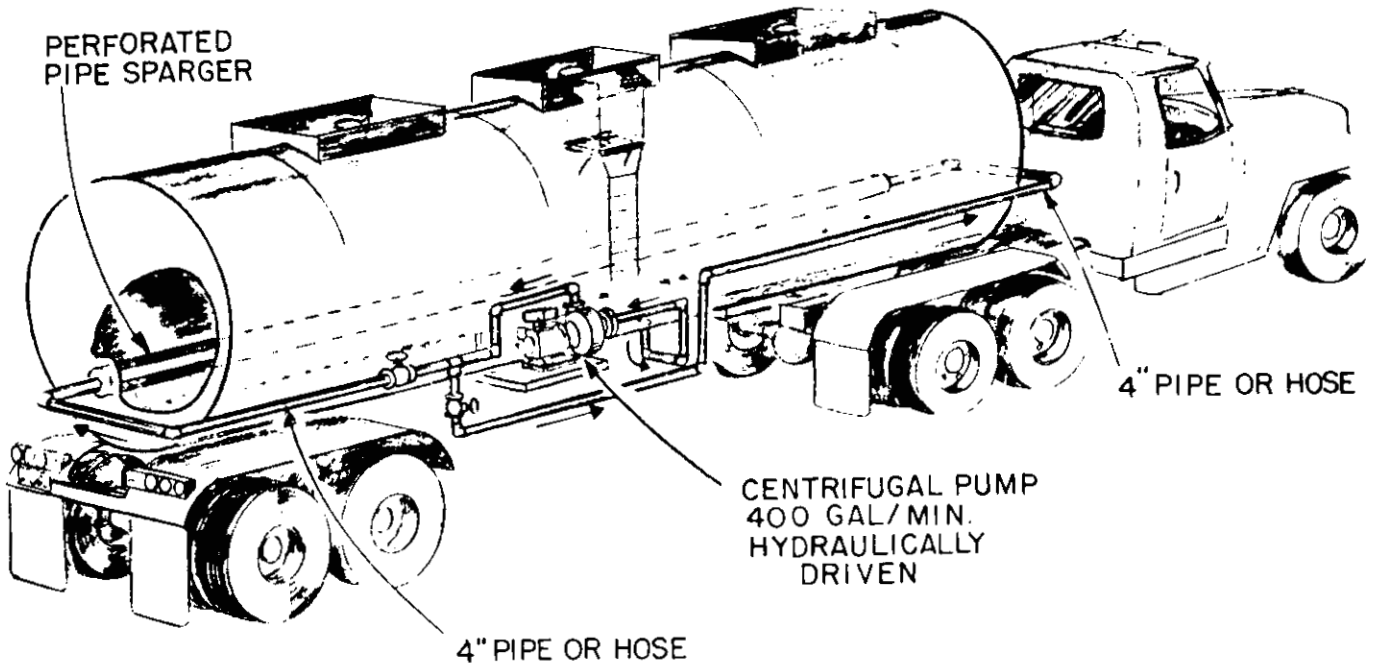

Figure 38. Transport truck with pipe sparger for suspension fertilizers

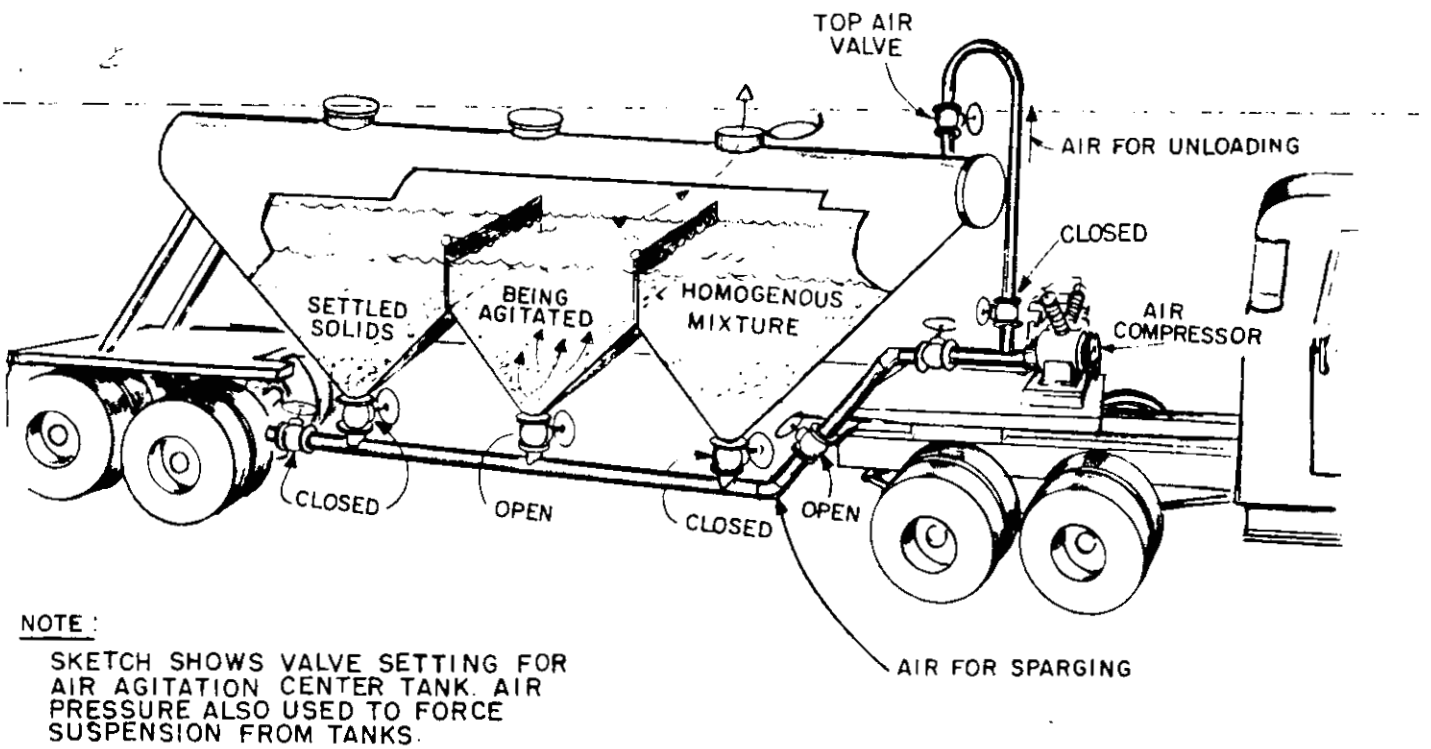

Figure 39. Cone bottom transport

at the base of each hopper and filters up through a diffuser pad to agitate the suspension and make it flow. When the appropriate pressure is built up in the tank (up to 25 psi), the discharge valve is opened so that air blown into the suspension forces it through the discharge line. Pressure remains constant and the flow rate is controlled by a butterfly discharge valve.

Other companies transport fluids in spherical tanks on flat-bed trucks. The spheres shown in figure 40 are made of polyolefin plastic and are excellent for storing and transporting suspensions. Materials that settle to the bottom are circulated to the top of the spheres. No difficulties have been reported with deterioration of the plastic over a period of 10 years.

Field experience has shown that causes for delay in keeping materials supplied to the large applicators are:

1. The size and number of transports used to haul suspensions to the applicator.
2. Time required to pump the suspension from the transport to the applicator.

One equipment company has developed a tilting type transport that can be emptied quickly into the applicators. A photograph of this transport is shown in figure 41. These tanks are self-supporting and hinged on one side.

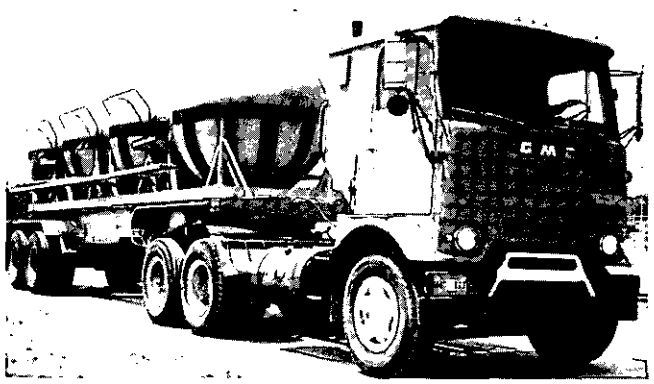

Figure 40. Spherical transport tank

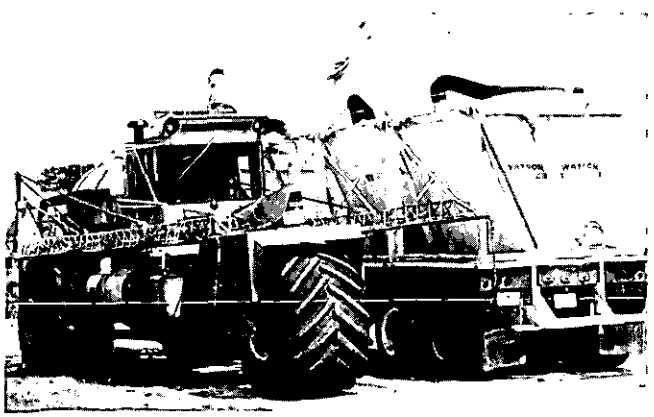

Figure 41. Tilting-type transport for suspensions

They have a hydraulic system which raises and quickly unloads the tank as it is dumped into the applicator. Other companies have installed large transfer pumps with capacities up to 300 gallons per minute.

The application of suspensions is discussed in chapter 9.

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Chapter 8

Specialty Grades of Fluid Fertilizers

By Eugene B. Wright, Jr.

Specialty fertilizers are frequently thought of as expensive, nonagricultural fertilizer products used mainly for feeding house plants or nursery stock. A popular form might be tablets or capsules of plant nutrients in a concentrated form which easily dissolves in water to yield a low analysis product. Such a picture is incomplete since it does not include those products used for fertilizing row crops by foliar application or feeding high-cost crops requiring special consideration, such as low chlorine content in tobacco fertilizers. To include these special use materials, this chapter will include those frequently used chemical compounds which supply one or more of the primary plant nutrients and are used or applied in a distinctive or unique manner in a liquid form.

The decade of the 1940s appears to be the beginning period of modern liquid fertilizer development at which time production of liquid mixed fertilizers started to become significant in the Pacific Coastal areas of the United States (1). This interest in liquids rapidly moved eastward during the next decade and a half. During this period, interest was demonstrated in nonchloride forms of potassium base liquids especially since the supply of potassium hydroxide periodically exceeded the normal demand and a natural outlet for this excess could be liquid mixed fertilizers. John D. Hatfield in an internal TVA memorandum outlined the solubility relationship of various potassium orthophosphates in the system K_2O-P_2O_5-H_2O at 32°F (0°C) which is shown in figure 42. The solid lines indicate the solubility relationship, the broken lines show constant fertilizer ratios, and the dotted line gives the solubility in the metastable region of dipotassium phosphate trihydrate. The solubilities for various ratios are given in table 24. The system K_2O-P_2O_5-H_2O is characterized by two regions of high solubility. The plant nutrient content increases from 29% for the 0-1-1 ratio to about 55% for the 0-6-7 ratio; it decreases to about 44% for the 0-3-4 ratio, increases to 55% for the 0-5-8, and then decreases again as the K_2O:P_2O_5 ratio increases. Because of the steep solubility gradient, small changes in composition may cause precipitation in the regions of highest solubility. For example, if the P_2O_5 content of 0-25.4-29.6 were 25%

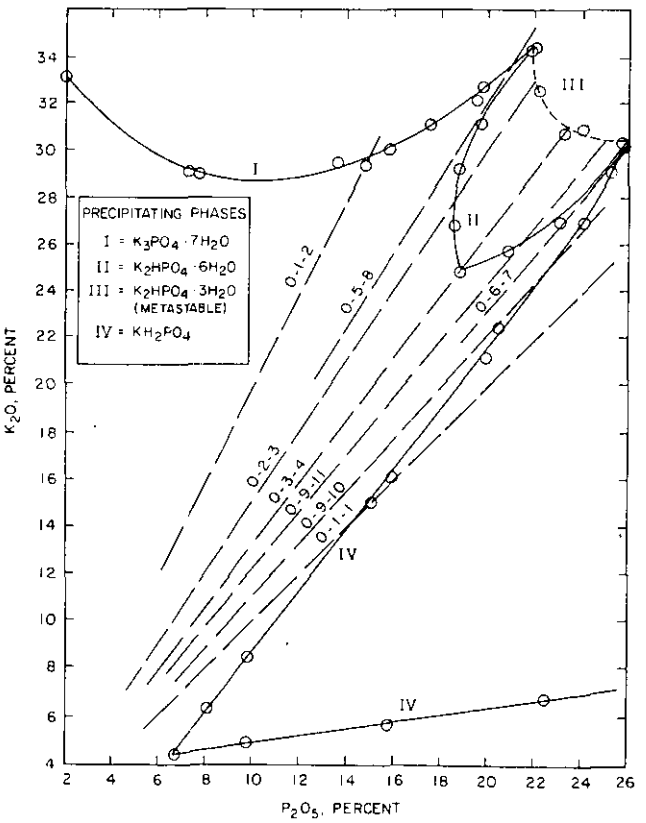

Figure 42. Solubility in the system K_2O-P_2O_5-H_2O at 32°F

instead of 25.4, precipitation would occur at 32°F (0°C) and the liquid would analyze 0-23-27.2.

Ratios such as 0-2-1 and 0-3-1 are of little interest in this system because of low solubility and high acidity of the solutions. Ratios such as 0-1-2 and 0-5-8 are questionable because of their alkalinity.

The addition of urea to the 0-1-1 ratio not only looks promising from the possibility of high analysis, but also permits the preparation of grades in ratios such as 1-5-5 and 1-4-4; these liquid grades are too corrosive when prepared from ammonia, phosphoric acid, and muriate of potash.

When dipotassium phosphate (0-40-52) is mixed with ammonium phosphate liquid, complete liquid grades of very high analysis are possible. Two such grades are 4-24-12 and 6-24-6.

A 5-20-20 polyphosphate grade with all the potash supplied as potassium hydroxide and with all of the nitrogen supplied as urea had a salting-out temperature of 18°F (-7.8°C) and urea was the crystallizing phase.

The introduction of electric furnace superphosphoric acid by TVA in mid-1950 led to the production of high analysis ammonium polyphosphate liquids on a commercial scale. Research also was directed toward liquid fertilizers based on superphosphoric acid (76% P_2O_5) and potassium hydroxide (2). Salt-out and saturation temperatures, crystalline phase, pH, and specific gravity measurements for several grades in representative ratios of low chlorine containing fluids from this study are shown in table 25. These grades were produced batchwise by adding in succession the potassium hydroxide, superphosphoric acid, water, and ammonia, if needed, while keeping the reaction mixture temperature below 180°F (82.2°C) by cooling; solid raw materials such as urea were added last. The product was then rapidly cooled below 100°F (37.8°C) to further lessen the hydrolysis of the polyphosphate which is enhanced at low pH and/or high temperature. Salting-out temperatures of the products were determined by cooling the solution at a rate of 4°F (2.2°C) per hour until crystals formed. The solution was then warmed at the same rate until the crystals dissolved to determine saturation temperatures. The maximum grade with a salting-out temperature below 32°F (0°C) was determined for each type of solution in the ratios studied. The liquids that had saturation temperatures below 32°F (0°C) also were tested in storage for 1 week at 32°F (0°C). The crystallizing phases for most of the liquids studied were identified by petrographic analysis. An electronic pH meter was used for pH measurements and a hydrometer was used for specific gravity determinations.

