NEW DEVELOPMENTS IN MANUFACTURE AND USE OF LIQUID FERTILISERS

By

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The manufacture and use of liquid fertilisers on a large scale is a relatively new practice--extending back over a period of only about 20 years. Thus it might be expected that an exposition of "new developments" would encompass the entire history of the industry. This is not necessarily true, however, because it has turned out that this new physical form of fertiliser offers a wide field of opportunity to the innovator, in which new developments have been, and continue to be, many and frequent. The past few years have provided a large body of subject matter. The purpose of the present paper is to review the liquid fertiliser field over the past 5 years or so and identify the significant new departures and trends.

We should note in passing, however, that the application of nutrients in liquid form is not new and, in fact, may well antedate the solid form. Even before the days of inorganic fertilisers, there was evidence of liquid application. In the early writings of the Greeks, for example, it is recorded that vegetable gardens and olive groves around ancient Athens were fertilised by city sewage carried in canals. And in more modern times, Sir Humphrey Davy tested inorganic fertiliser solutions as early as 1808 (1). Sir James Murray in 1843 even referred to solid fertiliser application as a "new" practice in England. He said that the new solid type was "exempt from loss by leakage,

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more safe, portable, etc.," as compared with the previous liquid products--which were normally sold in 30-gallon casks. At about the same time Bishop in Scotland reported on use of aqua ammonia to fertilise grass crops and gas house liquor subsequently came into general use.

Notwithstanding these early beginnings, liquid fertilisers were ahead of their time. As fertiliser technology developed and factors such as nutrient concentration, multinutrient combination, and production cost became more important, solids moved ahead--particularly for supplying phosphate and potash. Only in the past 20 years have various developments combined to bring liquids back into a competitive position, in which the intrinsic advantages of the liquid form can be realized without giving up good points such as high nutrient concentration and low production cost that have long been associated with solids.

The term "liquid fertiliser" as used in this paper refers to fertiliser solutions and suspensions, both multinutrient and single nutrient. Anhydrous ammonia is also a liquid and is a major fertiliser, but differs from solutions in so many respects that it seemed best not to include it. The discussion is based mainly on practice in the United States, where there has been more emphasis on liquids than in other parts of the world. However, an attempt has been made to cover developments in all areas.

Developments in Production

The objectives in liquid fertiliser production are much the same as in manufacture of the solid type:

1. Use of lowest cost raw materials.

2. Low operating cost.

3. High nutrient concentration--to reduce handling and shipping costs.

4. Good quality.

5. Low pollutant emission.

6. Product homogeneity--so that small amounts of materials such as micronutrients can be incorporated in the fertiliser and applied to the soil uniformly.

7. Product versatility.

8. Amenability to uniform application, so that incorporated pesticides can be applied to give complete ground coverage.

For some of these objectives, liquids are handicapped by their nature as compared with solids; this is particularly true in regard to cost of phosphate raw material and to nutrient concentration (although the gap is being narrowed). Product quality is also a problem because impurities introduced with the raw materials have a major adverse effect on the quality of liquids. (On the other hand, problems such as caking, dusting, segregation, and hygroscopicity encountered in production and use of solids is avoided.) Liquids have significant advantages, however, in regard to the other objectives, especially for product homogeneity and uniformity of application; the uniform composition and complete ground coverage, for example, are not only generally helpful but are particularly important in application of fertiliser-pesticide combinations.

Nutrient Concentration

Solution fertilisers have the built-in drawback that the nutrient concentration is reduced by the water required for holding the fertiliser salts in solution. Much of the research and development has been aimed at reducing the severity of this problem.

When liquid fertilisers first became significant in the fertiliser industry, in the early 1950's, the usual raw materials were ammonia, ammonium nitrate, urea, phosphoric acid (ortho), and potassium chloride. The solubility limitations for combinations of these materials are shown in Figure 1 (2). For the usual nutrient ratios the total nutrient concentration cannot exceed 20-35% if the crystallization temperature is to be held to 0°C or below.

(Figure 1)

In the late 1950's, the Tennessee Valley Authority (TVA) introduced polyphosphates as a means of increasing concentration, particularly for the nitrogen-phosphate base solutions that were coming into use at that time.

Substitution of polyphosphate for orthophosphate accomplishes other important objectives also (such as sequestering impurities in wet-process phosphoric acid), but the early emphasis was on increasing ammonium phosphate solubility, making it possible to manufacture and ship a 10-34-0 or 11-37-0 base solution as compared with about 8-24-0 if the industry were still depending on orthophosphate.

Today the standard practice in the United States is to make liquid fertiliser by mixing phosphate base solution with urea-ammonium nitrate solution and potash. Much of the development work of the past 5 years has been devoted to improving this practice.

Polyphosphate Chemistry: One of the main needs has been a better understanding of polyphosphate chemistry, especially in regard to solubility relationships between the various polyphosphate species that exist together in polyphosphoric acid as prepared commercially (usually called superphosphoric acid or "super" acid) and in ammonium polyphosphate solutions made from it.

The system is quite complex, mainly because superphosphoric acid is a mixture of orthophosphoric acid (H_3PO_4) and a series of linear polyphosphoric acids [e.g., pyrophosphoric ($H_4P_2O_7$), tripolyphosphoric ($H_5P_3O_{10}$), tetrapolyphosphoric ($H_6P_4O_{13}$), and so on]. The proportion of each depends on the total P_2O_5 concentration; as this increases the proportion of longer chain acids goes up and the ortho acid content is reduced (Table I). Further complication arises from the fact that the same species can form various ammonium salts, depending on the degree of ammoniation.

(Table I)

Recent studies by Farr, Williard, and Fleming (3) have elucidated the solubility relationships. In Figure 2, solubility curves are shown for the various systems involving ortho-, pyro-, tripoly-, and tetrapolyphosphate, the principal species involved. (For the usual grades of commercial super acid, only minor amounts of acids of chain length longer than this are present.)

(Figure 2)

The data show that solubility of the ammoniated acid species increases with chain length but that if the degree of ammoniation (expressed as $N:P_2O_5$ weight ratio) of the longer chain acids (tripoly and tetrapoly) exceeds about 0.22 the solubility decreases rapidly; at such a low ratio the resulting low pH promotes corrosion and polyphosphate hydrolysis. Ammonium pyrophosphate gives an intermediate solubility and the degree of ammoniation can be high enough to be in a practical range.

Since in practice mixtures of species are always obtained, the solubility curves of multiple phosphates in Figure 2 are the most significant. The combination of ortho and pyro, which are the main species in commercial super acids of relatively low polyphosphate content, gives high solubility and a fairly wide ammoniation plateau (A, D and B, D in the figure); the upper limit in grade, for crystallization at or below 0°C, is about 11-37-0. The highest solubility is obtained with all four species present (curves A, D, I, L and B, D, I, L); for a solution saturated with $(NH_4)_2HPO_4$, $(NH_4)_3HP_2O_7 \cdot H_2O$, $(NH_4)_5P_3O_{10} \cdot 2H_2O$, and $(NH_4)_6P_4O_{13} \cdot 2H_2O$--a nutrient content of 53% (grade, 12-41-0) can be attained at a reasonable ammoniation level (about 0.3 $N:P_2O_5$).

These data are for solutions in equilibrium with the solid phase of each of the component salts, whereas in practice the phosphate species would seldom if ever be present in the proportions to give a solution saturated with all components. For example, in the 12-41-0 solution described above the phosphate distribution was 25% ortho, 32% pyro, 14% tripoly, and 29% tetrapoly. Commercial superphosphoric acid seldom contains this much tripoly and tetrapoly to begin with, and part of it is lost by hydrolysis during ammoniation. Thus the actual solubility in the ammoniated solution usually lies somewhere between the NH_3-H_3PO_4-$H_4P_2O_7$-H_2O and NH_3-H_3PO_4-$H_4P_2O_7$-$H_5P_3O_{10}$ - $H_6P_4O_{13}$-H_2O isotherms, and the maximum concentration, at the optimum degree of ammoniation, is between 11-37-0 and 12-41-0. In practice, the content of long chain species in commercial superphosphoric acid has not been high enough and the ratio between species has not been close enough to the optimum to make 12-41-0 feasible, so the industry has settled generally for 11-37-0 as the maximum grade and 10-34-0 when the super acid, for process reasons, contains too little pyro acid to make 11-37-0 acceptable.