Table 24. Concentration of plant nutrients in the system K_2O-P_2O_5-H_2O at 0°C

Ratio	Grade	Total plant nutrient, %[a]
0:1:1	0-14.5-14.5	29.0
0:9:10	0-22.6-25.2	47.8
0:6:7	0-25.4-29.6	55.0
0:9:11	0-21.4-26.2	47.6
0:3:4	0-18.8-25.0	43.8
0:2:3	0-18.5-27.8	46.3
0:5:8	0-21.2-33.9	55.1
0:1:2	0-14.9-29.7	44.6

[a]Percent ($N + P_2O_5 + K_2O$).

Superphosphoric acid, potassium hydroxide, urea, and water were used in the production of 1:2:2, 1:2:3, 1:3:3, 2:4:5, 1:1:1, 1:2:1, and 1:3:1 ratio fertilizers. These products contained no chlorine. Ammonia was included in formulations for the 1:2:1 and 1:3:1 ratios, otherwise low pH products would result since the amount of potassium hydroxide was not sufficient to neutralize the acid. Most of the products were essentially neutral (pH 7.0 to 7.5) except those of 1:2:3 and 2:4:5 ratios, which had a high pH (8.3 to 11.9) because their ratio of K_2O to P_2O_5 was high. The caustic nature of the latter products would not present any serious corrosion problems with mild steel tanks and equipment; however, aluminum equipment would not be suitable.

In developing the data for table 25, it was found that the salting-out temperatures decreased and then increased as the concentration of the products increased. Water was the crystallizing phase at the lower concentrations, and increasing the concentration depressed the freezing point. At the 1:2:2 ratio, salting-out temperature of the 5-10-10 grade was 12°F (-11.1°C). Increasing the concentration to a 7-14-14 grade depressed the salting-out temperature to -5°F (-15°C). Further concentration caused urea to crystallize at a higher solution temperature of 36°F (2.2°C).

Although small, the differences between salting-out and saturation temperatures shown in the table indicate that there was some supercooling during salting-out determinations or overheating during saturation determinations. Nevertheless, the accuracy is believed to be sufficient for practical application in production of the grades listed. None of the solutions with saturation temperatures below 32°F (0°C) crystallized during storage for 1 week at 32°F (0°C). The superphosphoric acid was added to the potassium hydroxide rather than vice versa. This is believed to minimize hydrolysis and also avoids forming the relatively insoluble monopotassium phosphate.

Specimens of mild steel A 283 and stainless steel types 304 and 316 were tested for corrosion by a slightly basic potassium polyphosphate solution (3). A 0-24-26 grade with an initial polyphosphate content of 77% and a temperature of 130°F (54.4°C) was used. At the end of 2 weeks, the corrosion rate was measured and the samples were subjected to further possible attack in fresh solution for an additional 2 weeks. Attack on the stainless steel

Table 25. Low-chlorine fertilizers made from superphosphoric acid and potassium hydroxide

Grade	Formulation, lb/ton: H_3PO_4, 76% P_2O_5	Ammonia, 82.3% N	KOH, 37.7% K_2O	Urea, 46% N	Water	Temperature, °F: Salt Out	Saturation	Crystalline phase	Crystallized during storage for 1 week at 32°F	pH	Specific gravity at 85°F
					O-X-X ratio						
0-25-25	658	–	1,326	–	16	-14	-13	H_2O	No	7.1	1.561
0-26-26[a]	684	–	1,316	–	–	Room temperature		KH_2PO_4	Yes	–	–
0-29-31[b]	763	–	849		388	<-15	–	–	No	7.8	1.725
0-27-36[b]	711	–	986	–	303	<-15	–	–	No	11.4	1.785
					1:1:1 ratio						
10-10-10	263	–	531	435	771	15	18	–	No	7.0	1.270
11-11-11	290	–	584	478	648	30	32	Urea	No	7.2	1.286
12-12-12	316	–	636	522	526	47	51	–	Yes	7.2	1.317
13-13-13	342	–	690	565	403	65	68	–	Yes	7.3	1.355
					1:2:1 ratio						
9-18-9	474	73	477	261	715	0	4	–	No	7.0	1.278
10-20-10	526	81	531	290	572	22	26	Urea	No	6.9	1.361
11-22-11	579	89	584	319	429	51	56	Urea	Yes	7.3	1.400
					1:2:2 ratio						
5-10-10	263	–	531	217	989	12	14	H_2O	No	7.2	1.206
6-12-12	316	–	637	261	786	6	8	H_2O	No	7.2	1.250
7-14-14	368	–	743	304	585	5	10	H_2O	No	7.4	1.316
8-16-16	421	–	849	348	382	36	39	Urea	Yes	7.5	1.380
					1:2:3 ratio						
5-10-15	263	–	796	217	724	1	2	–	No	11.5	1.275
6-12-18	316	–	955	261	468	15	20	–	No	11.9	1.364
7-14-21	368	–	1,114	304	214	56	58	–	Yes	11.9	1.430
					1:3:1 ratio						
7-21-7	553	113	371	102	861	6	8	–	No	6.7	1.295
8-24-8	632	130	424	116	698	-4	-2	H_2O	No	6.7	1.360
9-27-9	711	146	477	130	536	87	92	Urea	Yes	7.3	1.474

Table 25 (continued)

Grade	Formulation, lb/ton: H_3PO_4, 76% P_2O_5	Ammonia, 82.3% N	KOH, 37.7% K_2O	Urea, 46% N	Water	Temperature, °F: Salt Out	Saturation	Crystalline phase	Crystallized during storage for 1 week at 32°F	pH	Specific gravity at 85°F
					1:3:3 ratio						
3-9-9	237	–	477	130	1,156	18	20	–	No	7.0	1.172
4-12-12	316	–	637	174	873	12	13	–	No	7.1	1.255
5-15-15	395	–	796	217	592	-1	+1	–	No	7.2	1.330
6-18-18	474	–	955	261	310	26	29	–	No	7.4	1.408
7-21-21	553	–	1,114	304	29	65	71	–	Yes	7.4	1.505
					2:4:5 ratio						
4-8-10	211	–	531	174	1,084	15	16	–	No	8.3	1.174
6-12-15	316	–	796	261	627	-2	0	–	No	8.9	1.310
7-14-18	368	–	955	304	373	35	40	–	Yes	10.1	1.390

[a] Used 47% KOH solution.
[b] Used Solid KOH (73% K_2O).

was negligible at the end of 28 days. Samples of mild steel placed in unaerated solution corroded at the rate of 10 mils per year based upon the 14-day test and 14 mils per year when reimmersed for an additional 14 days. Samples immersed in an aerated solution were corroded at nearly twice the unaerated rate (19 and 25 mils per year). A partially immersed cold worked sample of mild steel was attacked at the rate of 27 and 40 mils per year under static conditions. Grooving to a depth of 7 mils occurred at the liquid air interface.

Table 26 compares the maximum grade possible which would store at 32°F (0°C) for 7 days and 30 days at room temperature without salting out when the source of potash is potassium hydroxide instead of the normally used potassium chloride. The acid used was 76% P_2O_5 furnace acid and the polyphosphate level was about 50%. The data in general shows the grades to be two to three units higher when the potassium hydroxide supplied the potash requirements and supplemental nitrogen was supplied as urea. Supplying some of the potash as potassium chloride generally caused the salt-out temperature to increase as did supplying the supplemental N as UAN solution rather than urea. A 7-14-14 solution with all the potash supplied as potassium hydroxide withstood the storage tests at 32°F (0°C), but a 6-12-12 was the highest satisfactory grade when potassium chloride was included to supply 50% of the potash requirements. The maximum grade was further reduced to 5-10-10 when UAN solution was the source of supplemental nitrogen or when KCl was the only source of potash.

Table 26. Effect of source of potash on maximum grades of liquid fertilizer made with superphosphoric acid

	Maximum grade of liquid fertilizer made with indicated source of potash[a]	
Ratio	KOH	KCl
0:1:1	0-25-25	—[b]
1:1:1	11-11-11	9-9-9
1:2:1	10-20-10	8-16-8
1:2:2	7-14-14	5-10-10
1:2:3	6-12-18	3-6-9
1:3:1	8-24-8	7-21-7
1:3:2	8-24-16	4-12-8
1:3:3	6-18-18	3-9-9
1:4:2	6-24-12	—[b]
1:4:4	5-20-20	—[b]
1:6:6	3-18-18	—[b]
2:4:5	6-12-15	4-8-10

[a]Maximum grade that stored for 7 days at 32°F and 30 days at room temperature without salting out.

[b]Solution would be highly acidic using potassium chloride as the only source of potash.

A 0-25-25 grade was the most concentrated 0:1:1 ratio that salted out below 32°F (0°C). Water was the crystallizing phase. A 0-26-26 salted out at room temperature and potassium dihydrogen phosphate was the crystallizing phase. With 80% P_2O_5 electric furnace acid and KOH, a 0-30-30 solution containing 80% polyphosphate is satisfactory at 32°F (0°C) (4). Liquids of maximum plant food content can be produced from superphosphoric acid and potassium hydroxide when the P_2O_5:K_2O ratio is slightly less than 1. This is illustrated by the 0-29-31 and 0-27-36 grades with salting-out temperatures below -15°F (-26.1°C) (table 25). With orthophosphoric acid and potassium hydroxide, the maximum grade with a salting-out temperature below 32°F (0°C) for a 0:1:1 ratio is 0-14-14 (table 24).

The source of P_2O_5 for the specialty grades discussed so far has been electric furnace acid. So long as solubility relationships were not exceeded, a water clear solution resulted from the reaction of 76% and 80% P_2O_5 electric furnace acid and potassium hydroxide.

A slightly cloudy product resulted when extremely high polyphosphate electric furnace (83% P_2O_5 acid - 95% poly) was reacted with KOH to produce a 0-25.3-25.9 solution having a polyphosphate content of 91%. The pH and specific gravity at room temperature were 8.1 and 1.56 respectively.

TVA produced about 1,100 tons of nominal 0-26-25 potassium polyphosphate solution in the liquid fertilizer demonstration plant in 1976 to fulfill a crash agronomic study on the benefits of foliar feeding various crops—soybeans in particular. This product was made at a rate of about 15 tons per hour by reacting electric furnace superphosphoric acid containing about 80% P_2O_5 with 45% potassium hydroxide solution. The KOH solution, super acid, and a small quantity of water to adjust the product concentration were fed simultaneously to a mixing vessel. The temperature of the product in the mix vessel was maintained at about 114°F (45.6°C) by recirculating it in a closed loop through a shell and tube heat exchanger. Product overflowing the mixing vessel into a surge tank was further cooled to about 72°F (22.2°C) in a secondary cooling system before being pumped to storage. A tabulation of representative chemical analysis and pH measurements is shown in table 27. The nominal foliar grade produced from the 0-26-25 was 10-2.4-4 with 0.6% sulfur. Agronomic results of these studies were summarized by Gray in a paper presented to The Fertiliser Society of London on October 14, 1977 (6).

Limited research has also been conducted using wet-process acid of varying polyphosphate content as the source of P_2O_5. A 0-25-26 grade was produced using wet-process acid produced from both calcined and uncalcined rock. The polyphosphate level varied from 0% to 50%. As found when electric furnace acid is used, the solubility of 0-25-26

Table 27. Production of 0-26-25 potassium polyphosphate liquid fertilizer (8)

Grade	Percent of P_2O_5 as polyphosphates	P_2O_5:K_2O ratio	pH	Sp. Gr.	Temp, °F
0-25.2-24.6	69	1.024	7.4	1.527	107
0-26.2-25.3	73	1.036	–	1.554	113
0-25.7-25.4	82	1.012	7.4	1.551	114
0-25.8-25.5	81	1.012	7.3	1.554	114
0-26.3-25.7	76	1.023	7.2	1.553	116
0-26-0-25.0	76	1.040	7.2	1.553	116
0-25-7-25.9	81	0.992	7.5	1.551	114
0-26.6-26.0	85	1.023	7.3	1.552	114
0-26.5-25.3	83	1.047	7.1	1.551	113
0-26.5-25.0	82	1.060	7.0	1.550	112
0-26.3-25.1	76	1.048	7.1	1.550	120

grade is more favorable than that of either 0-25-25 or 0-26-25 grades. The acid was added to the potassium hydroxide to keep the solution basic which allowed production without going through the minimum solubility area where the K:P mole ratio is 1 (KH_2PO_4 is the least soluble of the potassium orthophosphate salts). In all tests, considerable precipitation occurred which was determined to be K_2SO_4 along with some iron and aluminum salts analogous to those produced by ammoniation of wet-process acid. Also present were crystals of KH_2PO_4. These dissolved upon dilution with 26% K_2O solution (31% KOH) when the grade reached 0-23-26 (pH about 8.0). Further dilution with water to 0-14-16 grade dissolved the potassium sulfate. Upon standing, some of the 0-14-16 grade produced with low polyphosphate gelled. The undissolved solids tend to precipitate rapidly from the wet-process solutions so that relatively clear liquid can be separated either by decantation or filtration.

Sources of potassium other than KOH to produce potassium phosphate solutions have been studied. These include potassium bicarbonate, potassium carbonate, cotton burr ash, and reaction of KCl and acid at high temperatures (7). The salting-out temperatures of 0-20-20 solutions produced with potassium bicarbonate as the source of K were similar to those made with potassium carbonate and with potassium hydroxide. Considerable foaming occurred when the acid was mixed with solutions of either K_2CO_3 or $KHCO_3$; however, the foaming can be managed by providing extra free board in the mixing vessel and a means of foam breaking. A mechanical foam breaker similar to a whisk which is attached to the agitator worked well.

Samples of cotton burr ash which contained about 37% K_2O as carbonate, were leached with about 3 parts water per unit of ash to yield a 10% K_2O solution removing about 80% of the K_2O from the ash. The remaining 20% K_2O remained in the residue which was separated from the liquor. This 10% solution could be neutralized with 76% superphosphoric acid to supply about half the K_2O in a 5-10-10 specialty grade. Leaching with less than about 3 parts water per unit of burr ash resulted in unsatisfactory extraction of the K_2O from the ash.

A process for producing fertilizer grade KH_2PO_4 was discussed at the ISMA Technical Conference in Sandefjord, Norway, in September 1970 (8). In this process, KCl is reacted with hot H_2SO_4 [400°F (202.2°C)] to evolve relatively pure HCl and form a residue of $KHSO_4$ in H_2SO_4. The latter is reacted with rock phosphate to form a slurry of KH_2PO_4, gypsum, H_3PO_4, and impurities from the rock. Gypsum is filtered from the slurry; crystals of KH_2PO_4 are centrifuged from a mixture of the filtrate and methanol, after which the methanol is recovered by distillation leaving a still bottom rich in H_3PO_4. About the same time Pennzoil United, Inc., and Goulding Fertilizer, Ltd., Ireland, announced similar processes for producing potassium polyphosphate (9). Neither process has been fully developed to commercial scale.

TVA demonstrated a somewhat similar process producing a solid product using wet-process acid and KCl at the 5th Demonstration of Fertilizer Technology in 1964. Heating KCl and wet-process acid to about 600°F (315.6°C) for 1 hour produced a melt which was sticky and very hygroscopic upon cooling (7). Addition of calcined dolomite to the melt yielded a dry product analyzing about 0-48-26 which had good physical characteristics; however, while 90% of the P_2O_5 was citrate soluble, only about 48% of the P_2O_5 was water soluble. If, instead of adding dolomite, the cooled melt was ammoniated to a pH of 6.5, a 4-24-12 liquid grade resulted with all of the P_2O_5 water soluble and 60% of it present as polyphosphate. Heating the KCl-acid mixture to temperatures between 600°F (315.6°C) and 1,400°F (760.0°C) caused the reaction products to solidify. Continued heating to 1,500°F (815.6°C) refluidized the reactants and produced a melt analyzing 0-56-36 with 98% of the P_2O_5 as highly condensed polyphosphates. The product was unsuitable for production of high analysis liquids since gels formed in mixtures of cooled melts and 1 to 2 parts water.

The addition of sodium tetraborate prior to heating to 1,500°F (815.6°C) to furnish 2% boron reduced condensation of the phosphates to only pyro and tripolyphosphates thereby increasing the solubility of the solid melt in water. A 0-25-16-1B liquid having good storage characteristics resulted when equal parts of melt and water were mixed.