Another approach to higher solubility is to use a lower degree of ammoniation even at the expense of greater sensitivity to hydrolysis. From Figure 2 it is evident that dropping back to an $N:P_2O_5$ ratio of 0.27-0.28 gives a nutrient solubility of 56-57% (12-44-0 grade). Such a product was introduced recently by TVA and shows promise. However, especial care must be taken to minimize hydrolysis.

Super acid of higher P_2O_5 content can be made, of course, as a means of getting a higher long-chain content and consequently a higher solubility of ammoniated acid. However, there is a limit in this respect. Studies by Potts, Shaffer, and Nix (4) have shown that the polyphosphate content of the ammoniated product is optimum at about 80% of the total P_2O_5; above this the solubility falls off, apparently because the ammonium salts of the longer chain acids are not as soluble. However, further departure from optimum ratio between species could also be a factor. The chemistry in this area has not been explored.

In view of the work of Farr et al., this raises the possibility that there is a species, either tetrapoly or an acid of longer chain length, that gives maximum solubility of the ammonium salt.

To obtain the optimum 80% in the poly form, acid of 80-82% P_2O_5 content is used.[1] This actually contains more than 80% of the P_2O_5 as poly species (Fig. 1) but some is lost by hydrolysis during ammoniation.

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[1] This refers to phosphoric acid of high purity, commercially available as furnace-type acid. Unless otherwise specified, furnace-grade acid is the type referred to in subsequent discussions. In acid containing impurities, such as wet-process acid, the diluting effect of the impurities reduces the optimum P_2O_5 content.

Hydrolysis is a major problem both in production and use of polyphosphate-based liquid fertilisers. The hydrolysis mechanism has been studied recently by Farr, Williard, and Hatfield (5). The various poly species in a mixture all hydrolyze at the same time but the longer chains hydrolyze much faster. The mechanism involves splitting off an end $-PO_4$ group, so that tetrapoly hydrolyzes to tripoly, tripoly to pyro, and pyro to ortho. Determination of the species ratio after a given period of hydrolysis is complicated because the intermediate species are being formed and hydrolyzed at the same time; for example, tripoly is being formed by hydrolysis of tetrapoly but also is being hydrolyzed to pyro, so that at a given point the tripoly content may be either increasing or decreasing depending on conditions. Farr et al. have developed equations describing the hydrolysis of each species, plus a computer program to determine the constants in the equations.

Data are also reported by Farr et al. on the effects of pH and temperature on rate of hydrolysis. Like other polyphosphate systems, low pH promotes hydrolysis as does increase in temperature. Thus the acid should be ammoniated to as high degree as is feasible without unduly reducing solubility and the ammoniation should be carried out at as low a temperature as possible.

Magnesium suppresses hydrolysis of the tripolyphosphate species but not the higher polyphosphates, presumably because of the stability of the magnesium tripolyphosphate complex. Aluminum and iron accelerate the hydrolysis of all polyphosphates above pyrophosphate to about the same extent; thus their effect is additive.

Other recent work on polyphosphate chemistry has included studies by Frazier, Scheib, and Lehr (6) on the solubility of potassium pyrophosphates. Solubility was generally much higher than in the orthophosphate system; for example, at comparable pH pyro gave an 0-33-30 solution (at 25°F) whereas the maximum grade in the ortho system was only about 0-20-20. Adding ortho to the pyro helped a little, raising the maximum grade to 0-34-30.

Frazier et al. have recently completed studies of the system NH_3-K_2O-H_3PO_4-$H_4P_2O_7$-H_2O which will be published. In this mixed alkali system, they found that solution composition is controlled by new solid phases rather than by the recognized solid phases in the respective alkali systems.

Practical Aspects of Polyphosphate Use: When polyphosphate was first made available to the liquid fertiliser industry it was considered that superphosphoric acid would be shipped to liquid fertiliser plants and there ammoniated as was the procedure at that time with orthophosphoric acid. In other words, super acid would replace ortho acid in the existing practice. However, there were problems in shipping and handling super acid, mainly because of its relatively high viscosity and tendency to crystallize ("salt out") during shipment and storage. These problems could be minimized, and satisfactory shipping and handling properties attained, by setting the P_2O_5 content at about 76%. This concentration gives an ortho:pyro ratio that is near the eutectic and therefore the crystallization temperature is relatively low, about 16°C (61°F). However, only about half the P_2O_5 is in the poly form at this concentration (Table 1) whereas a much higher poly content is needed for maximum solubility. For acid containing 80-82% P_2O_5, which is best for solubility, the viscosity and crystallization temperature are so high as to make shipping difficult. Such acid is normally neutralized immediately after it is produced and before it cools.

Thus the practice developed of ammoniating super acid at the point of production and shipping the resulting ammonium polyphosphate solution. The nutrient content was reduced somewhat but shipping and handling properties were vastly improved. Moreover, the many liquid fertiliser mixing plants built after the advent of polyphosphates could avoid the expense of acid storage and acid neutralization. Instead of ammoniating acid ("hot mix"), they could merely combine the ammonium polyphosphate base solution with other constituents in a simple and inexpensive mixing operation ("cold mix").

This is not to say, however, that shipment of super acid is not feasible. Fairly large quantities of both the furnace and wet-process types are shipped successfully. The tendency to supercool helps by minimizing crystallization during shipping and storage. Viscosity is a major problem, however, especially for the wet-process type which is difficult to pump and meter at temperatures under 60°C. The usual practice is to ship it hot in insulated tank cars and convert it to 10-34-0 before cooling.

Some eutectic-type furnace acid (76% P_2O_5) has been shipped and stored as such but the practice is not prevalent. Insulated or heated storage tanks are used. Furnace acid in the 80-82% P_2O_5 range has been shipped also (in insulated stainless steel cars) but storage is not feasible; like wet-process super acid, it is neutralized upon arrival and before cooling. For such acids, the temperature must be above 60°C to avoid handling problems. Positive displacement pumps (e.g., gear pumps) normally are used.

The first ammonium polyphosphate base solution, made by TVA before knowledge of the solubility relationships was developed, was an 11-33-0 (0.33 N:P_2O_5). This was soon changed to 10-34-0 (0.29 N:P_2O_5) to get a lower salt-out temperature. Later a higher concentration of super acid was used to raise the polyphosphate concentration from about 50 up to 65-70% of the P_2O_5 and thus make it possible to go to an 11-37-0 grade (0.3 N:P_2O_5). More recently, in 1968, the acid concentration was raised still higher, to 80-82% P_2O_5, so that "high poly" 11-37-0 of optimum poly content (80% of the P_2O_5; actual range, 75-82%) could be made. This is the current TVA product. In addition, TVA recently introduced 12-44-0 (0.27 N:P_2O_5) which, as mentioned earlier, is more subject to hydrolysis in storage than is 11-37-0. Special attention is given to cooling before shipping and storage during the summer months is discouraged.

The ammonium polyphosphate base solutions have become a major factor in the United States liquid fertiliser industry, providing a combination of high nutrient concentration and good handling properties that has made them grow rapidly in popularity. There are now over 3000 plants in the United States producing multinutrient liquid fertilisers and it is estimated that 75% of them use polyphosphate base solution to supply the phosphate.

The main advantage of such base solutions is the high concentration and the consequent reduction in cost of transporting phosphate to mixing plants. There is also some increase in grade of the NPK mixtures produced (as compared with using orthophosphate), but the materials added in formulating such mixtures--such as urea, ammonium nitrate, and potassium chloride--severely reduce the beneficial effect of polyphosphate on solubility (7). The advantage of the polyphosphate is greatest for high phosphate grades and for grades containing no potash and is least when ammonium nitrate and potassium chloride are constituents of the solution (potassium nitrate, which has low solubility, becomes the equilibrium solid phase over a wide range of grades). For example, 6-18-6 can be increased to 7-21-7 by use of base solutions and 14-14-0 raised to 19-19-0, whereas 7-7-7 is about the best that can be done with either ortho or polyphosphate when ammonium nitrate is present.

The recent development of "high-poly" solutions (about 80% of the P_2O_5 as polyphosphate) has improved the situation further for some grade ratios (8).

Nutrient ratio	Products[a] made from			
	Ortho acid	10-34-0[b]	11-37-0[c]	12-44-0[c]
3:1:0	15-5-0	21-7-0	24-8-0	24-8-0
2:1:0	16-8-0	20-10-0	22-11-0	24-12-0
1:1:0	13-13-0	17-17-0	20-20-0	21-21-0

[a] Made from polyphosphate base solution and urea-ammonium nitrate solution.
[b] 43% of P_2O_5 as poly.
[c] 80% of P_2O_5 as poly.

In addition to increasing the grade of the final mixture somewhat, base solutions supply polyphosphate for other functions, including sequestering of impurities from wet-process phosphoric acid and increasing solubility of micronutrient compounds. These uses will be discussed in a later section.

Urea is generally better than ammonium nitrate as a source of supplemental nitrogen in regard to grade of NPK solutions. The main problem is that the low solubility of urea makes the shipping of urea solution somewhat expensive. (Solid urea could be used but is more expensive and solids handling is costly.) The usual source of supplemental nitrogen is urea-ammonium nitrate solution because the two compounds together have high solubility (28-32% N). One solution to this problem is to ship a urea-ammonium polyphosphate solution (e.g., 16-16-0). TVA is currently planning to produce solid urea-ammonium polyphosphate in its existing ammonium polyphosphate plant; with some minor alterations, this same plant could be used to produce a urea-ammonium phosphate liquid.

A few producers use straight urea, making grades such as 10-10-10 and 14-14-7 as compared with 7-7-7 and 10-10-5 with urea-ammonium nitrate solution (base solution, 10-34-0).

Base solutions have become so popular that about 120 plants now produce them. These range widely in size and scope, from large central plants making their own super acid and selling base solution over a wide area to small plants that buy super acid and ammoniate it for their own use (typical "hot mix" operation). Although super acid is viscous and difficult to ship, there are six companies that make and ship it in the United States.

A further method of supplying polyphosphate to mixers is to produce ammonium polyphosphate in solid form. In 1966, TVA started production of a solid product (15-62-0) that contained 50% or more of the P_2O_5 as polyphosphates; it is made by ammoniating super acid without addition of water. (The super acid is essentially anhydrous and thus gives a solid product directly.) The solid is shipped to liquid fertiliser producers in fairly large quantities where it is dissolved in water, often with further ammoniation to give a 10-34-0 base solution or to produce mixtures such as 7-21-7 and 4-11-11. The main disadvantage is the added cost for solids handling in existing liquid plants. Bulk blenders who want to convert partially to production of liquids find it particularly advantageous to use solid ammonium polyphosphate. They already have storage available for the material and need only to install a mix tank. Also, in the United States the freight cost for solid ammonium polyphosphate is significantly less than for liquid ammonium phosphate (77 vs 48 units of plant food).

One obstacle to getting high concentration in NPK liquids is the low solubility of potassium chloride and its reaction products, a problem that could be avoided by use of either potassium orthophosphate or polyphosphate. Several research organizations have worked toward this as an objective, but finding an economical method for potassium phosphate production has been a problem. For the orthophosphate system, only certain of the several potassium phosphate species have high solubility, and, as might be expected, these are the hardest to produce. The potassium polyphosphates, on the other hand, appear to be quite soluble. There is some commercial production in the United States of 0-26-27 from potassium hydroxide and super acid.

Recent developments in this field include the process developed by Pennzoil Research and Goulding Fertilisers. In this method, chlorine or hydrochloric acid is produced in addition to the potassium phosphate. The economics depend on the return that can be realized from these byproducts, plus any premium obtainable in the sales price of the potassium phosphate because of its high analysis and solubility.

In recent work at TVA (8), potassium phosphates--both ortho and poly--have been made by an electrolytic method (mercury amalgam type) in which potassium chloride is electrolyzed and the potassium stripped from the resulting amalgam by phosphoric acid. With ortho acid, the grade produced was 0-23-27; the range was 0-27-29 to 0-32-32 with super acid, depending on the polyphosphate content of the acid. The distribution of polyphosphate species in the product was about the same as in the original acid. A full economic evaluation of the process has not yet been made.

Suspensions: Although polyphosphates have afforded a means of increasing liquid fertiliser concentration significantly, there are some drawbacks--including that of reduced effectiveness when supplementary materials are added to the ammonium polyphosphate solution. Thus polyphosphate is quite effective in raising phosphate concentration for the trip from the phosphate producer to the smaller companies that mix it with other materials, but some other method is needed if the concentration of the final mix is to approach that of solid fertilizers. This has become even more important in the past few years because of increases in the speed of application, which has become so high that it is difficult to keep the applicators supplied (by transport from the mix plant directly to the farm) unless a highly concentrated fertiliser is available.

The use of suspensions has been the general answer to this problem. By carrying salt crystals in suspension very high analysis can be obtained; polyphosphate usually is still helpful because it holds more phosphate in the solution phase but the crystals carry a major portion, usually at least half, of the total nutrient. The suspension approach is particularly helpful when the grade is relatively high in nitrogen or potash. Examples are as follows:

Clear liquid	Suspension
8-8-8	15-15-15
3-9-9	7-21-21
2-6-12	5-15-30
10-5-5	20-10-10

The suspension grades compare well with the highest attained in the solid mixes commonly used.

Most suspensions are formulated in the same way as for clear liquids--by simple mixing of a base phosphate solution (10-34-0 or 11-37-0), urea-ammonium nitrate solution (28-0-0 to 32-0-0), and potassium chloride (9). A small amount of clay (about 2% of attapulgite or sodium bentonite) is added and thoroughly dispersed to slow the settling of crystals and also to make the solids easy to resuspend after settling during storage. It is necessary to impose shearing force to accomplish good clay dispersion, which is usually done in a special premixing step with clay and water. Recirculation of the clay-water mixture several times through a centrifugal pump usually gives excellent gelling of the clay.

There have been few recent developments in this type of suspension manufacture. The method is simple and effective, the main problem being high viscosity if too high a grade is attempted or if the ambient temperature drops to a low level. The latter is not usually a problem because suspensions are seldom stored very long, but for spring application in the colder areas viscosity sometimes causes difficulty. The optimum viscosity is generally considered to be 250-1000 centipoises (measured at 70°F).

There has been some development of base suspensions--grades such as 12-40-0 and 13-41-0 that are counterparts of the 10-34-0 and 11-37-0 base solutions (10, 11). In addition to the increase in concentration, excess clay is added so that in the final mixing little clay is needed (sometimes none), thus simplifying the operation for the mixer. TVA produces such base suspensions and they have been used in the industry to a limited extent.

Work has also been done on 14-47-0 but there has been no commercial use. The main problem is in production, where deposition of crystals on heat transfer surfaces makes the cooling operation difficult. One approach (12) is to spray the hot suspension into a cooled oil bath, thereby accomplishing cooling directly.

The 14-47-0 is a "clayless" type suspension. It has been found that if the polyphosphate content is high enough, on the order of 85% of the total P_2O_5, the very fine polyphosphate crystals formed stay suspended well without need for a suspending agent (13).

In some cases it might be desirable to use solid urea as the source of supplemental nitrogen rather than urea-ammonium nitrate solution. Tests have shown that high-analysis final mixes of good quality can be made in this way. The highest grade mixes of acceptable viscosity and storage properties were as follows:

	Supplemental N as	
$N:P_2O_5:K_2O$ wt. ratio	Urea-ammonium nitrate solution	Solid urea (micro prills)
1:1:0	21-21-0	23-23-0
1:1:1	15-15-15	16-16-16
1:2:2	10-20-20	10-20-20
1:2:3	9-18-27	9-18-27
3:1:0	27-9-0	30-10-0

In other tests, it was shown that ammonium nitrate can be substituted for the urea-ammonium nitrate solution without reducing the grade.