Although reaction of KCl with phosphoric acid has not become commercially feasible, reaction of KCl with nitric acid to make large tonnages of KNO_3 has been accomplished. Southwest Potash in Vicksburg, Mississippi, successfully operated a patented process which also yields chlorine gas as a secondary product beginning in 1963

(10). The Israel Mining Industries at Haifa, Israel, reacts KCl and nitric acid to produce hydrochloric acid and potassium nitrate. Laboratory tests were made at TVA to determine the suitability of potassium nitrate for production of 1:1:1 and 1:2:2 ratio tobacco fertilizers using 8-24-0 and 11-37-0 grade base solutions. When needed, supplemental nitrogen was supplied as urea-ammonium nitrate solution and supplemental potash as potassium chloride. The maximum grades that were satisfactory at 32°F (0°C) were 5-5-5 and 3-6-6, when made with both base solutions. Comparative tests resulted in the same maximum grades when using potassium sulfate, the usual source of potash for tobacco. An 8-25-3 made by blending 10-34-0 liquid ammonium polyphosphate and KNO_3 had a salt-out temperature below 20°F (-7°C).

The solubility relationship of several potash salts with water at various temperatures are shown in table 28. Very slight interest has been shown in solutions of these salts even as specialty products because of their low analysis or high cost. The economics of foliar fertilization with them is yet to become favorable.

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6. R. C. Gray, "Foliar Fertilisation With Primary Nutrients During Reproductive Stage of Plant Growth," Fertiliser Society of London, Proceeding No. 164, October 1977 (TVA Reprint Number X 388).
7. New Developments in Fertilizer Technology, 5th Demonstration, October 6-7, 1964.
8. *Fertilizer Abstracts*, Number 1317, No. 8, August 1976.
9. *Chemical Week*, 110 (15) 14 (April 12, 1972).
10. *New Fertilizer Materials*, Chemical Process Review, Noyes Development Corporation, Chapters 9 and 11, 1968.

Table 28. Percentage of plant foods in saturated solutions at different temperatures of potash salts used or formed in the formation of fluid fertilizers

Temperature	Potassium nitrate		Potassium chloride		Potassium sulfate		Mono-potassium phosphate		Dipotassium phosphate	
°F	K_2O	N	K_2O	Cl_2	K_2O	S	K_2O	P_2O_5	K_2O	P_2O_5
				%						
32	5.4	1.6	13.8	10.4	3.7	1.3	4.3	6.4	30.8	23.3
35	5.8	1.7	14.0	10.5						
40	6.6	2.0	14.3	10.8			4.7	7.0		
45	7.4	2.2	14.7	11.0						
50	8.1	2.4	14.9	11.3	4.6	1.6	5.2	7.7	32.3	24.1
55	9.0	2.7	15.2	11.5						
60	9.9	3.0	15.6	11.7	5.6	1.9	5.9	8.6	32.6	24.5
65	10.8	3.2	15.9	11.9						
70	11.7	3.5	16.1	12.1			6.4	9.6	33.3	25.1
75	12.7	3.8	16.4	12.4			6.9	10.2	33.9	25.6
80	13.4	4.0	16.7	12.6			7.0	10.5	34.2	25.8
85	14.5	4.3	17.0	12.8	6.1	2.1	7.4	11.0	34.7	26.1

Chapter 9

Application of Liquids and Suspensions

By Michael F. Broder

The applicability of fluid fertilizers (suspensions and liquids) has contributed to the steady growth in the use of these materials in the U.S. Fluids can be broadcast at high speeds or can be uniformly distributed to multiple outlets on tillage and planting equipment. Fluid flow rates can also be accurately metered permitting accurate application. Fluid fertilizers are carriers for agricultural chemicals and they can also be injected into irrigation water. The decline in fertilizer consumption by farmers in 1983 heightened competition among fertilizer dealer/applicators. More efficient application methods, weed control, and other services were offered by fertilizer dealers in an effort to boost fertilizer sales. Liquid fertilizer, well suited for these services, continues to occupy an important part of the fertilizer market.

Application Techniques

All fluid application techniques can be combined into two broad classes, broadcast and band application. Broadcast application is usually done with ground driven equipment. Though most broadcast application is done prior to planting or seedling emergence, some crops typically are topdressed by broadcasting liquid fertilizer onto the established crop. For some crops, aircraft are often used to broadcast fluid fertilizer. In arid parts of the U.S., liquid fertilizer, particularly nitrogen, is broadcast with irrigation water through sprinkler irrigation systems. Another technique for applying liquid fertilizers is known as foliar feeding; low rates of fertilizers are applied directly onto crop leaves either by aircraft or high clearance applicators. Foliar feeding is commonly used to apply micronutrients such as iron and zinc on certain crops. Many unanswered questions exist, however, concerning use of primary nutrients in foliar feeding.

Band application is a general term referring to several application techniques. Surface banding is the application of fertilizer in continuous strips on the soil surface. This can be done by dribbling the liquid at low pressure and is termed "dribble application." Dribbling is often done on pastures. Surface banding is used to apply fertilizer between rows of established crops. This is often referred to as "sidedressing." However, sidedressing also includes the injection of fertilizer into the soil between crop rows. Strip application is the term commonly used to describe the procedure whereby liquid is applied to the soil surface in strips, spaced as are crop rows but not necessarily aligned with crop rows, then lightly disced into the soil prior to planting.

Row application, in this discussion, refers to the application of fertilizer in a strip near the seed during planting. The juxtaposition of the seed and fertilizer band is dependent on the amount and type of fertilizer used and the crop. For wheat, the fertilizer is often placed directly with the seed. On corn, care is taken to place the fertilizer slightly below and to one side of the seed to prevent germination damage. Starter or pop-up fertilizer is similar to row applied fertilizer in that it is applied near or with the seed at planting; however, unlike row fertilizer, starter fertilizer furnishes only part of the crop's fertilizer requirement.

Another type of band application is referred to as "root zone" or "deep" banding. Deep banding is the application of fertilizer 6 or more in. (15.2 cm) below the soil surface. The bands may or may not lie below the seed. With anhydrous ammonia, the location of fertilizer and seed is

crop and time dependent. In row crops, planting may take place immediately after application of ammonia, in which case seeds are planted between strips of ammonia. In grains, planting is delayed to allow ammonia to be converted to nitrate and the seed and fertilizer rows may be perpendicular or may coincide. When ammonia and phosphate fertilizer are banded together, the process is referred to as "dual application." Dual application is becoming a common practice in the U.S. Wheat Belt.

Broadcast Application Equipment

Most fluid broadcast applicators are either trucks which have been adapted to spray liquids or are special-built high flotation vehicles. The high flotation vehicles are often tricycle-type and are commonly referred to as "floaters" (figure 43). Booms on either side of the applicator are hinged at the rear of the applicator and can be folded forward for highway travel. Most applicators have booms that span 50 feet (15.2 m); however, some models have booms that fold at two points and span 80 feet (24.4 m).

In most applicators, fluid is pumped to the nozzles by a centrifugal pump driven by a power takeoff of the applicator engine. Figure 44 shows the flow diagram of liquid in the truck. Note that pressure at the nozzle is usually controlled by the amount of material bypassed to the applicator tank. The regulating valve and the pressure gauge are usually located in the truck cab. In some applicators, a regulating valve is also located in the product line permitting nozzle flow control independent of recirculation.

Generally, broadcast applicators handle both liquids and suspensions. Since suspensions comprise a large part of the fluid broadcast market and require large plumbing and pumping capacity, manufacturers have increased the diameter of applicator main lines to 3 in. (7.6 cm) with 3/4-in. (1.9 cm) fittings supplying each nozzle. Pumps are rated as high as 300 gallons (1,136 l) per minute at 100 pounds per square in. (68.9×10^4 Pa) fluid pressure. Agricultural chemicals and solids are sometimes held in suspension by use of a sparger (a pipe with holes oriented to spray material tangentially around the applicator tank).

Two distinctions between solution and suspension applicators are the nozzles and strainers used. Of the three nozzles most commonly used to apply fluid fertilizer, flat fan nozzles (right side of figure 45) are only suitable for solutions. Solids in suspensions tend to clog the small orifices in flat fan nozzles. Flat fan nozzles are preferred when uniform distribution of fine droplets is required. Such is the case when herbicides are used. Sprays can drift, however, under windy conditions. When winds are strong enough to cause spray drift, flooding and hollow cone nozzles are preferred. Flooding nozzles (left side of figure 45) emit drops the same size as average rain drops; there is little or no drift. They also give uniform application across the swath if proper overlap of adjacent nozzle sprays is maintained.

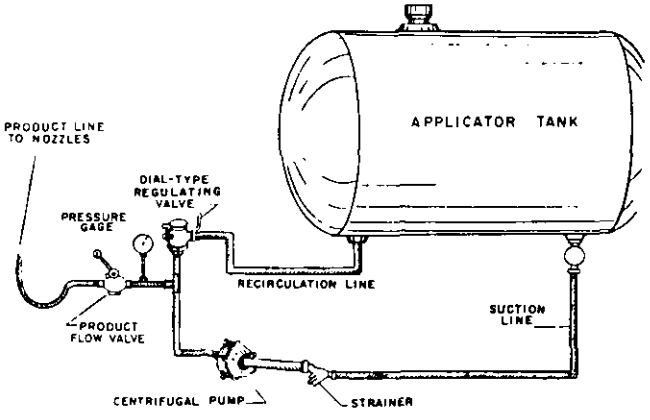

Figure 44. Flow diagram for fluid fertilizer applicator that uses pump bypass to control pressure at nozzle

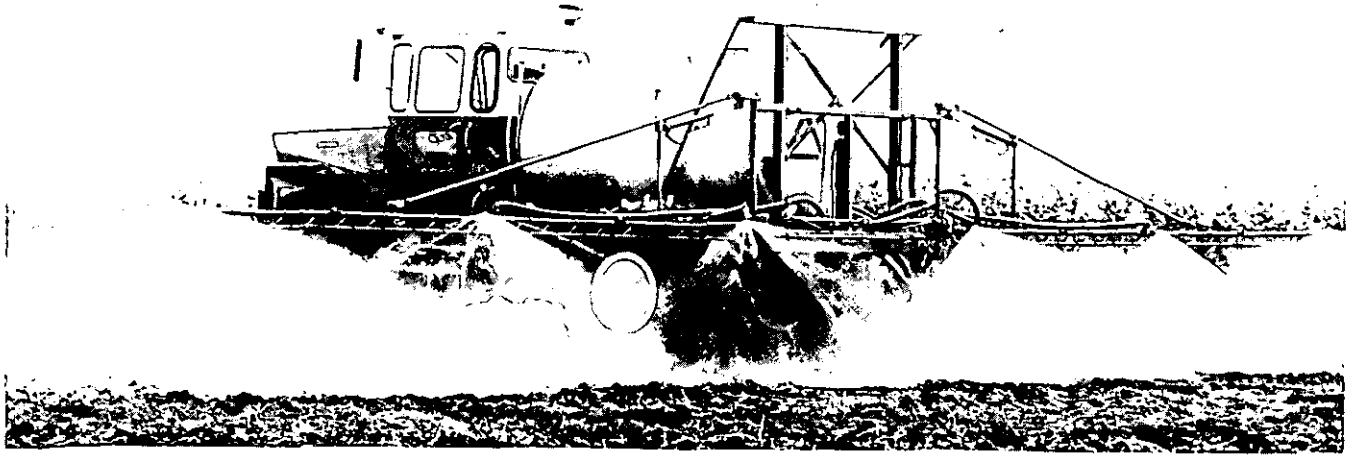

Figure 43. High flotation applicator

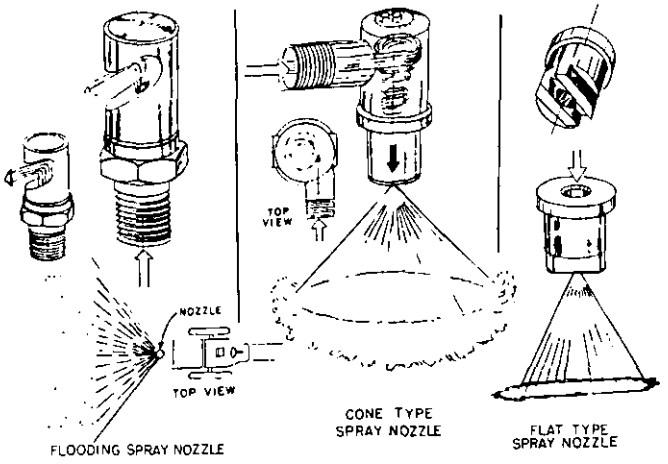

Figure 45. Nozzles used to broadcast and apply fluid fertilizers

Figure 46 (1) shows the importance of proper overlap. Broadcast application is most uniform when 100% overlap (double overlap) is used. Double overlap is achieved when the width of a nozzle spray striking the ground is double the nozzle spacing. Since most applicators have a fixed nozzle spacing, the boom height is used to adjust spray overlap. Spray overlap increases with an increase in boom height. Some applicator manufacturers tilt the nozzles to spray at 45°, instead of vertically downward, to increase spray overlap.

A nozzle designed to reduce drift and produce larger droplets than flood nozzles is rapidly being adopted. This nozzle produces a hollow cone pattern and is shown in the center of figure 45. The large droplets are produced in a swirl chamber which also decreases fluid velocity. The orifices in these hollow cone nozzles are, therefore, slightly larger than orifices in flood nozzles of similar capacity.

In suspension applicators, strainers are sometimes not used because suspension is screened while filling the applicator. If strainers are used they are bar type or at least 6-mesh (3.36 mm) size. For solution application, strainers are sized to allow passage of crystals half as large as the diameter of the smallest nozzle orifice encountered.

Manufacturers of fluid broadcast equipment use different methods for controlling application rate. Though a proportional flow valve is generally used to control nozzle flow rate, the valve is preset on some applicators while on others the valve can be adjusted during application. Some applicators employ a pressure and ground speed sensor connected to electrical controls which automatically regulate a valve to maintain a constant application rate. Automatic rate controllers are becoming popular because they eliminate the need to monitor pressure. A few applicators have pumps driven by a ground wheel. Ground driven pumps can be geared to maintain a fixed application rate regardless of driving speed.

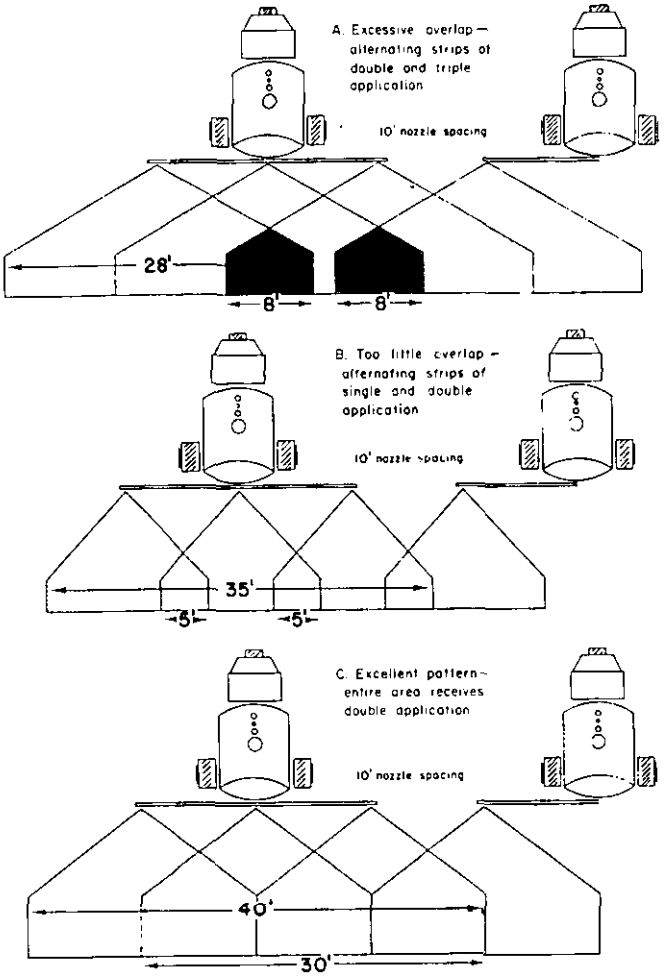

Figure 46. Spray patterns

A few companies use air pressure applicators. Pressure required to spray liquid is supplied by a small air compressor driven by a power takeoff from the truck engine. Air is added to the applicator tank through a sparger to agitate the mixture as it is applied. Pressure is monitored and controlled during application by adjusting an air escape valve inside the cab of the applicator.