In work on NK suspensions, it was found that a satisfactory 20-0-20 grade can be made from solid urea and finely divided potassium chloride. With urea-ammonium nitrate solution the formation of potassium nitrate and ammonium chloride prevents attainment of high analysis.

Many companies have produced and marketed potash base suspensions such as 5-15-30 and 3-10-30. These are usually shipped to satellite stations where they are mixed with 12-40-0 or 10-34-0 ammonium polyphosphate suspensions and urea-ammonium nitrate solution to produce various NPK suspensions. No clay addition is required at the satellite station because both the potash and phosphate base suspensions contain clay.

One of the research needs in the suspension field has been a better knowledge of suspension rheology. In recent work at TVA (13), a torsion wire gelometer (Fig. 3) has been developed for use in studying gelation during preparation of suspensions; by use of different torsion wires, the yield point can be determined over a wide range.

(Figure 3)

The objective in suspension manufacture is to develop rheological properties such that a thixotropic gel forms on standing and crystal settling is thus inhibited. Upon agitation the gel should break up and the viscosity decrease to a point that the suspension will flow easily through pumps and piping. Then, upon further standing the gel should reform to prevent settling.

Tests with the gelometer showed that a high degree of shear is necessary to prepare gels of maximum strength (for a given amount of clay) but that there is an optimum; excessive stirring decreased the yield point by over 50%. The gel strength increased for a time after preparation, for example, from 4.5 g-cm after 15 minutes to 19 g-cm after 64 hours. Thereafter the strength declined, typically by over 60% in 6 weeks. Type, size, and amount of suspended solids were important.

Raw Material Cost

In comparison with solid fertilisers, the cost of raw materials is a more important consideration in formulating liquids because, for clear liquids, the solubility requirement rules out some of the low-cost materials. Much of the research in the field has been centered on development of combinations and procedures that reduce formulation cost.

Wet-Process Phosphoric Acid: In the beginnings of the liquid fertiliser industry the practice was based almost entirely on furnace-type phosphoric acid. Wet-process acid was a little cheaper, but the impurities dissolved in it precipitated during ammoniation and prevented attainment of the desired high degree of product clarity.

When polyphosphates came into the picture, the clarity problem was decreased considerably because the polyphosphates held the ammoniated impurities in solution by a sequestration mechanism. Nevertheless, furnace acid was still preferable because it was difficult to get a high polyphosphate content in wet-process superphosphoric acid, which is made by boiling the water out of wet-process orthophosphoric acid (usually about 54% P_2O_5). The impurities in the latter cause high viscosity if the ortho acid is dehydrated enough to give high poly:ortho ratio--and removal of water becomes more difficult as the polyphosphate content increases. In contrast, furnace acid is practically free of impurities and high poly is obtained merely by reducing the amount of water used to hydrate phosphorus pentoxide.

Thus for several years the premium for furnace acid was considered justifiable. The economic trends, however, have gone against furnace acid. The costs of electric power and coke have risen steadily while the sulfuric acid used in making wet-process phosphoric acid has declined in price to a low level. There is no current indication that these trends will reverse in the foreseeable future; sulfur recovered from sour natural gas and from waste gases likely will continue to depress the market, and the cost of power, in view of mounting environmental pressures, probably will increase rapidly. Thus furnace acid may well disappear from the liquid fertiliser industry in a few years. Because of this there has been a major research effort aimed at avoiding the shortcomings of wet-process acid.

The technique for <u>conversion of wet-process acid to super acid</u> is well known and there have been no significant recent developments. The P_2O_5 content is usually between 68 and 72% and the polyphosphate level from 45 to 55% of the total P_2O_5. The conversion to super acid increases the cost somewhat, but the long shipping distances in the United States generate freight savings that reduce or eliminate this disadvantage.

Because of the relatively low polyphosphate content in the wet-process super acid, the base solution grade is limited to 10-34-0; only one producer is known to have attempted 11-37-0 by simple ammoniation and this was discontinued--apparently because of salting-out difficulties.

Since wet-process super acid is relatively difficult to produce, a process has been developed that eliminates the need for the acid; instead of super acid, ortho acid is ammoniated under conditions such that the free water is evaporated and the orthophosphate is dehydrated to polyphosphate (14, 15). The resulting melt is then dissolved in water (with ammoniation and cooling) to give 10-34-0. This is an attractive method because the heat from reaction of acid and ammonia is not wasted--as it is when super acid is ammoniated--but supplies most of the heat required for water evaporation and polyphosphate formation. The heat requirement is only about 15% of that required if the super acid route is followed. Moreover, super acid handling problems are avoided and the cooling load for cooling the 10-34-0 is reduced by about one-third.

The direct process may become the preferred method for making polyphosphates, except perhaps where long shipping distances generate freight costs that outweigh the cost of making super acid and ammoniating it at the destination. Several producers use the process in the United States--including Jon-T Chemicals, Swift Agricultural Chemicals, and Goodpasture, Inc.--and there is at least one producer in France (Etablissements Gardinier). The processes used differ in some respects but usually include the steps of (1) preheating the wet-process orthophosphoric acid, (2) reacting the acid with preheated ammonia in an insulated reactor at 250-350°C, (3) dissolving the polyphosphate melt in water, and (4) adding ammonia to give the desired N:P ratio. Gardinier (16) reports use of separate steps for disengaging steam and ammonia from the melt and recovering the ammonia, while Swift (17) disengages in the melt dissolution tank. A flowsheet of the Swift process is shown in Figure 4.

(Figure 4)

Although the direct process is economical, the heat available in the system (reaction heat plus that which can be added feasibly as reactant preheat) is not sufficient to give a polyphosphate level higher than about 50% of the total P_2O_5. Supplemental heat could be applied to the reactor, of course, but mechanical problems make this unattractive. Another approach, now coming into use, is to remove part of the water from the orthophosphoric acid before introducing it into the direct process system. In other words, wet-process super acid of relatively low polyphosphate content is used as the acid reactant. Process cost is increased because of the separate step required for concentrating the ortho acid, but the high polyphosphate content generated in the resulting ammonium polyphosphate solution improves the quality so much (see later discussion) that the additional expense seems justified.

The TVA flowsheet for this method (8) is shown in Figure 5. Feed acid, containing 20 to 50% of the P_2O_5 in the poly form, is fed continuously to a pipe reactor where it reacts with a continuous stream of gaseous ammonia.

The reaction temperature is 330-345°C, which can be maintained without acid preheat (other than that required for adequate flowability) because the lower water content results in less evaporative cooling in the reactor. The melt flows from the reactor into a loop-type dissolution-cooling system, from which the product is 11-37-0 containing 75-85% of the P_2O_5 in the poly form. In pilot plant tests good results were obtained when 60% of the ammonia was fed to the reactor and the remaining 40% was introduced with the melt-dissolution water fed into the loop downstream from the reactor.

(Figure 5)

The 11-37-0 is cooled by a combination of heat exchange with water and with vaporized ammonia. The latter supplies about 25% of the cooling load. A final temperature below 65°C is required to minimize hydrolysis.

The process has the advantage that "low conversion" super acid (25-35% of the P_2O_5 as polyphosphate) produces a final polyphosphate level almost as high as when standard super acid (50% of P_2O_5 as poly) is used. The low-conversion acid can usually be produced at higher rate in a given concentrator.

The melt could also be solidified and the resulting solid ammonium polyphosphate shipped to mixers, where the additional ammonia would be added during dissolution and mixing. The melt is difficult to granulate, however, and the physical properties are not as good as for the furnace type. TVA pilot plant tests on granulation in a pugmill (13) have shown that granulation is improved by reducing the polyphosphate level and that above 30-35% it is quite difficult to induce crystallization in the viscous melt. Such a poly content, of course, is lower than desirable for liquid fertilisers. In recent tests, attempts have been made to further ammoniate the melt before cooling--on the basis that the higher degree of ammoniation should induce crystallization. Some improvement has been noted but a satisfactory method of making acceptable ammonium polyphosphate (at least 50% of the P_2O_5 in the poly form) from wet-process acid is not yet available.

Another approach to solving the low polyphosphate problem is to use high-poly (80%) 11-37-0 along with low-poly (50%) 10-34-0 (in cold-mix plants) or wet-process ortho acid (in hot-mix plants) to get a higher poly level. The latter is a relatively old and established practice. Furnace-type 11-37-0 has been used mainly but the new high-poly 11-37-0 made by the wet-process route is also suitable.

Still another approach is that used by some furnace acid producers who have incorporated limited amounts of wet-process ortho acid into the furnace acid manufacturing operation. For the past 3 years TVA has added wet-process acid to the hydrator in the furnace acid plant to supply up to 25% of the P_2O_5 content in the product super acid. The wet-process acid supplied the water required for P_4O_{10} hydration. Substitution of more than 25% may be feasible and TVA is attempting to increase the proportion of wet-process acid; tests have indicated that as much as 32% can be attained.

The suspension route also offers a means for using wet-process acid--without the necessity for generating polyphosphate to give high analysis and to sequester impurities (18). One approach is "hot slurry" operation, which is restricted to local practice because the process involves mixing wet-process acid (ortho), ammonia, nitrogen solutions, and potash, followed by application while still hot to avoid excessive crystallization and settling. Fairly high grades can be attained (e.g., 14-14-14) but the product characteristics are such that adequate agitation must be provided from the time of production to application. The product is really not a true suspension as no attempt is made to develop thixotropic properties that would make it suitable for storage.

Although there are problems in handling and applying, the simplicity and low raw material cost of the "hot slurries" have given them considerable commercial success. The raw material cost in some instances has been even lower than for bulk blends made from 18-46-0, ammonium nitrate, and potash. The practice is restricted to broadcast application, however, since the product quality is not good enough for row-applied fertiliser.

Work has also been done on storable suspensions (no polyphosphate), mainly at TVA (8). Base suspension grades satisfactory in regard to viscosity and crystal settling as high as 12-40-0 can be made by a procedure involving two-stage ammoniation. In the first stage, carried out at 225°F, about 75% of the ammonia is added (to a pH of 4) and the mixture held at the high temperature for about 30 minutes; the slurry is then cooled to 160-180°F and the rest of the ammonia introduced (final pH, 5.9; retention time, about 10 minutes; clay addition, 1.5%). The two-stage technique is believed to cause precipitation of metal-based impurities as crystalline compounds rather than amorphous materials that limit the grade in single-stage ammoniation because of high viscosity. The 12-40-0 has excellent long-term storage properties and can be used to make high-analysis NPK suspensions.

There is a limited suspension practice in which only solid raw material such as diammonium phosphate (18-46-0), urea, and potassium chloride are used. Since the 18-46-0 is made from wet-process acid, this is another way of getting the cost advantage of the acid. The materials must be mixed long enough to dissolve the granules, at least partially, in order to reduce their size. Some companies use liquid grinders to grind the granules during mixing. It is also helpful to add a little phosphoric acid to adjust the $N:P_2O_5$ ratio to a level that gives higher solubility.

There has been some development, particularly in Europe and Canada, of "powdered" monoammonium phosphate (made from wet-process phosphoric acid) for use as a low-cost intermediate in granulation of mixed fertilisers. Limited studies have been made by TVA (13) on use of the material in preparation of suspension fertilisers; the powdered form makes it superior for such use as compared with the usual granular ammonium phosphate products. Supplementary materials in the tests were urea and potassium chloride, plus ammonia to adjust the $N:P_2O_5$ ratio to that optimum for solubility. Acceptable 15-15-15, 11-22-11, and 22-11-11 could be made without clay.

The use of monoammonium phosphate depends on the supply, which is currently limited in the United States but perhaps adequate in other areas.

All these ramifications in use of wet-process acid to reduce raw material cost make the situation confusing. The following tabulation is offered in an attempt to clarify the practice (mainly in the U.S.).

Method	Status	Significance[a]
10-34-0 made from super acid at acid production point; shipped to mixer	Commercial	One of the principal methods; estimated to account for 40% of 10-34-0 production[b]
Super acid shipped; 10-34-0 made at regional plant and shipped to mixer	Commercial	Also a major method; estimated at 20% of 10-34-0 production
Super acid shipped; 10-34-0 made and used by mixer	Commercial	20% of 10-34-0 production
Direct process; 10-34-0 or 11-37-0 (high poly) shipped to mixer	Three producers using orthophosphoric acid; ten producers using low-poly super acid (also two in Europe)	20% of 10-34-0 production
Direct process by mixer	Production planned	-
Hot-mix slurries	Commercial	25% of suspensions produced in this manner
Cold-mix suspensions	Commercial	70% of suspensions produced by this method, using ammonium polyphosphate base solutions. About 10% of this tonnage is stored and the remainder applied immediately
Suspensions from solid materials	Limited practice	New equipment now being introduced to improve this procedure

Method	Status	Significance[a]
Wet-process ortho acid used by mixer with supplementary 11-37-0 (furnace or wet process) to sequester impurities	Commercial	25% of total P_2O_5 used in liquids
Solid ammonium polyphosphate	TVA is the only producer	Limited
Wet-process acid used in furnace super acid production	Only TVA and one commercial producer	Limited

[a] Percentages given are rough estimates only. Percentages are not additive since some overlap.

[b] 10-34-0 is estimated to supply about 70% of the P_2O_5 used in making clear liquid fertilisers, and clear liquids account for about 70% of the total in all fluid fertilisers (including suspensions).

Nitric Phosphate: A few years ago, when sulfur was in short supply and high in price, there was considerable activity in reducing raw material cost by production and use of nitric phosphate suspensions (19, 20). Nitric acid took the place of sulfuric acid in acidulating phosphate rock, producing phosphoric acid containing calcium nitrate in solution. Then when ammonia was added the calcium precipitated as calcium phosphates and the ammonia was combined as ammonium nitrate.

Since the calcium remained in the product, the nutrient concentration at acceptable viscosity was relatively low; typical grades were 9-9-9, 6-12-18, and 6-12-12. Because of this, a local operation was visualized with small, relatively simple acidulation plants serving a limited area; about eight such plants were built in the central section of the United States.

Several factors have worked against the success of this method, with the result that most of the plants have been shut down or converted to other types of liquid fertiliser (it is understood that only one plant is still operating).

1. The low grade gave relatively high handling cost.

2. Nitric acid is relatively dilute and thus involved high shipping cost.

3. The continuing decrease in sulfur price removed much of the formulation cost advantage.

4. Corrosion and atmospheric pollution were problems.

5. It was difficult to precipitate the calcium phosphates in a form available to plants; basic calcium phosphates insoluble in citrate were formed. This could be avoided by various means but all increased cost.

Nitrogen Materials: Since all the nitrogen in fluid fertilisers can be supplied as liquid materials (e.g., 32-0-0 and 11-37-0) nitrogen cost is usually lower than for solid fertilisers, particularly those for which the formulation is such that solid nitrogen materials must be used. On the other hand, in making a solid such as diammonium phosphate more low-cost ammonia can be used than in liquid fertilisers. Thus the nitrogen tied up with phosphate is usally cheaper in solids but the supplemental nitrogen costs less in liquids. The net balance, of course, depends on the grade.

Although urea and ammonium nitrate are the usual supplementary nitrogen materials, in the past few years formulation cost of liquid fertilisers has been reduced in some cases by using ammonium sulfate. Sulfate is not normally regarded as an economical fertiliser material but growth in production as a byproduct, mainly from caprolactam plants, has changed the situation somewhat, and the possibility of recovering sulfur oxides from power plant and smelter waste gases as ammonium sulfate may make the material even more economical in the future. The main drawback is high shipping cost because of the relatively low nitrogen content, but this could be offset by the low price level resulting from its byproduct status.

Ammonium sulfate also supplies nutrient sulfur, as discussed later, but this is a special use for limited areas. For general use, only the nitrogen provides practical economic value.