All of the methods used to control liquid application rates have limited accuracy due to variations in fertilizer flow properties. Pressure and ground speed sensing errors as well as nozzle wear can cause application error. Nozzle flow rates at a given set of application rate settings are used to improve application accuracy. This information, obtained by calibration, is often required to achieve accurate application. Equipment fabricators usually calibrate nozzles with water; a more effective calibration is obtained with the fluid to be applied. Fertilizer flow measurements take into account flow variations due to fluid density and viscosity. Fertilizer flow is difficult to predict using water data with correction factors and equations. Data obtained by calibration can improve the accuracy of rate controls and can

ensure that the recommended amount of fertilizer is deposited on the entire field.

Pumps Used for Fluid Fertilizer Application

Five types of pumps are used for fluid fertilizer application: centrifugal, piston, hose (squeeze), roller, and diaphragm. Centrifugal pumps are most common for broadcast application because they can handle high volumes required for high speed application at the low pressures [10 to 40 psig (6.9 to 27.6 x 10^4 Pa)] required for broadcasting. Centrifugal pumps are durable, inexpensive, and can handle suspensions. Two disadvantages of centrifugal pumps are that they must be driven at high speed (2,500 to 3,600 rpm) and that they are not positive displacement. That is, output is not necessarily proportional to pump speed.

Piston pumps (figure 47) are often used for band application and are used for broadcasting, particularly when the applicator is tractor drawn. The slow rotational speed of piston pumps makes them ideal for driving off a ground wheel. Since they are positive displacement, application rate is constant when ground driven, regardless of driving speed. Rates of application are varied by changing the length of the piston stroke. Piston pumps are more expensive than centrifugal pumps and operate at higher pressures. Piston pumps seldom have high enough output for recirculation agitation. A separate centrifugal pump is often used for suspension agitation. Piston pumps can clog when pumping high potash suspensions at low rates. If the pump is set above 30% of full stroke, however, clogging of potash suspensions should not occur.

Roller pumps are used for solution and herbicide spraying. Roller pumps are vane-type pumps in which resilient rollers are used instead of sliding vanes. They can be driven by power-take-off (P.T.O.) shafts and are common on tractor-mounted spray rigs. Roller pumps produce higher pressure than centrifugal pumps but are not positive displacement. A disadvantage of roller pumps is that they are subject to abrasion by suspensions.

Squeeze or hose pumps are very popular for band application of suspensions. Hose pumps are much less expensive than piston pumps but are not as accurate. Since flow is divided in the pump manifold, flow dividers are not required. There are two types of hose pumps in use. Figure 48 shows a pump using round hoses and a spring loaded backup plate. Figure 49 shows flat hoses and no backup plate.

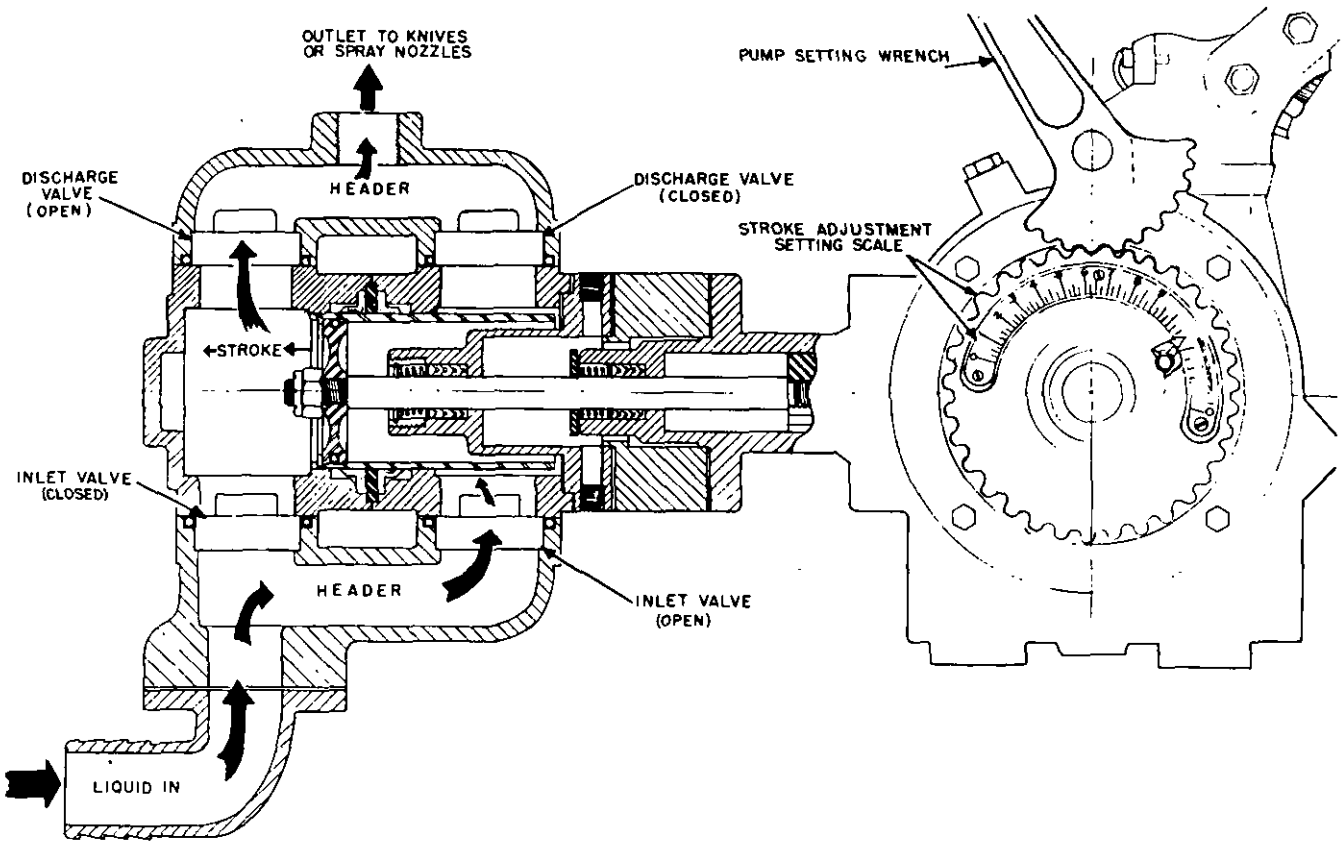

Figure 47. Liquid fertilizer—piston type metering pump

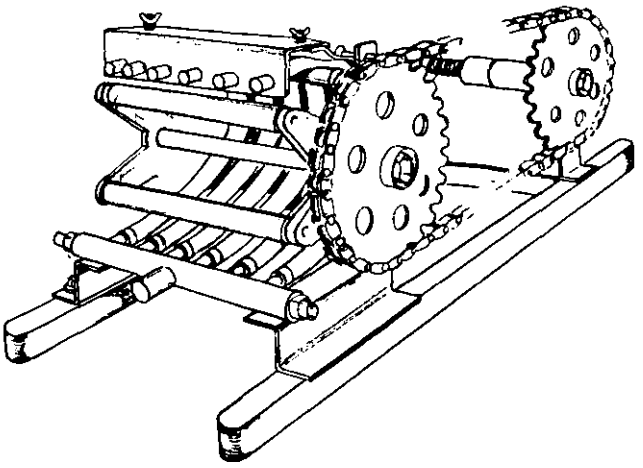

Figure 48. Squeeze pump with round hoses and back plate

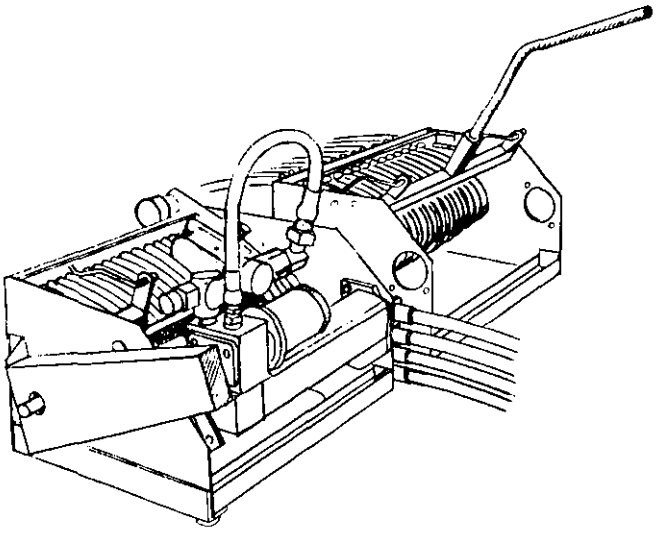

Figure 49. Squeeze pump with flat hoses and hydraulic drive

Diaphragm pumps are used to inject fluid fertilizers into irrigation water. High pressures produced by diaphragm pumps are required to pump against the pressure in irrigation lines. Recently, diaphragm pumps have been used for deep placement of liquid phosphate in dual application. The rotational speed of the pump is matched to tractor P.T.O. shaft speed.

Applying Fluids Through Irrigation Systems

Applying fertilizers in irrigation water, fertigation, is becoming more popular and widespread because it is inexpensive and agronomically efficient. The cost of fertigation can be 10 times less than conventional application. Periodic application of nutrients, "spoon feeding," is an agronomically beneficial practice that is commonly done by fertigation.

Sprinkler fertigation tests have shown that an ordinary tap into the irrigation piping system is all that is required to get uniform mixing of fluid fertilizer in irrigation water (2). To ensure mixing, fertilizer is injected into the system just ahead of a tee or an elbow in the irrigation line. Turbulence in the water created by the pipe fittings aids in mixing. The velocity of water in the irrigation line at the region where the fertilizer and water meet also affects mixing. A water velocity of 6 feet (1.82 m) per second is recommended (2). A system designed to provide uniform distribution of irrigation water will also provide uniform application of fertilizer if the two are well mixed.

Injecting fertilizers into sprinkler irrigation systems is easily accomplished but installation must include devices to prevent pollution of ground water. One method to prevent pumping of fertilizer when an engine driven irrigation pump shuts down is to drive the injection pump from a belt on the irrigation pump.

In installations having an electric motor on the irrigation pump, the injector pump can be powered by an electric motor interlocked electrically with the motor on the irrigation pump (figure 50). Therefore, injection of fertilizer stops automatically if the irrigation pumping plant stops. Note the vacuum breaker and check valve between the irrigation pump discharge and the point of fertilizer injection into the irrigation pipeline. This prevents back-siphoning of fertilizer into the well if the irrigation pumping plant fails. The check valve on the injection line stops flow of water from the irrigation system into the fertilizer tank in the event the injection pump stops while the irrigation pump continues to run (3).

In some installations, a normally closed solenoid valve interlocked electrically with the engine or motor driving

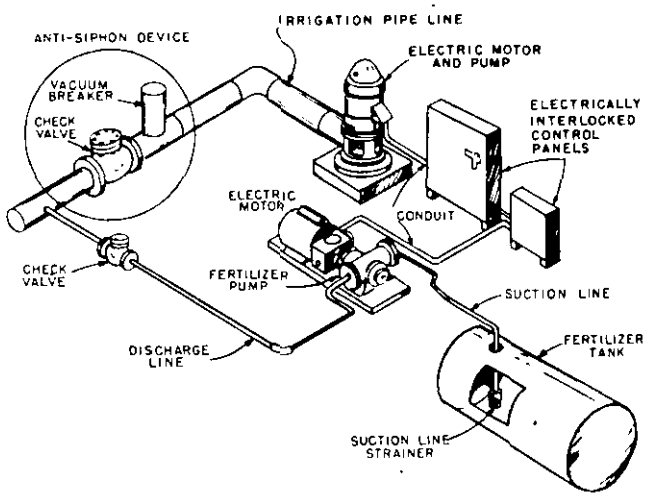

Figure 50. Anti-pollution device on fertigation system

the injection pump is placed in the injection line. With this, neither fertilizer nor water can flow in either direction through the injection line if the injection pump stops (3).

Use of fertilizer in drip irrigation systems is practical in areas where water costs are high or where high value crops are grown. Areas where the topography makes conventional irrigation impossible are also commonly irrigated by a drip system.

One problem in fertigation with drip systems is precipitation of solids when ammonium phosphate is used in hard water. Precipitates clog drip irrigation emitters making fertigation difficult. Phosphates with high polyphosphate content or acidic solutions help reduce the formation of insoluble precipitates. Both approaches are effective in sprinkler irrigation systems; however, fertigation with hard water in drip systems still presents problems.

Surface Band Application

Band application, traditionally done by farmers, is rapidly becoming a service offered by many fertilizer dealer/custom applicators. With current fertilizer prices favoring ammonia and dry fertilizer materials, fluid fertilizer dealers are using band application as a marketing tool. Though the benefits of band application may be exaggerated by some fluid fertilizer dealers, research has shown that banding is superior to broadcasting on many soil/crop systems.

Dribble application is a common practice for pasture fertilization. Row crops are often sidedressed by dribble application and phosphate is sometimes dribbled and disked into the soil to enhance its effectiveness.

Though dribble application implies that liquid is dribbled from an opening and falls by the force of gravity, some dribble applicators have nozzles which produce a solid stream under pressure (figure 51). Farmer operated equipment generally does not have nozzles. Farmers often attach dribble equipment to a tillage implement. A ground driven squeeze pump delivers liquid through hoses with open ends aimed downward and equally spaced on a tool bar in front of disks or some other tillage devices.

Ground driven piston pumps are also commonly used for farmer operated dribble application. Piston pumps, unlike squeeze pumps, have a single outlet from which flow must be equally divided into as many tubes as there are dribble outlets. Several devices can accomplish this. On small rigs the pump outlet can be divided and subdivided by ordinary plumbing fittings. The lines to each knife must be equal in diameter and length to ensure uniform application.

Larger rigs require more elaborate flow dividers. Several types of manifold flow dividers are available. Cylindrical or disk-like manifolds are common. In these manifolds there is typically a 3/4-in. (1.9 cm) or larger inlet in the center of the disk with 8 to 16 outlets spaced around the circumference of the disk. The outlets are 1/4 to 3/8 in. (0.63 to 0.95 cm) in diameter. Some of these manifolds are open. Others have spring loaded needle valves in each outlet. The latter type is for solutions and will clog when using suspension fertilizers.

Flow dividers designed especially for suspensions have recently been introduced. One system uses a hollow cone nozzle mounted in the top of a pot (figure 52). The pot has from 8 to 15 equally sized compartments each of which drains into a single line. Since the compartments drain faster than they are filled, equal length lines are not

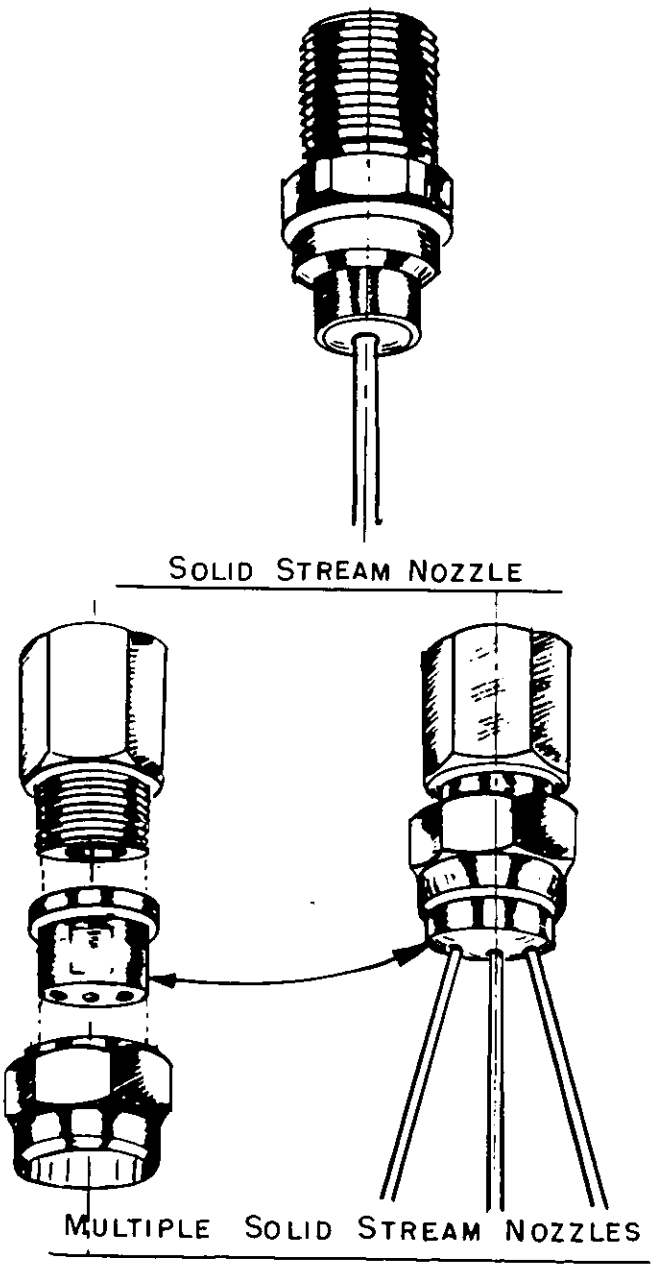

Figure 51. Nozzles used for dribble or surface band application

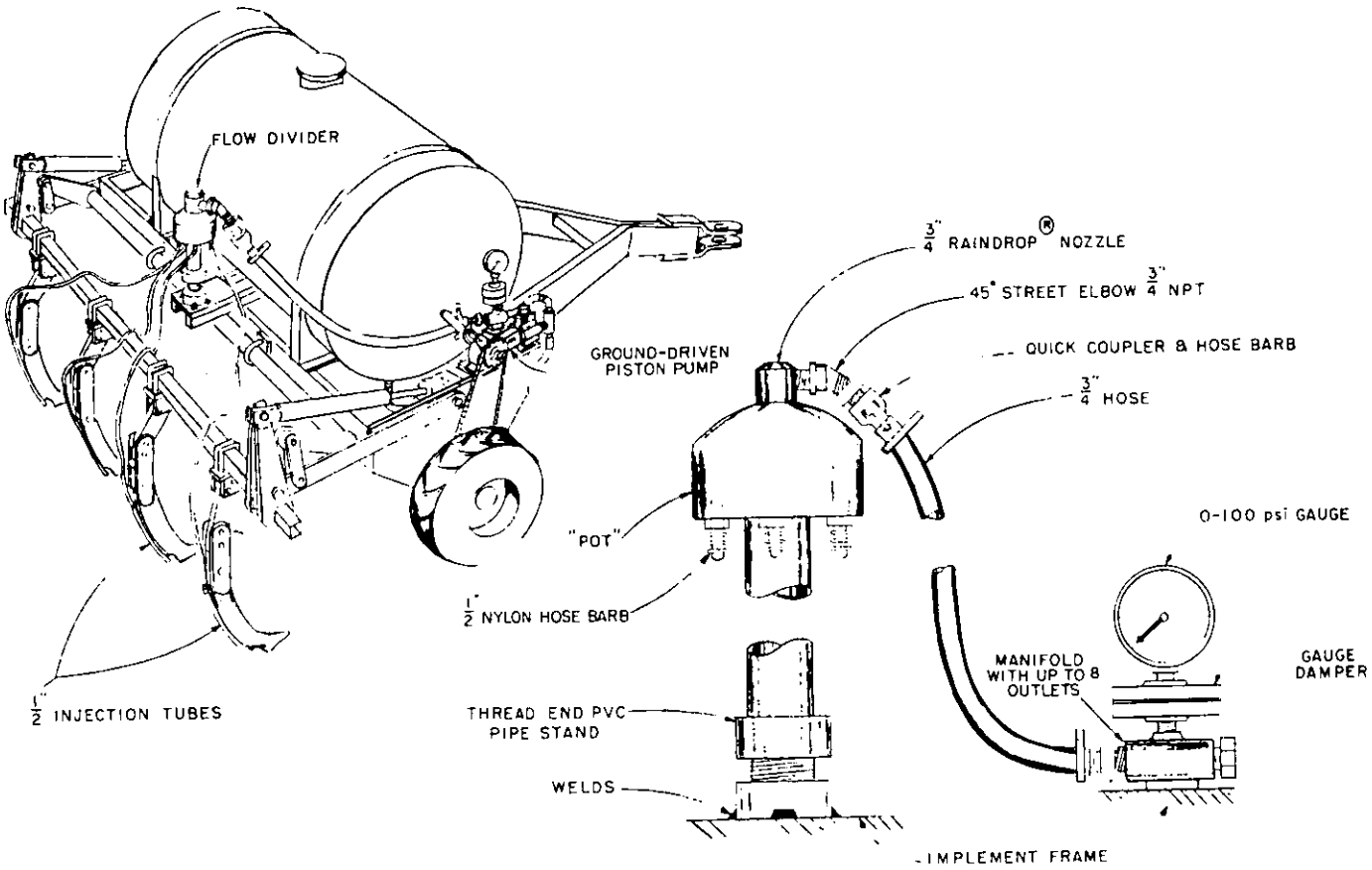

Figure 52. Flow divider for suspension injection

required. Since liquid flows by gravity from the pot, extremely viscous suspensions may cause flow stoppages.

A second type of suspension flow divider uses multiple orifices in series to achieve the low application rates desirable for band application (figure 53). Multiple orifices are made large enough to allow passage of suspension. The flow rate of suspension through the series of orifices, however, is much less than the flow of suspension through a single orifice of the same size.

Broadcast spray equipment can be used for dribble application by replacing broadcast nozzles with solid stream nozzles. This is done with many solution applicators which otherwise use flat fan nozzles at close spacing. Multiple solid stream nozzles are also used (figure 51). These nozzles produce two or three divergent streams and are designed for solutions. Multiple solid stream nozzles must be spaced properly to produce strips that are uniformly spaced on the soil.

Suspensions present problems because the spacing of nozzles for dribbling [12 to 30 in. (30.5 to 76.2 cm)] is 2 to 10 times narrower than the nozzle spacing for suspension broadcasting. Orifices must, likewise, be smaller. For

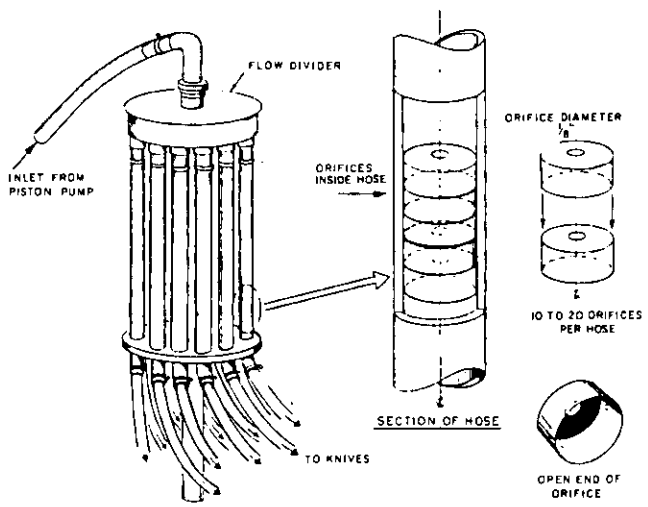

Figure 53. John Blue flow divider for row application of liquids

this reason the flow dividers previously mentioned are common for suspension dribble equipment. Both the pot and multiple orifice system divide the flow in a manner

which permits application of fertilizer at low rates and narrow outlet spacing.

One manufacturer has converted a high flotation broadcast applicator to a dribble applicator by splitting the flow from each nozzle into two equal flows. The outlet spacing is reduced from 60 to 30 in. (152.4 to 76.2 cm). The strip kits, as they are called, attach to the boom as do nozzles and produce solid streams which are not affected by wind as are streams that are dribbled. This particular rig was designed especially for application of liquid phosphate fertilizer in the Corn Belt. This practice is typically called strip application.

Subsurface Band Application

Subsurface injection equipment is similar to dribble or strip application equipment in that similar pumps and flow dividers are used. Tractor drawn subsurface applicators generally have ground driven piston or squeeze pumps. Since ground wheels are not practical on some tillage tools (V-blades), hydraulic drives are sometimes used to drive fertilizer pumps (figure 49).

One subsurface applicator is unique in that it has no pump and relies on gravity to transfer liquid into the soil (figure 54). The gravity flow system is used for starter fertilizer or row application. An air-tight tank behind each planter unit supplies liquid to or near the seed furrow at a constant rate regardless of the liquid level in the tank. A constant head is maintained by allowing air which replaces liquid drained from the tank to enter the tank via a breather tube which extends to the bottom of the tank. The small orifices used to control application rates do not allow passage of suspensions. Suspension fertilizers must be pumped in subsurface injection systems.

Injection knives or chisels are used to inject liquids beneath the soil surface. Spargers or nozzles are also placed under V-blades to inject liquids with ammonia in dual application systems (figure 55).

Though most subsurface banding is done by farmers with planters or tillage equipment, some equipment manu-

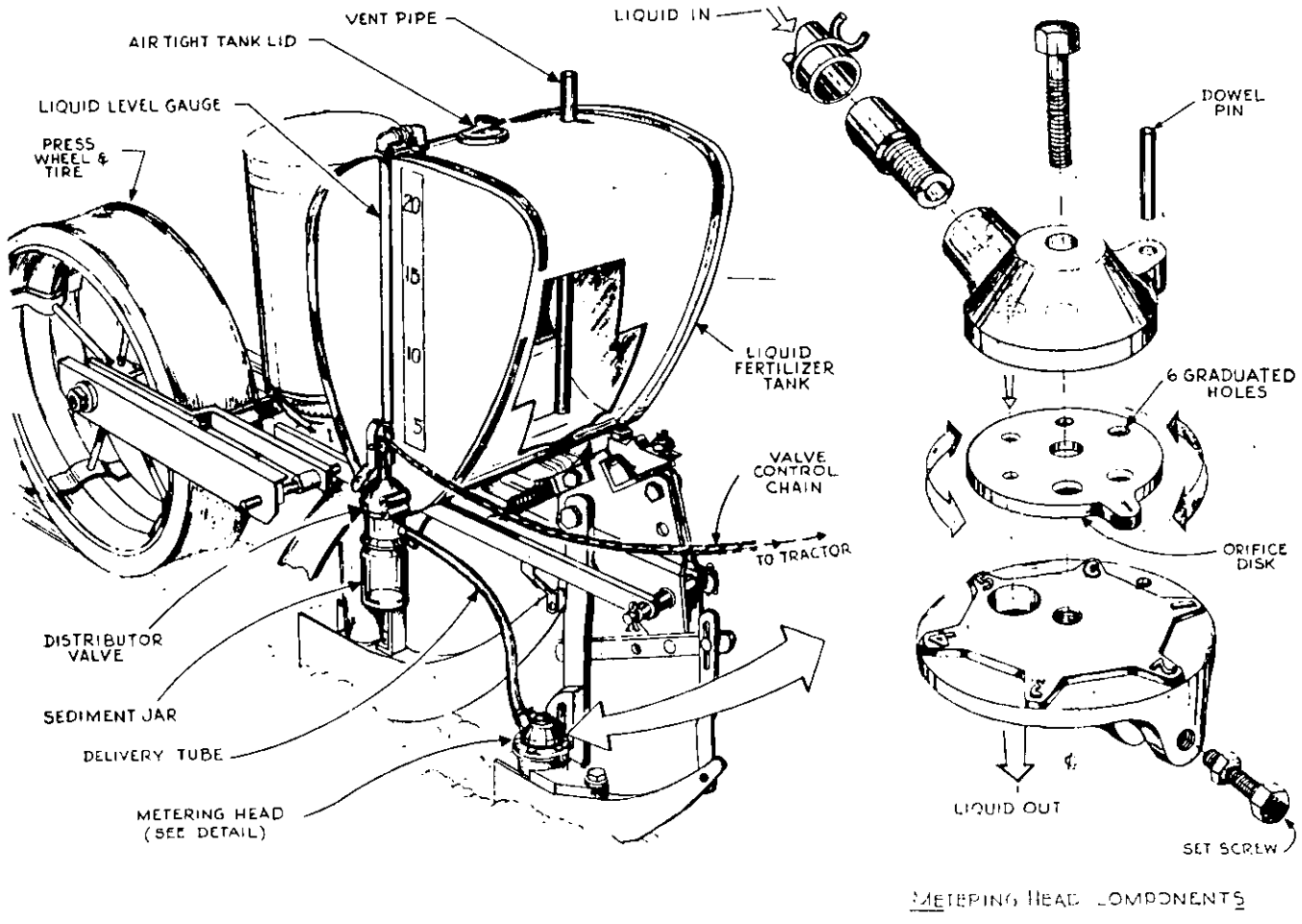

Figure 54. Constant-head gravity-flow fluid fertilizer applicator and orifice plates

facturers have adapted custom fluid broadcast equipment for subsurface application. All custom subsurface injection equipment is high flotation and 4-wheel drive is sometimes necessary to develop the traction required for pulling injection knives through soil. A typical custom subsurface applicator has a tool bar which is between 30 and 40 feet long (9.14 to 12.19 m), depending on the knife spacing. The tool bar is generally attached to the applicator frame and the knife or chisel depth is controlled hydraulically. V-blades are not used on custom subsurface applicators. Unlike tractor drawn equipment, centrifugal pumps are used on custom equipment.

Dual Application

Dual application of anhydrous ammonia and liquid ammonium phosphate fertilizer is becoming widespread in the U.S. Wheat Belt. Ammonia is generally metered at a constant rate by an adjustable orifice. The liquid ammonium phosphate is pumped by centrifugal pumps on custom applicators and by piston or squeeze pumps on tractor drawn units. V-blades are commonly used on tractor drawn units and separate lines for ammonia and liquid phosphate are attached to the underside of the V-blades. Ammonia and phosphate outlets are in line and spaced 12 to 15 in. apart (30.48 to 38.10 cm) under the V-blade (figure 55).

When injection knives or chisels are used for dual application, the phosphate tube is welded to the ammonia tube (figure 56). This arrangement often causes freezing of the liquid phosphate near the expanding ammonia. Conveying phosphate through a plastic tube helps eliminate the freezing problem (figure 57).

A variety of tank arrangements are used for dual application. The ammonia tank is generally pulled behind the tillage implement on a trailer. The liquid phosphate tank is mounted on the tillage implement, pulled on a trailer, or twin tanks are mounted on either side of the tractor. High flotation custom applicators which are adapted for dual application use the regular applicator tank for fluid phosphate and the ammonia tank is trailered behind the applicator.