Unfortunately, ammonium sulfate is not very soluble in liquid fertiliser systems; Achorn and Scott (21) report relatively low grade (e.g., 10-24-0) for clear solutions made from sulfate and 10-34-0.

Thus the suspension approach is more promising. By mixing sulfate 13-41-0 (polyphosphate base suspension), and potassium chloride, grades such as 12-12-12, 14-7-7, and 16-8-4 with acceptable properties have been produced. These are somewhat lower than for suspensions made with urea or urea-ammonium nitrate but are still high enough to be attractive.

There has been some limited use of sulfate suspensions in the United States--made from sulfate, 10-34-0, and potash. The main grades have been 20-8-4 and 4-12-12, with 2-3% clay. The product is not stored but is applied immediately by broadcasting from an applicator truck equipped with a recirculation system to prevent settling.

Potash Materials: Most liquid fertiliser producers use "liquid grade" potash--finely divided white potassium chloride (62% K_2O)--which usually costs slightly more than the standard potash (60% K_2O) used in production of homogeneous granular mixed fertiliser. The advantage of the liquid grade material is that it dissolves faster in manufacture of clear solutions and suspends better in suspensions. The coarse or granular potash used in bulk blends usually costs more than the liquid grade.

Product Quality

Development and maintenance of high quality is a matter of major importance in the liquid fertiliser industry. In contrast to solid fertilisers, quality requirements are somewhat more rigorous because of the special problems encountered in storage and application. This is not to say that there are not quality problems in production and use of solids, but getting the grade within the prescribed limits and controlling caking are the main solids problems whereas liquids involve such diverse troubles as salt crystallization in cold weather, precipitation of impurities in the form of gels during storage, off color, polyphosphate hydrolysis, and, for suspensions, nutrient segregation, crystal growth, and difficulty in redispersing solids after storage.

The situation is affected considerably by the type of application. For starter or sidedress fertiliser, which mainly involves application by injecting the liquid below the soil surface, the requirements are much more severe because the fertiliser must be applied with accuracy and in relatively small amounts; clear liquids or suspensions of very good quality are much preferred. In contrast, broadcast application allows much more leeway, especially if applicators of the type described later are used. The continuous stirring and large nozzles allow use of fluid fertilisers that otherwise would be regarded as too low in quality to be acceptable.

Impurity Precipitation: The sequestering effect of polyphosphates has made it possible to prepare clear liquid fertilisers from wet-process phosphoric acid and thereby allow substitution of the acid for the furnace type to reduce cost. There is still a problem, however, because the impurities often precipitate in storage even though the product was clear initially. A large amount of the recent research effort has been concerned with this adverse effect on quality.

The chemistry of impurity precipitation is quite complex. In the first place, phosphate rock contains numerous compounds that are extracted with the phosphate during wet-process acid production; typical analyses of acid made from Florida rock (18), for the usual shipping-grade concentration (54% P_2O_5) and also for super acid, are as follows (in weight percent):

P_2O_5 Total	P_2O_5 Ortho	Fe_2O_3	Al_2O_3	MgO	F	SO_3
54.0	54.0	1.3	1.4	0.5	1.0	3.0
70.7	39.5	1.8	1.6	0.8	0.3	2.4

The general range of impurities, for shipping-grade acid made from Florida and western U.S. rocks, is

Constituent	Range, wt %
Fe (as Fe_2O_3)	0.4-1.8
Al (as Al_2O_3)	0.5-1.8
MgO	0.2-0.8
K_2O	0.003-0.06
Na_2O	0.01-0.2
F	0.1-1.1
SO_3	0.1-0.9

These constituents combine to form a large number of compounds that precipitate slowly from the supersaturated solution even without ammoniation; this has been a major problem for a long time in shipping and storing wet-process acid regardless of its end use.

Lehr and coworkers (22) in recent years have made major progress in elucidating the nature and properties of these compounds, both before and after ammoniation. The subject is so complex that no attempt will be made to cover the full scope; in general, the major precipitates from the acid are compounds of the general formula $(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$ and from the ammoniated acid a series with a wider range of composition corresponding roughly to $(Fe, Al, Mg)_x(H, NH_4)_y(PO_4)_z \cdot nH_2O$.

Removal by settling is the time-honored method for reducing impurity content of the acid, made necessary in the United States by the need to get at least partial clarification to improve shipping and handling properties.

There are several recent patents on use of additives such as coal tar derivatives to promote precipitation before or during settling, but it is not known whether or not these are actually used. The main development seems to have been an intensification of efforts by producers, by expanding settling and centrifuging facilities to provide acid of better quality for liquid fertiliser customers.

Calcination of phosphate rock is practiced fairly widely as a means of removing organic matter, decomposing carbonates (to improve grade), and promoting settling rate of impurities. Recent work (13) has also shown that calcination can contribute to metal compound removal in another way, particularly for magnesium which gives the most trouble in liquid fertilisers. Calcination of the rock at 1000°C for 30 minutes followed by extraction with a dilute acid (H_2SO_4, H_3PO_4, or HNO_3) removed as much as 90% of the magnesium and only 4-5% of the P_2O_5. This work was exploratory only but seems promising.

Solvent extraction is now a commercial practice (in Israel and Mexico) for making high-quality phosphoric acid of low impurity content. The process, developed by Israel Mining Industries, involves extraction of phosphate rock with hydrochloric acid followed by solvent extraction to separate the phosphoric acid from the calcium chloride. The solvent-extracted acid is relatively free of impurities except for iron; typical contents (wt %) are Fe (as Fe_2O_3), 0.53; Al (as Al_2O_3), 0.0002; MgO, 0.0048.

The acid can also be made by the standard method, extraction with sulfuric acid, and the impurities separated from the product by solvent extraction.

Solvent-purified acid has recently begun to enter the U.S. liquid fertiliser industry, where it is converted by the direct process to high-poly 11-37-0. This is a clear, light green product, which remains free of precipitation for storage periods up to 6 months.

Another solvent method (23), developed by Bohna Engineering and Research in the United States, may become significant; it has been tested only on a pilot plant scale so far but may be commercialized. Three flowsheets are proposed, two involving acidulation of phosphate rock with ammonium bisulfate (which is recycled) followed by solvent extraction--and the third solvent extraction of ordinary superphosphate. Very low impurity content, except for magnesium, is claimed.

Pilot plant tests have been carried out by Azote et Produits Chimiques (24) on phosphate rock extraction by nitric acid followed by solvent extraction and ammoniation. Monoammonium phosphate with only a small impurity content precipitates.

Typpi Oy, in Finland, has worked on a somewhat similar process (25) and has announced plans for a plant. A solid mixture of ammonium phosphate and ammonium nitrate is obtained; the objective, however, is to make a high-quality solid fertiliser rather than a liquid type.

Although these methods have produced considerable improvement, the quality of phosphate supplied by wet-process acid is still not good enough--with the possible exception of some types of solvent-purified acid--to allow production of a clear, stable liquid fertiliser unless some polyphosphate is present. The main effect of the higher quality ortho acid now available has been to increase its use by mixers in hot-mix plants. Supplementary polyphosphate to sequester residual impurities is still required for clear products, but less sequestrant is needed. Also, if the suspension route is followed, the lower impurity content gives a better product.

Sequestration by polyphosphates is now a relatively old procedure and is fairly well standardized. Several patents have been issued on use of sequestrants other than polyphosphates but these appear to be of little importance.

The main problem has been the relatively low polyphosphate content of products made from wet-process acid, which often has not been high enough to give adequate sequestration. The new developments in attaining higher poly level, discussed earlier, should solve this problem--although even with the high-poly product it is economical to restrict the amount when it is used in conjunction with wet-process ortho acid in a hot-mix plant. Therefore research has proceeded on ways to maintain clarity when the minimum amount of polyphosphate is used.

The main trouble has been with magnesium which, being divalent, is more difficult to sequester than the trivalent iron and aluminum. Ferrous iron (Fe^{++}) can also give trouble by precipitating as $Fe(NH_4)_2P_2O_7 \cdot 2H_2O$, but tests have shown that this can be prevented by adding a small amount of ammonium nitrate or other oxidizing agent to oxidize the ferrous iron to the trivalent ferric form.