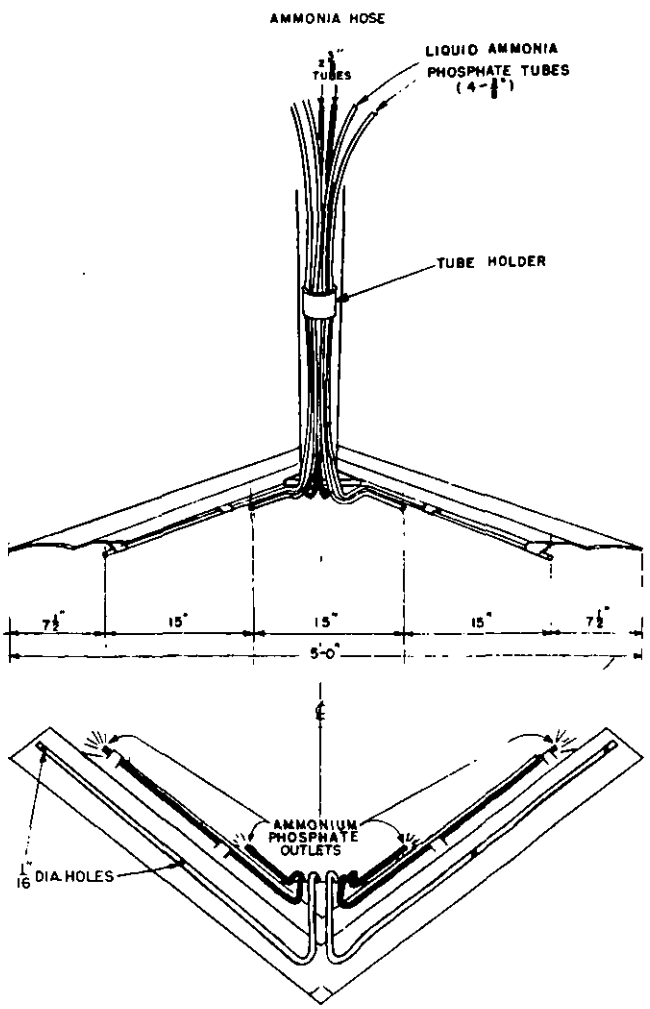

Figure 55. V-blade equipped with ammonia sparger and liquid phosphate injection assembly

Aerial Application

The use of aircraft in agriculture has increased greatly in the past few years. Most aerial application involves the

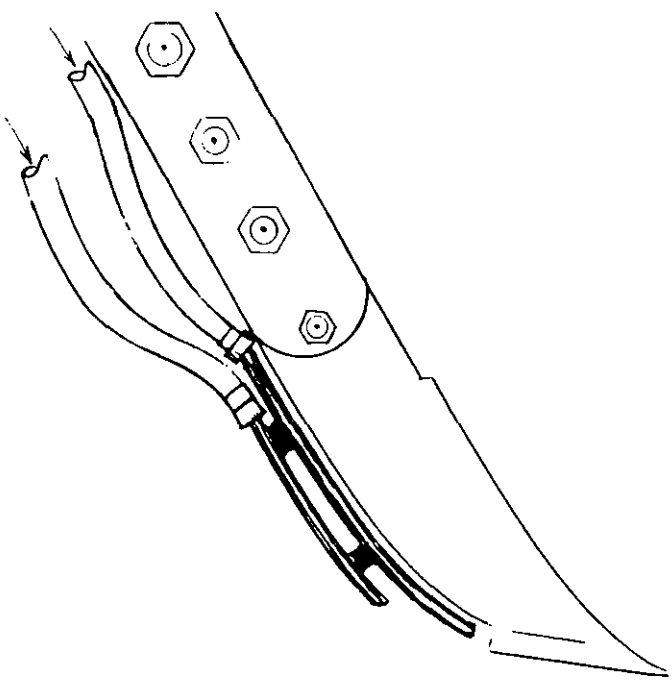

Figure 56. Dual application knife with ammonia and phosphate tubes separated

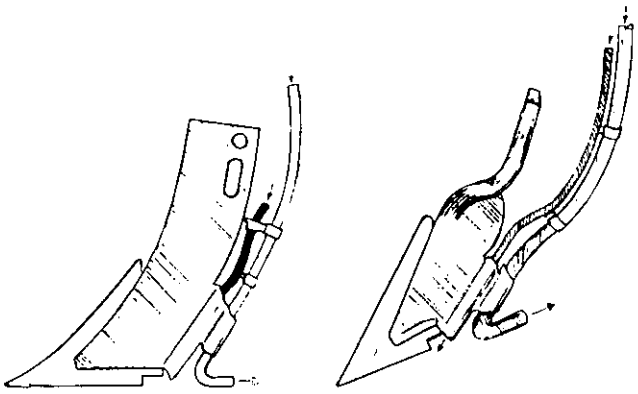

Figure 57. Ammonia knives equipped for dual application

use of herbicides and pesticides. Fertilizer, however, is applied extensively by aircraft on some crops. Rice and citrus producing areas in the southern regions of the U.S. are often fertilized by aircraft. Forest producers use aircraft to apply slow-release nitrogen fertilizer (sulfur-coated urea). Since aircraft have limited carrying capacity, application of dry materials is more common than fluid application. Aerial spraying, however, is common for correcting micronutrient deficiencies or primary nutrient deficiencies that can be corrected by foliar feeding after a crop is established.

Aerial application equipment is largely derived from ground equipment. Centrifugal pumps and bypass recirculation are common. Fixed wing aircraft and helicopters are commonly fitted with booms and nozzles at close spacing. Flat fan nozzles are common; however, the problem of spray drift has turned interest to drift reduction (hollow cone) nozzles.

The difficulty in eliminating spray drift is illustrated by the distances that spray droplets can be carried from the path of aircraft. A fine spray drifts 48 feet (19.63 m) in a 3-mile-(4.83 km)-per-hour wind while falling only 10 feet (3.05 m). An aerosol droplet can travel 21 miles (33.8 km) under the same conditions. To reduce spray drift, one aerial sprayer manufacturer has placed extra nozzles on the right side of the fuselage to help compensate for prop wash which moves spray from right to left. Other methods involve wing modifications on airplanes to modify their wake and nozzles which control droplet size.

Helicopters are becoming more popular for aerial application because they can reach areas inaccessible by plane and travel slow enough to supply fertilizer at high rates. Bi-winged aircraft are also common because they are easier to maneuver than single winged crafts and travel at slower speeds.

Trends and Recent Innovations

The threat of high fertilizer prices has spurred interest in agronomically efficient application techniques. Incorporation of nitrogen and placement of fertilizer near the roots of plants are becoming more popular. Farmers and dealers are also shifting to energy efficient application methods. Equipment is available which can perform several field operations at once. Planting, fertilization, tillage, and weed control can be accomplished in a single pass.

Among the innovations which have recently been made in fluid fertilizer application are custom applicators which can broadcast, dribble, or inject fertilizer beneath the soil surface. One such applicator is used for broadcast application by day and for subsurface injection at night when the tillage marks enable the operator to see where he has been.

Custom broadcast application equipment has been built to apply fertilizer at a speed of 2.5 acres per minute (1 ha/min). Boom movement is hydraulically dampened to permit application at higher speeds. Onboard microprocessors monitor application rate and acres covered and adjust the application rate automatically, providing extremely accurate application.

Pneumatic dry fertilizer and seed planting equipment is becoming more popular. Pneumatic systems are capable of distributing dry materials from a single hopper to several outlets spaced across a large implement. Tillage equipment and liquid fertilizer delivery systems are being coupled with these pneumatic planters. The result is a precision planter/fertilizer applicator that covers 60 feet (18.3 m) in a single pass.

The many innovations in fluid fertilizer application indicate how the science is changing to meet the demands for higher production. The threat of higher energy and fertilizer costs will surely bring about further advancements in fluid fertilizer application.

Chapter 10

Materials of Construction for the Fluid Fertilizer Industry

By F. P. Achorn and H. R. Horsman

Corrosion costs the fluid fertilizer industry millions of dollars each year. Corrosion and erosion are functions of temperature, pH, concentration, velocity, and solids loading. Together corrosion and erosion can destroy an expensive piece of equipment in a short time. The most susceptible to corrosion-erosion attack is equipment that is exposed to fast-moving fluids that contain solids. Liquid fertilizers are excellent electrolytes, and the corrosion products that form on the metal slow down the corrosion rate; but erosion strips away the protection, and the result is accelerated metal loss. Carbon steel, the most common material of construction, is attacked by both nitrogen solutions and fluid fertilizer mixtures. Aluminum is resistant to most nitrogen solutions, but is attacked by NPK mixtures. The stainless steels are resistant to both nitrogen solutions and mixtures. They are also resistant to the fluids in combination with micronutrients, herbicides, and pesticides. The disadvantage of stainless steel equipment is its high initial cost, and some alloys are subject to pitting attack. Corrosion-resistant plastics applications have been used successfully by the fluid fertilizer industry; however, they are susceptible to impact damage and damage from organic solvents often used in herbicides and pesticides.

The purpose of this chapter is to supply information that might be used to help select the most economical material of construction for each individual application.

Nitrogen Solutions

Much has been written concerning corrosion-resistant equipment and procedures for handling nonpressure nitrogen solutions [28%, 30%, and 32% N urea-ammonium nitrate (UAN) solutions] (1, 2, 3, and 4). These solutions usually contain a corrosion inhibitor; however, corrosion test results with solutions that do not contain inhibitors show that such solutions are not corrosive to most aluminum alloys, stainless steels (300 series), or polyvinyl chloride (PVC) plastics. Corrosion tests by TVA showed that solution containing 32% nitrogen was less corrosive to carbon steel than more dilute UAN-solution or ammonium nitrate (AN) solutions containing 19% nitrogen. Also urea solutions containing 19% nitrogen were less corrosive than either the 19% AN or 19% UAN solution and about the same as the 32% UAN solution (5). Carbon steel exposed to these solutions has been effectively inhibited with each of the following inhibitors:

1. Ammonium polyphosphate or ammonium orthophosphate (0.05% to 0.2% P_2O_5)
2. Anhydrous ammonia
3. Ammonium thiocyanate (0.1%)
4. Sodium arsenite (0.1%)
5. Sodium dichromate (0.1%)

The ammonium phosphates and ammonia are the most frequently used inhibitors since they are readily available in the fertilizer industry and they are environmentally acceptable. Ammonium phosphate forms a coating of iron phosphate on carbon steel, providing a barrier to further corrosion by the nitrogen solution. Tests show that about 10 pounds (4.5 kg) of ammonia will treat a ton of solution (increase pH from 7.0 to 7.5) and the treated solution will not corrode mild steel. The data given in table 29 show that AISI 304 stainless steel is usable at 80° and 120°F (27° to 49°C) exposed to AN (19% N) solution, and at 80° and 120°F (27° to 49°C) exposed to UAN (32% N, pH 6.7). Also annealed carbon steel is superior to cold-worked carbon steel.

Table 29. Suitability of AISI type 304 stainless steel and mild steel for use in nitrogen solutions

	Suitability and corrosion rate (mils/yr) at indicated temperature[a]					
	AISI type 304 sst at 80° or 120°F		Carbon steel at ambient temp[b]			
			Cold worked		Annealed[c]	
	Usable	Rate	Usable	Rate	Usable	Rate[d]
Nitrogen solutions WITH corrosion inhibitors[e]						
AN solution (19-0-0 grade)						
54.3% AN, 45.7% H_2O	Yes	–	NR	–	–	–
UAN solution (28-0-0 grade)						
30.5% urea, 39.5% AN,	–	–	Yes	–	–	–
30.0% H_2O, initial pH = 6.8						
UAN solution (32-0-0 grade)						
34.8% urea, 45.1% AN	–	–	Yes	–	–	–
20.1% H_2O, initial pH = 6.8						
Nitrogen solutions WITHOUT corrosion inhibitors						
Urea solution (19-0-0 grade)						
41.3% urea, 58.7% H_2O,	–	–	NR	16[f]	Yes	1
initial pH = 8.9, final pH = 9.4						
AN solution (19-0-0 grade)						
54.3% AN, 45.7% H_2O,	–	–	NR	87-117[f]	Yes	1, Pm
initial pH = 8.5, final pH = 7.9						
UAN solution (19-0-0 grade)						
20.7% urea, 27.2% AN, 52.1% H_2O,	–	–	NR	350[f]	NR	22
initial pH = 6.4, final pH = 7.5						
UAN solution (28-0-0 grade)						
32.1% urea, 37.8% AN, 30.1% H_2O,	–	–	NR	99[f]	?	P3
initial pH = 8.0, final pH = 7.8						
UAN solution (32-0-0 grade)						
Urea:AN ratio unknown,	Yes[g]	<1	–	–	–	–
initial pH = 6.7, final pH = 6.9						
UAN solution (32-0-0 grade)						
37.4% urea, 42.5% AN, 20.1% H_2O,	–	–	NR	13-20[f]	Yes	Pm
initial pH = 8.1, final pH = 6.4						

[a] NR = not recommended. ? = questionable. Yes = should be suitable when used under the conditions specified. Corrosion rate determined by measuring weight loss of specimen after exposure in nitrogen solution. Corrosion rate may vary depending upon degree of aeration and velocity of fluid flowing past the alloy.

[b] Ambient atmospheric conditions, see footnote c.

[c] Two-inch disk made from an annealed (hot-rolled) plate. Disk was suspended in the bucket (footnote f) and submersed in unaerated liquid without corrosion inhibitor. Exposure conditions for the disk were less severe than for the bucket.

[d] P indicates pitting to depth in mils shown by number (m = minute).

[e] Information furnished by two nitrogen solution producers from actual field storage. Several corrosion inhibitors were available and used by manufacturers of nitrogen solutions. For corrosion rates with specific corrosion inhibitor, contact supplier of nitrogen solution.

[f] Severely cold-worked 5-gallon bucket half filled with unaerated test liquid without corrosion inhibitor and exposed in field unprotected from weather.

[g] Laboratory test. Specimen was 2-inch-diameter coupon (disk).

Ammonium Polyphosphate Base Solutions

Ammonium polyphosphate (APP) solutions of various grades (10-34-0, 11-37-0, 9-30-0, 12-44-0) contain from about 20% to 80% polyphosphate. Plant experience and laboratory corrosion tests have shown these liquids can be stored in carbon steel tanks without excessive corrosion resulting. Chemical and microscopic examinations show the APP solution reacts with the iron to form ferrous phosphate film on the walls of the tank, protecting it from further corrosion (6, 7). The film will deteriorate somewhat at the liquid-air interface on the surface of the liquid which tends to cause corrosion rings to form around the tank. Corrosion rings are usually not evident except when the fluid is kept at the same level for extended periods. This problem can be avoided by floating a film of oil on the surface of the liquid (8). Used motor oil is excellent for this purpose and an oil film thickness of about 1/8 in. (3 mm) seems to work well. This formula may be used for calculating the gallons of oil required for the 1/8-in. oil film.

$$\text{Gal oil} = \left(\frac{\text{tank diameter, feet}}{4}\right)^2$$

$$= \left(\frac{\text{tank diameter, meters}}{1.22}\right)^2$$

APP solutions pumped through carbon steel pipes will not corrode them if the fluid velocity is kept reasonably low. Optimum fluid velocity is unknown but most operators find that if the flow is kept below 8 feet (2.4 m) per second corrosion is kept within tolerable limits. Corrosion increases with temperature; thus, the solution should be kept at less than 150°F (66°C). At higher fluid velocities and temperatures, the protective iron phosphate film deteriorates and corrosion of the steel increases. Entrained air at high fluid transfer rates may contribute to the increased corrosion. Cast iron is not subject to severe corrosion by APP solutions and it is recommended for impellers in transfer pumps. Solutions apparently do not corrode stainless steel (type 316) until fluid velocities exceed 16 feet (4.9 m) per second.

In TVA's prototype plant for the production of APP suspension, 9-32-0 grade, merchant-grade phosphoric acid (0-54-0) is reacted with ammonia in a pipe reactor to produce a fluid that contains suspended solids. Experience in this plant has shown that carbon steel pipe and cast iron pumps are not serviceable, especially in the high fluid velocity areas. Cast iron impellers, pumps, casings, and carbon steel piping have been severely damaged after only a few hundred hours service. Stainless steel impellers and pump casings (American Casting Institute CF-8M, CD-4MCu) have shown only slight evidence of wear in the same amount of time. This operation has shown that the use of ball and plug cock type valves for flow control and throttling increases corrosion-erosion on the downstream side of the valve body and in the first foot or so of the downstream pipe. Control and throttling valves that direct the fluid flow through the center of the valve body (gate, globe, needle, etc.) into the downstream pipe minimize corrosion-erosion damage to valve and pipe walls. PVC has worked well in some piping of the plant; however, it was not tested in the pipes where severe corrosion occurred.

Corrosion due to high fluid velocities has occurred in many fluid fertilizer plants which use TVA's pipe reactor process for production of high polyphosphate solutions (10-34-0 and 11-37-0). Since orthophosphate is believed to be the film-forming species, the corrosion may be due, in part, to the low orthophosphate content (about 25%-35%) as compared to the liquids formerly dominating the fluid industry (minimum orthophosphate 50%).

Chlorinated polyvinyl chloride (CPVC) and other PVC plastics have been used for years in the fluid fertilizer industry. They are lightweight and do not require a lot of equipment or highly skilled labor for installation. The most commonly used PVC is PVC-1. Its biggest disadvantage is its low impact strength. CPVC costs about twice as much as PVC. PVC Type II is an excellent low cost construction material for liquid transfer lines where the fluid temperature does not exceed 140°F (60°C). It is flexible, yet has a high impact strength.

PVC resists corrosion by the polyphosphate liquids, but some formulations lose more strength than others at elevated temperatures. Table 30 shows some thermal and physical properties of PVC and CPVC compared to steel.

CPVC is recommended where fluid temperatures exceed 140°F (60°C). This material resists heat distortion at temperatures up to 210°F (99°C) at about 260 lb/in^{2}g (1.8×10^6 Pa). It does not have the impact strength of PVC Type II, but it is an excellent plastic for use in hot-mix fluid fertilizer plants if properly supported and protected. The support of all plastic lines is important and a dependable method is to lay the pipe in an angle iron as shown in figure 58.

Table 30. Thermal and physical properties of PVC and CPVC compared to steel

Property	PVC-I	PVC-II	CPVC	Steel
Specific gravity	1.40	1.35	1.55	7.80
IZOD impact strength, ft-lb/in. of notch[a]	0.8	8	3.0	30
Ultimate tensile strength, lb/in^2	8,000	5,500	8,400	60,000-90,000
Upper temperature limit, °F	140	140	210	>1,000

[a]ASTM standard tests, D 256 for plastic and E 23 for metals.

Plastics have good overall balance of properties at least cost.

Liquid Mixtures

Chlorides in liquid mixtures corrode carbon steel but not at a rapid rate. The main source of chlorides is from potash. Many companies have found that carbon steel mix tanks with 1/4-in. (6 mm) thick walls have not corroded through after 5 years of operation. Carbon steel nurse and application tanks have been used for years in the application of NPK mixtures. These tanks will usually last at least 5 years. Some companies have found that they can extend the life of these tanks if they are frequently washed with water or liquid fertilizer, such as 10-34-0 or 32-0-0, to lower the chloride level on the surface of the metal. Others have found that if the tanks are kept full of liquid and a film of oil is floated on the surface, there is less likelihood of corrosion. Some companies fill their applicator tanks with water or liquid fertilizer when they are not in use, thus avoiding the corrosive chloride-air combination.

Some companies coat the inside walls of their mild steel tanks with corrosion-resistant paints. These three types of paints have been effective.

1. Epoxies and epoxy tars
2. Vinyl esters
3. Some polyethylene and phenolic resins

Proper preparation of the metal prior to painting is essential for good service life. Most paint companies recommend that the metal in new or old tanks be thoroughly cleaned by sandblasting to white metal for immersion service (Steel Structure Paint Council-SP5, National Association of Corrosion Engineers No. 1). After carefully inspecting the metal to ensure that it has been thoroughly cleaned, a corrosion-resistant bonding primer should be applied, followed by application of a vapor barrier primer

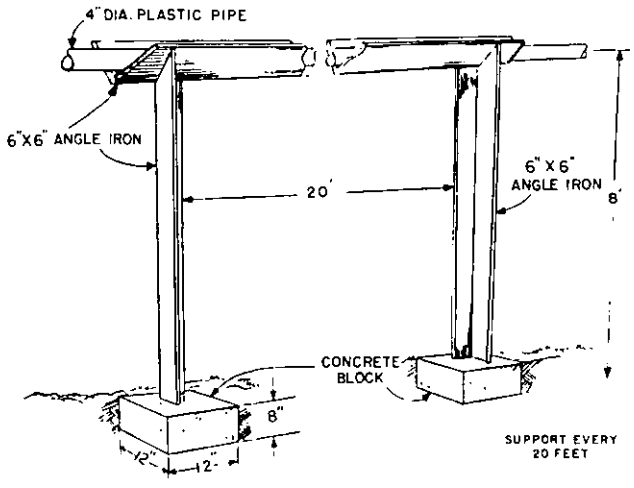

Figure 58. Support for PVC plastic pipe

or intermediate coat. Not all coating systems require an intermediate coat, but one is often used to obtain the desired total film thickness. Also, three coats are required to ensure that there are no pinholes. Using a different color paint for each coating is an excellent inexpensive method to ensure complete coverage. Once the paint films are penetrated and corrosion starts, the corrosion will spread on the metal beneath the film and the paint will start to peel. To ensure good coverage, some companies apply as many as five coats of paint. The total film thickness should be at least 5 mils (0.125 mm) for stationary tank walls and 9 mils (0.225 mm) for mobile equipment. A relatively simple method to ensure the desired dry mil thickness is to use a wet mil paint thickness gauge. The dry mil thickness is then determined by multiplying the measured wet mil thickness by the percentage solids supplied by the coating manufacturer. Companies that plan to use these protective coatings should get specific instructions concerning metal preparation and painting from the paint suppliers.

Most 300 series stainless steels are resistant to corrosion by liquid mixtures. There have been a few reports that some 304 and 316 stainless steels have been corroded by mixtures containing potash; however, others have reported no corrosion of these types of stainless steel by NPK mixtures. Type 304 stainless steel is more susceptible to chloride induced pitting than the molybdenum containing 316 and 317 stainless steels.

One steel company reported crevice corrosion of type 304 stainless steel by salts in the areas affected by fused-metal splatter during welding. They recommend that the tanks be flushed with water after each use to prevent buildup of salt deposits on the metal (9). There has been only one report of corrosion to type 316 and 317 stainless steel, and these are recommended for use with all the conventional fluid fertilizers. These two metals are also the most expensive. PVC plastic is an excellent relatively low cost material for pipes and tank liners exposed to fluid mixtures. Care should be taken to select the type of PVC that suits the type of plant and process (hot-mix or cold-mix).

Some companies store liquid mixtures in neoprene-lined nylon bags as shown in figure 59. This is a photograph of a rubber bag with a capacity of 500,000 gallons (1.9×10^6 l) installed in a pit. If the bag ruptures, the liquid is trapped in the pit and can be pumped immediately into another container. Some companies have used these bags to store phosphoric acid.

Figure 60 is a photograph of a transport truck on which are installed several spherical type tanks made of polyolefin plastic. These tanks are excellent for storage of liquids and suspensions. The material that tends to settle in the bottom can be easily withdrawn and recirculated to the top of the

sphere. No difficulties have been reported with deterioration of the plastic. Some have been in use for as long as 10 years.

Storage and Transfer of Phosphoric Acid

The container most frequently used for storing phosphoric acid is a rubber-lined carbon steel tank. The types of rubber most frequently used are Butyl and natural rubber. Type 316 stainless steel is also an excellent construction material for storage tanks and transfer lines. Table 31 shows the suitability of various alloys for use in wet-process orthophosphoric acid and table 32 shows the suitability of various alloys for use in wet-process superphosphoric acid. Tanks with the rubber lining or stainless steel are still in service after 20 years or more. These require a high initial investment.

To avoid high cost, some companies store acid in less expensive fiberglass reinforced plastic tanks. Many tanks of this type have given excellent service for more than 10 years but some have ruptured after only a few months of service. Many different plastic resins (PVC, polyolefins, polyesters, polyethylene, phenolics, and others) are used with fiberglass reinforcement and with varied construction techniques. The resin provides the corrosion resistance, and the fiberglass and its application method provides the tank with its strength. The strongest vessels are wound with continuous strands of fiberglass. The buyer of tanks should investigate the performance history of the supplier's tanks to ensure their reliability. Also, most wet-process phosphoric acid contains fluorine compounds which attack fiberglass. The tank manufacturer can protect against this damage by applying several coats of the resin (sometimes

Figure 59. Neoprene-lined nylon bag (capacity: 500,000 gallons)

Figure 60. *Transport trucks equipped with plastic tanks*

called a veil) over the fiberglass. Some lining materials tested by TVA in phosphoric acid are found in table 33.

Occasionally, old tanks are lined. When this is done, the tank walls should first be smoothed, sandblasted, and coated with a vapor barrier primer (see section on coating inside of tanks). Some coating companies recommend a high build (about 50 mils or 1.25 mm thick) spray applied butyl rubber system.

In the past 10 years there have been numerous pit storage containers built for storing phosphoric acid. Considerable care was taken with the construction of the first pits to avoid puncturing the liner. Later there were some complaints concerning ruptured pit linings and investigations showed that in most instances the lining was not properly constructed or the support surface beneath the lining was not properly prepared.

Table 31. Suitability of various alloys for use in wet-process orthophosphoric acids

	Suitability and corrosion rate (mils/yr) at indicated temperature[a]					
	150°F		200°F		250°F	
	Usable[b]	Rate	Usable[b]	Rate	Usable[b]	Rate
20% P_2O_5 acid						
AISI Type 304 sst[c]	–	–	Yes	6	–	–
AISI Type 316 sst	–	–	?	7	–	–
Lead, 10% antimonial	–	–	Yes	<1	–	–
29% P_2O_5 acid						
AISI Type 316 sst	Yes	3	?	9	–	–
AISI Type 317 sst	Yes	1	Yes	4	–	–
Carpenter 20	Yes	1	Yes	5	–	–
20%-40% P_2O_5 acid						
Alloy 20 (cast, CN-7M)	Yes	1	Yes[d]	5	–	–
Lead, chemical	–	–	Yes	<1	–	–
39%-56% P_2O_5 acid						
AISI Type 304 sst	No[c]	<1	–	–	–	–
AISI Type 316 sst	Yes	<1-4[e]	NR	18-36	NR	40-750
51%-55% P_2O_5 acid						
AISI Type 317 sst	Yes	1	?	6-8	NR	40-85
AL 6X	Yes	<1	Yes	4	NR	55
AL 29-4	Yes	<1	Yes	4	?	12
Alloy 20 (cast, CN-7M)	–	–	?	10	NR	125
Carpenter 20	–	–	Yes	6	NR	24-49
E-Brite 26-1	Yes	<1	Yes	3	NR	35
Hastelloy C	Yes	<1	–	–	NR	30
Hastelloy G	Yes	<1	Yes	3	NR	32
Illium G (cast)	–	–	–	–	NR	81
Inconel 625	Yes	<1	Yes	2	NR	25
Jessop 700	Yes	<1	Yes	4	NR	47
60%-66% P_2O_5 acid						
AISI Type 316 sst	–	–	Yes	2-8	–	–

[a]Corrosion rate determined on laboratory scale by measuring weight loss of coupon (2-in-dia x 1/8-in-thick disk) after exposure in test tube containing 750 ml of acid for 28 days. Corrosion rate may vary depending upon degree of aeration and velocity of fluid flowing past the alloy.
[b]NR = not recommended. ? = questionable. Yes = usable under the conditions specified.
[c]AISI Type 304 stainless steel is susceptible to pitting attack by wet-process acid.
[d]Intergranular corrosion; metal should be solution annealed to improve corrosion resistance.
[e]Four mils per year was in 42% P_2O_5 acid at 185°F.

Figure 61 is a sketch of an excellent design for an acid storage pit. The pit bottom slopes at an angle of about 0.2 to 0.3 in. per foot (1.7-2.5 cm/m) from one end to the other. Usually one end has a depth of 6 feet (1.8 m) and the other end 8 feet (2.4 m). All four walls of the pit should be sloped at an angle of 45° or less so that no stress is applied to the liner as fluid is added.

It is important that a drainage device be installed as shown in figure 61 so that if a rupture occurs, the acid will drain into a sump from which it can be recirculated until the pit can be emptied and the liner repaired. This sump is often used to detect small leaks by filling it with water and checking the pH of the water daily. A drop in pH indicates a leak. This design shows reinforcing wire on the bottom of the pit and drainage trench. Over the wire is a layer of sand over which a layer of asphalt is sprayed. The perforated plastic pipe is laid in the drainage ditch and crushed rock is laid around the pipe. Next, the layer of asphalt and rock is covered with sand so that there is a smooth surface onto which the PVC liner is laid.

Prior to installing the liner (usually 30 mils or 0.75 mm minimum thickness), it should be inspected for holes. This can be done by first laying the liner in the pit and then blowing air between the sandfloor and the PVC liner to lift and buoy the film. A high intensity light directed on the surface will reveal holes to an operator beneath the liner. Holes can be patched with a suitable solvent and PVC material. It is usually advisable when repairing the liner to place a patch on both sides of the hole so that there are three thicknesses of PVC around the hole.

The acid is withdrawn from the sump end through an open-end pipe or a perforated pipe sparger. Companies that use the sparger find that as new acid is added to the pit, the streams from the sparger resuspend the solids that settle in the acid. Most companies cover their pits with an A-frame type of wooden roof covered with a standard composition material. Some cover their pits with an additional PVC liner which floats on top of the fluid. Figure 62 shows a pit with a floating cover.

Some companies have used these pits as long as 12 years to store phosphoric acid, UAN solution, and APP base solutions. They report no difficulties in the storage of these liquids in a properly installed pit. The estimated installation cost (1975) of pit storage for phosphoric acid was $34 per ton of P_2O_5. This is considerably less than the $98 per ton of P_2O_5 for rubber-lined storage tanks (17,000 gallons) (6.4×10^4 l).

Conduit

PVC or PVC-coated conduit is the most corrosion-resistant for use around fluid fertilizer plants. PVC,

Table 32. Suitability of various alloys for use in wet-process superphosphoric acid[a]

	Acid, % P_2O_5	Suitability and corrosion rate (mils/yr) at indicated temperature[b]			
		80°-200°F		300°F	
		Usable[c]	Rate	Usable[c]	Rate
Stainless steel					
AISI Type 304 sst[d]	70-74	Yes	<1	?	5-13
AISI Type 316 sst	69-74	Yes	<1	?	3-13
AISI Type 317 sst	70-74	Yes	<1	?	3-23
Carpenter 20Cb	72-74	Yes	<1	?	5-8
Hastelloy C	70-75	Yes	<1	Yes	<1-4
Illium G (cast)	70-74	Yes	<1	Yes	<1-4
Incoloy 825	69-74	Yes	<1	?	1-9
Uranus B6	69-75	–	–	Yes	2-4
Lead, 10% antimonial	68-75	?	<1-11	Yes	4
Lead, chemical	69-75	?	<1-64	Yes	2-4
Red brass	69-72	?	1-11	?	11-16
Red brass	69-72[e]	NR	29-330	–	–

[a] The acids used in the laboratory-scale corrosion tests were from many different sources. Some of the factors that affect the corrosive properties of wet-process acid are: type and quantity of impurities in the phosphate rock, pretreatment of phosphate rock (if any), method of P_2O_5 extraction, product acid concentration, purification or subsequent treatment, and temperature.