Results obtained in laboratory studies of solubility in the system $MgO-NH_3-H_3PO_4-H_4P_2O_7-H_5P_3O_{10}-H_2O$, and $MgO-NH_3-H_3PO_4-H_4P_2O_5-H_5P_3O_{10}-H_6P_4O_{13}-H_2O$ at 25°C (13) showed (1) that the magnesium ammonium pyrophosphates $Mg(NH_4)_2P_2O_7 \cdot 2H_2O$ and $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$ were the only precipitating phases, (2) that tripolyphoshate is the most effective of the condensed phosphates for sequestering magnesium, thereby preventing or delaying the precipitation of magnesium pyrophosphates in ammonium polyphosphate fertiliser solutions, (3) that lowering the pH of the solution from about 6.5 to 5.5 delays appreciably the precipitation of magnesium phosphates, and (4) that the principal beneficial effect of the tetrapolyphosphate was to maintain or to increase the tripolyphosphate content of the solutions through hydrolysis of tetrapoly to tripolyphosphate as the initial step of the hydrolysis mechanism. These results together with those obtained in a study of the simpler system, $MgO-NH_3-H_5P_3O_{13}-H_2O$ at 25°C indicate that the MgO content of ammonium polyphosphate liquid fertilisers stored in excess of a few weeks at 25°C should not exceed about 0.7%.

The magnesium problem has been and continues to be a serious one, probably the major current operating problem in the liquid fertiliser industry. Several methods for improving the situation have been tested, none with complete success. The best approach seems to be use of base solution with very high polyphosphate content, on the basis that such solutions contain a relatively high proportion of tripoly and longer chain species which the above studies indicate to be more effective, per atom of phosphorus, in sequestering magnesium.

Other tests have shown (13) that the storage life of 10-34-0 (time until appearance of magnesium precipitate) can be correlated directly (for a given storage temperature) with the initial weight ratio of high-poly P_2O_5 (P_2O_5 in chains longer than pyrophosphate) to MgO. The amount of high-poly P_2O_5 required may depend on the lime content, since calcium is also difficult to sequester. (Low temperature storage, of course, minimizes the problem because polyphosphate loss by hydrolysis is reduced to a low level.)

As a practical matter, if the magnesium content of the phosphoric acid is such that the product solution will contain more than about 0.7% MgO, it is probably better to produce a suspension rather than attempt a clear solution.

The presence of fluorine may complicate the magnesium problem (26) by causing precipitation of a sludge of $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ (27). Further studies of this compound established that it can exist in two crystalline forms--the insoluble crystal dimorph that causes the sludge, and a much more soluble crystal dimorph that is stable at higher fluoride concentrations. It has thus been established that there is a critical range of fluorine content within which the insoluble crystal dimorph of this compound will precipitate, and that on either side of this range the problem is eliminated. The amount of fluorine present depends on whether the liquid fertiliser is prepared by the super acid route, in which case much of it will have been driven off in manufacture of the super acid, or by the direct process, which does not evaporate as much. In either case, if the fluorine content is in the critical range, a fluoride can be added to prevent precipitation. The amount required depends on the amount of magnesium present and on the iron and aluminum content. The relative effect of each can be expressed empirically by the ratio: $F:(MgO + 2.5Al_2O_3 + 0.33Fe_2O_3)$. This is a convenient simplified chemical expression of the optimum complex-ion equilibria between fluorine and aluminum, magnesium, and iron. The value for this ratio necessary to prevent precipitation also depends on the content of pyrophosphate, since this is the precipitating phosphate species; as pyro content increases, the optimum fluorine content also increases slightly.

Several soluble inorganic fluoride compounds were found suitable for the addition in laboratory tests; ammonium bifluoride was used in pilot plant tests with good results. Waste fluosilicates also appear to be acceptable, although the ammonium salts are preferred over sodium or potassium forms to avoid further impurity contamination. The range of minimum acceptable fluorine ratio in the tests (small scale and pilot plant) was about 0.1 to 0.5.

Another magnesium problem is formation, under certain conditions, of a gel rather than a precipitate--sometimes to the extent that the liquid is converted to a clear, semisolid mass. It has been found (26) that this is a function of the $MgO:Al_2O_3$ weight ratio, the pyrophosphate content, and the fluorine:metal oxide ratio; only when the $MgO:Al_2O_3$ ratio is larger than 1.0, 25-40% of the P_2O_5 is present as pyrophosphate, and the fluorine:metal oxide ratio is 0.1-0.2 does the gel form. Either fluorine or Al_2O_3 can be added to move the composition away from these ranges.

Urea phosphate production is another new development aimed at improving liquid fertiliser quality (8). Work on urea phosphate has been carried out in Europe (28) and in India (29), and TVA recently began a program on production of relatively pure material suitable for use in making high-quality clear liquid fertiliser.

In bench-scale work with wet-process orthophosphoric acid, addition of urea precipitated about 80% of the P_2O_5 as urea phosphate [$CO(NH_2)_2 \cdot H_3PO_4$] containing only about 10% of the acid impurities. The nutrient grade was 17.7-44.9-0. Exploratory tests indicate that the urea phosphate can be converted to ammonium polyphosphate by ammoniation; at the elevated temperature developed in ammoniation, the urea dehydrates the orthophosphate to polyphosphate and is itself hydrolyzed to ammonia and carbon dioxide.

In operation of the process, it would be expected that the impurity-laden mother liquor (about 7-27-0) from the urea phosphate crystallizer would be used in making suspension or solid fertilisers.

Color: The furnace-type phosphoric acid used in the liquid fertiliser industry normally gives a clear solution almost visually undistinguishable from water. With wet-process acid, however, the solution has some color, ranging from green to amber even if completely devoid of solids. Ordinarily, this type of coloration is acceptable; in fact, the green color, especially when associated with sparkling clarity, seems to be a characteristic preferred by consumers.

However, liquid products often appear murky and dirty, even black in color, because of finely divided carbonaceous matter--not enough to be termed an impurity precipitation problem or to class the product as a suspension but enough to reduce customer acceptance because of the poor appearance.

A good way of avoiding the problem is to calcine the phosphate rock, which destroys the organic compounds present in the rock and usually produces the desired green color. (Some rocks, notably Kola, do not require such treatment.) Since calcination is costly, however, research has been done on removing the carbonaceous material from the acid or from base solution.

Filtration is one approach. At least one producer in the United States filters 10-34-0 before shipping. The carbonaceous matter can also be oxidized. In work at TVA (13) on clarifying products made when wet-process acid was added in furnace super acid production, oxidants such as nitric acid, ammonium nitrate, sodium chlorate, alkali dichromate, and potassium permanganate were effective. Nitric acid or ammonium nitrate is used currently in the plant, with good results except that foaming and corrosion have been problems. Flotation and filtration also gave good results in small-scale tests.

Polyphosphate Hydrolysis: Since sequestration is depended on to keep impurity precipitation from affecting quality, it is important to prevent or minimize loss of polyphosphate by hydrolysis during shipping and storage. Although research has been done on inhibition of hydrolysis, nothing of consequence has developed. The only practical approaches, therefore, are to keep temperature down, pH up, and the storage period as short as possible.

It has always been considered in the liquid fertiliser industry that the final mix should not be stored very long, mainly because it is simpler and cheaper to make the mix only when the farmer is ready to use it and haul it directly to the farm; this is feasible because the simple mixing units have high capacity. The main storage is in the nurse tanks that supply the applicators and this is short-term storage.

Intermediates, however, are in a different category. The mixer likes to buy 10-34-0, for example, and store it so that a supply is available throughout the busy mixing season. And if any is left over, he would like to keep it until the next season. Also, some producers store base solutions such as 10-34-0, 32-0-0, and 4-10-10 at "satellite" stations near farming centers, mixing on order in the customer's nurse tank or applicator. Agitation is not required because the materials mix themselves as they are pumped into the tank.