[b] Corrosion rate determined on laboratory scale by measuring weight loss of coupon (2-in-dia x 1/8-in-thick disk) after exposure in test tube containing 750 ml of unaerated acid for 28 days. Corrosion rate may vary depending upon degree of aeration and velocity of fluid flowing past the alloy.

[c] NR = not recommended. ? = questionable. Yes = usable under the conditions specified.

[d] Type 304 is susceptible to pitting by wet-process acid.

[e] Acid was aerated at about 0.02 ft^3/min.

schedule 40 and 80, is the only nonmetallic conduit at the present time approved by the National Electric Code for use above ground. Carbon steel and aluminum need to be coated if exposed to strong free acids. Aluminum is not resistant to strong alkalies.

Ammonia

Carbon steel can be used for piping and tanks. Zinc, tin, copper, and copper-base alloys should not be used

Table 33. Suitability of nonmetallic sheet materials, liners, and coatings for use in wet-process orthophosphoric and superphosphoric acids

	Suitability at indicated temperature[a]				
	80°F	120°F	150°F	200°F	300°F
Orthophosphoric acids					
31%-34% P_2O_5 acid					
Butyl rubber	–	–	Usable[b]	?[c]	–
EPDM[d]	–	–	Usable[b]	Usable[b]	–
Hypalon[e]	Usable	Usable	Usable	Usable	–
54%-55% P_2O_5 acid					
Buta-bond rubber	–	Usable	Usable	–	–
Butyl rubber	Usable	Usable	Usable	–	–
Natural rubber	Usable	–	?	–	–
Neoprene	–	Usable	Usable	–	–
Penton plastic	–	Usable	Usable	–	Usable
Polyethylene Type I	–	Usable	–	–	–
Hypalon[e]	Usable	Usable	Usable	Usable	–
57% P_2O_5 acid					
Penton	–	–	–	–	–
Superphosphoric acid					
70%-74% P_2O_5 acid					
Liners, sheet[g]					
Natural rubber	Usable	–	?	–	–
Butyl rubber	Usable	–	Usable	?	–
Neoprene	Usable	–	Usable	?	–
PVC II	Usable-?	–	Usable-?	Usable-?	–
Tygon	Usable	–	Usable	?	–
Polyethylene Type III	–	–	Usable	–	–
Polypropylene	–	–	Usable	–	–
Teflon	Usable	–	Usable	Usable	Usable
Coatings, applied[g]					
Heresite,[h] p-403 + L-66	Usable	–	Usable	Usable	–
Neobon[i]	Usable	–	Usable	–	–
Nukemite No. 40[j]	Usable	–	Usable	–	–

[a] After the samples of plastics and elastomers were exposed to liquids at the desired temperature, they were evaluated as being usable, questionable, or not recommended according to their appearance, hardness, strength, swelling, weight, and disintegration.
[b] Tested at 175°F.
[c] Tested at 225°F. ? = questionable.
[d] Ethylene-propylene diene monomer.
[e] Chlorosulfonated polyethylene. All suitability data from Du Pont literature.
[f] Tested at 285°F.
[g] All materials of a similar base type were not equally resistant to deterioration by the acids because of differences in formulations and curing methods.
[h] Phenol-formaldehyde resin, thermosetting.
[i] Neoprene base.
[j] Vinyl copolymer resin.

where moisture may be present as they are corroded rapidly by wet ammonia gas or aqua ammonia.

Most alloys of aluminum are resistant to corrosion by anhydrous ammonia and aqua ammonia except for dilute aqua ammonia (1%-5% NH_3); this corrosion can be controlled by the addition of nitrates (10). Aluminum alloys that contain copper should be avoided, especially the 2000 series that contains copper as the principal alloying element.

Anhydrous ammonia does not corrode carbon steel at atmospheric temperature. However, contaminants such as carbon dioxide and air (oxygen) in ammonia cause stress corrosion cracking of carbon steel (11). Some mechanical properties of steels used in tests (11) to show the effects of strength and hardness on their susceptibility to stress corrosion cracking are shown in table 34.

The high-strength steels are more susceptible to cracking than medium- and low-strength steels. The addition of 0.2% minimum of pure water to anhydrous ammonia inhibits stress corrosion cracking of carbon steel. Vessels that are stress relieved after fabrication are less susceptible to stress cracking than those in the stressed condition (cold formed and welded). Installation of elbows immediately downstream of restriction orifices should be avoided for anhydrous ammonia.

Fluid Fertilizer Additives

Fluid fertilizers are an excellent medium for the application of micronutrients and pesticides. They are usually added to the mixture in the applicator; therefore, there is some concern about corrosion to the applicator. If pesticide-fertilizer mixtures are allowed to stand in tanks for an extended period of time, they may separate (float on top or fall to the bottom). Also they may soften some plastic tanks, especially those that have additives that depend on organic solvents to stay in solution. Also, many additives contain fluorine and chlorine which become ionic

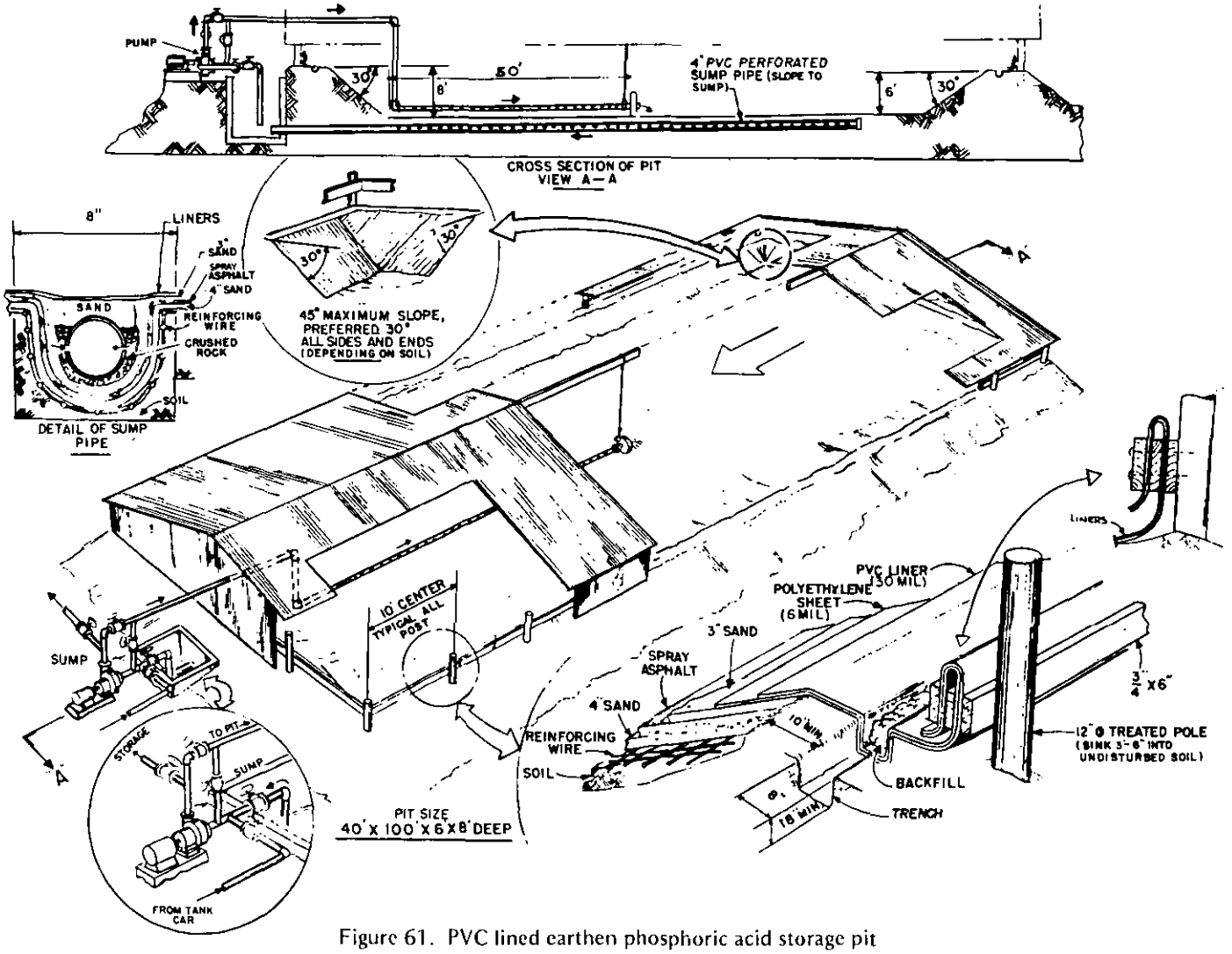

Figure 61. PVC lined earthen phosphoric acid storage pit

when the additive degrades, and they contribute to pitting attack in metal equipment. Copper compounds cannot be used safely in aluminum tanks because of the unfavorable galvanic relationship between copper and aluminum. Usually no corrosion problems can be attributed to the micronutrient compounds that are added to fluid fertilizer.

Cooling Equipment

During the past 5 years, several liquid fertilizer producers have used evaporative type coolers that are normally constructed for the refrigeration industry (figure 63). The coolers are packed with redwood slat-type packing which lasts for about 5 years in a liquid fertilizer plant.

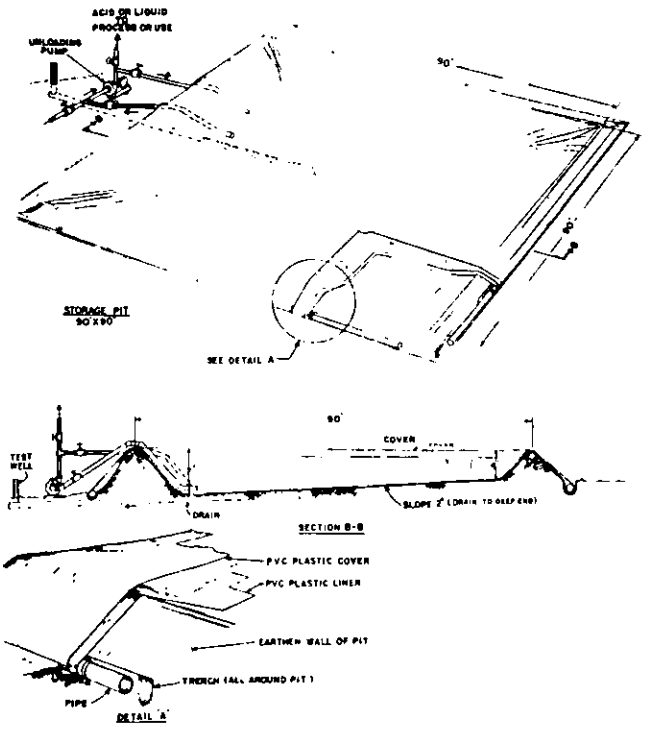

Figure 62. PVC lined storage pit with floating PVC plastic cover

Table 34. Mechanical properties of steels used in stress corrosion cracking tests

	Yield strength, lb/in^2	Tensile strength, lb/in^2	Hardness
ASTM A 285	37,000	59,000	RB 66
ASME case 1056	48,000	79,000	RB 85
ASTM A 212 grade B	51,000	83,000	RB 84
ASTM A 202 grade B	57,000	93,000	RB 94
T-1 steel	116,000	125,000	RC 25
AISI 4130	119,000	134,000	RC 29

Some of the coolers have been redesigned, as in figure 64, and packed with PVC plastic Intalox saddles or Pall ring packing. The plastic will not deteriorate and the saddles or rings provide a large evaporative surface area per unit volume.

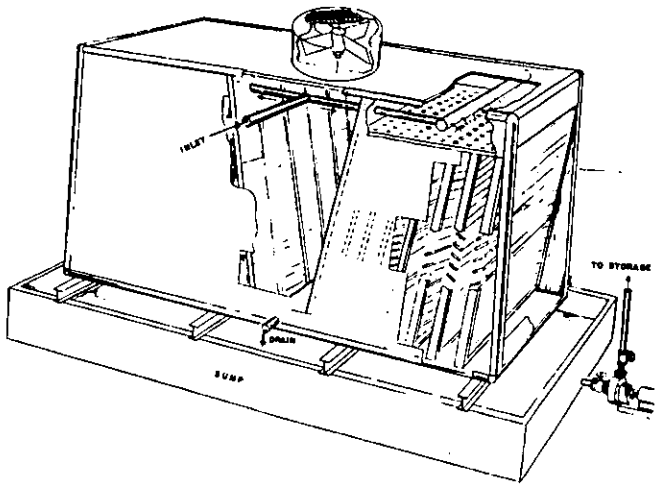

Figure 63. Evaporative-type cooler (from refrigeration plant)

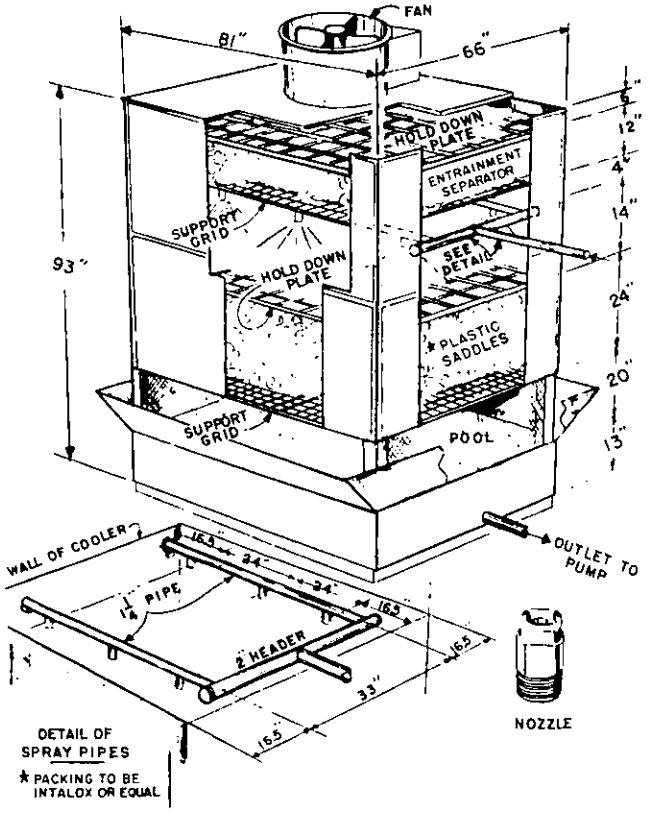

Figure 64. Evaporative cooler (with plastic packing)

Summary

This chapter by no means covers all of the corrosion-resistant materials used in the fluid fertilizer industry but should serve to highlight important materials and practices for reducing troubles with corrosion and erosion. Those personnel responsible for choosing the materials of construction in this industry should weigh all the information that is available to make suitable and economical selections of materials. The manufacturers of equipment and materials continue to develop new materials and methods that give each construction material better corrosion and erosion resistance. All carbon steels, aluminums, stainless steels, coatings, and liners are not equally resistant even if they have the same generic name. Different manufacturing methods and formulations give different characteristics. The one recommended for each specific application should be selected. Beside textbooks and reference books that provide general information on each material, the manufacturers provide specific information about the performance of their products. This information is provided through the home office or their local representative. Other organizations will provide useful material properties and application information. Some of these organizations are:

Aluminum Association (AA)
818 Connecticut Ave., NW
Washington, D.C. 20006

National Association of Corrosion Engineers (NACE)
P.O. Box 986
Katy, TX 77450

National Association of Plastic Distributors (NAPD)
Gilson Road
Jaffrey, NH 03452

National Fertilizer Solutions Association (NFSA)
8823 North Industrial Road
Peoria, IL 61615

Society of the Plastic Industry (SPI)
355 Lexington Avenue
New York, NY 10017

Steel Founders' Society of America (SFSA)
20611 Center Ridge Road
Rocky River, OH 44116

Steel Structure Paint Council (SSPC)
4400 Fifth Avenue
Pittsburgh, PA 15213

All sources of information should be utilized since minimizing corrosion lowers operating costs by minimizing maintenance, limiting unscheduled downtime, and maximizing equipment life.

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