The main development in this respect is that producers have generally accepted polyphosphate solutions as having limited "shelf life" and have adapted their practice to accommodate this. The very high polyphosphate level in recently developed solutions is also helpful, because there is more leeway for hydrolysis without getting the polyphosphate level unacceptably low.

Suspensions: Suspension fertiliser is also a short shelf-life item. As noted earlier, the thixotropic properties of N:P:K suspensions deteriorate in extended storage (maximum good storage about 3 months) and no way to give long storage life has yet been found. The N:P base suspensions can be stored for relatively long periods, however, usually longer than for base solutions because polyphosphate level is not as important.

Although complete stability (no crystal settling) is desirable, in practice there is usually some settling. This is acceptable as long as a settled layer difficult to redisperse is not produced. Crystal growth in storage can also be a problem by plugging lines and nozzles. The main developments in regard to these problems are improved clay incorporation procedures that optimize the thixotropic properties and application equipment designed to maintain homogeneity and minimize plugging.

Product Versatility

In addition to supplying the primary nutrients, fluid fertilisers are more versatile than solids in ability to carry other materials to the soil. In fact, one of the main factors in the current popularity of suspension fertilisers is that micronutrients and pesticides can be incorporated more easily and applied more effectively than when combined with solid fertilisers.

Micronutrient compounds can be dissolved in clear liquids if the chelated type is used or if the ordinary inorganic types are sequestered with polyphosphate. The suspension route can also be used as a means of supplying low-cost micronutrient sources in amounts sufficient to fulfill agronomic requirements. The micronutrient sources--typically sodium borate, copper sulfate, zinc oxide, manganese oxide (Mn_3O_4), and sodium molybdate--are merely mixed with water and introduced along with the other constituents. The only requirement is that the particle size be small, no larger than 60 mesh. The agitation necessary to develop thixotropic properties gives adequate mixing of the micronutrients, much more easily and uniformly than in solid fertiliser production where the finely divided micronutrient tends to segregate from the larger fertiliser particles. Application is also more uniform since the agitation in the applicator ensures homogeneity.

The suspension route is especially desirable in pesticide incorporation. Since the usual types of pesticides are not soluble in clear liquid fertilisers, segregation occurs in storage and continuous agitation is needed during application. In compatibility tests with suspensions, however (30), thirty of the thirty-two pesticides tested were found to be compatible, that is, they remained dispersed throughout a quiescent suspension for prolonged periods.

Addition of an emulsifying agent gives further stability, but ordinarily is not used unless the pesticide is added to clear liquid fertiliser and the application equipment is not fitted with an agitator.

Incorporation of pesticides in fertilisers saves time and expense by applying the two together. However, application of solid fertilisers usually is not uniform enough to give the high degree of distribution uniformity needed for the pesticide. For this reason, along with the simple mixing, suspension-pesticide mixtures have grown rapidly in popularity.

Incorporation of nutrient sulfur is another area in which suspensions are advantageous. Achorn and Scott (21) have shown that satisfactory grades such as 12-6-6-11.5S and 11-11-11-8.6S can be made by combining ammonium sulfate with 13-41-0 base suspension and potash. A clay content of about 1% was adequate for good suspension properties. In commercial practice, grades such as 20-8-4-3S and 4-12-12-5S have been made with low-poly 10-34-0; 2-3% clay is used and the products are applied immediately.

Ammonium thiosulfate is used commercially in combination with 11-37-0, giving a clear solution of 11-24-0-9S grade. Ammonium polysulfide (20-0-0-45S) is used in conjunction with aqua ammonia and urea-ammonium nitrate solution; it is not compatible with phosphate. The older practice of using byproduct ammonium sulfite-bisulfite solution continues in the western part of the United States and in Canada, but the sulfur-ammonia solution pioneered by TVA several years ago has lost popularity because of handling problems in the field.

Application of nutrient sulfur by incorporation in liquid fertilisers is growing in the United States, both because sulfur deficiency is increasing and because the liquid fertiliser route is convenient and time-saving. Ammonium sulfate as a sulfur carrier is especially important in states such as Nebraska, Kansas, and Texas.

Manufacturing Techniques

Since one of the main advantages of liquid fertilisers is the simplicity of production, major developments in manufacturing technique would not be expected. However, there are some recent departures that have given significant improvement.

Pipe Reactor for Polyphosphate: A simple device for reacting ammonia with phosphoric acid (ortho or super) in the direct process for making ammonium polyphosphate has been developed (31,8). The usual corrosion and scaling in the reactor can be reduced by cooling the reactor walls with a water jacket;

the arrangement used in the TVA pilot plant is shown in Figure 6. The acid and ammonia are mixed by a concentric tube arrangement that is quite simple but gives good mixing.

(Figure 6)

The pipe reactor is being adopted widely by the liquid fertiliser industry; an example of a plant so equipped is shown in Figure 7. Ammonia is added through a 2-inch-diameter stainless steel pipe installed in the vertical section of the reactor tee, and wet-process superphosphoric acid (20-35% of P_2O_5 as polyphosphate) is fed through a 4-inch-diameter side inlet of the tee. Ammonium polyphosphate melt is discharged into the hot well of the tank-type cooling tower. The melt is discharged about 2 inches above the surface of the liquid in the hot well. All the ammonia used in the process is added in the pipe reactor. The liquid from the hot well is recirculated through the top of the cooler and sprayed onto a bed of Pall-ring packing by spray nozzles mounted on a manifold.

(Figure 7)

The packing is supported in the cooler by a screen. Air is blown into the cooler by a fan that has a capacity of about 10,000 cfm and which discharges beneath the screen. The liquid passing through the packing impinges onto a baffle that covers about two-thirds of the bottom of the tank and discharges the cooled liquid into the hot well. The hot well overflows through a weir into the product well, from which the solution passes to a heat exchanger in which further cooling is induced by partial vaporization of the liquid ammonia feed. The cooled product is pumped to storage. The ammonia passes from the heat exchanger through a second vaporizer heated with steam to complete the vaporization and to supply superheat.

Some producers use only the hot liquid fertiliser to vaporize the ammonia, while others prefer to use the arrangement shown. However, those using the extra vaporizer have fewer startup problems.

All producers that use the pipe reactor still report some problems with scale formation inside and on the walls of the reactor. However, although the scale is hard, it can be removed by chiseling or other mechanical means. Shutdown can be avoided by having two reactors available (piped in and connected) so that one can be cleaned while the other is operated. Most plant operators report that the scale is troublesome but that they can usually operate the plant with a minimum of downtime. One operator reports: "We can usually live with this minor scale problem." Another has recently installed a large diameter reactor (6 in.) since the relatively large size makes it easier to remove the scale.

Hot-Mix Cooler: Cooling of the product has always been a problem in mix plants that use wet-process acid along with other materials. Cooling water must be supplied and heat transfer surfaces tend to foul. Natural-draft air cooling of the direct type has been adopted recently in some plants as a means of simplifying the operation. The liquid is pumped to nozzles that spray down into an air chamber, typically 4 x 8 x 12 feet; the spray area is enclosed by an open assembly of wooden slats to prevent droplet drift with the air that passes through the space as the result of natural draft.

Some producers have used forced-draft evaporative-type coolers (packed with redwood slats) such as those employed in commercial refrigeration units. The hot liquid is dribbled onto the packing and air is drawn across the packing by an exhaust blower.

Portable Base Solution Plant: There has been some departure from the general practice of ammoniating wet-process super acid immediately upon arrival and then shipping the resulting base solution to hot-mix, cold-mix, and satellite plants. At least two producers have developed portable 10-34-0 units of the continuous reactor type (as opposed to the batch reactors normally used in hot-mix plants). The unit is mounted on a truck and moved from plant to plant to fill 10-34-0 storage tanks. A pipe-type reactor is used but solution is circulated and water added in the reactor, thus making the operation different from that in which polyphosphate is generated in the reactor.

Punched Card Formulation: Most plants, both hot and cold mix, are still of the batch type; ingredients are added to a batch mixer mounted on scales for direct weighing. The relatively high operator time required for the batch operation has been reduced by automating the system. A punched card inserted into the scale activates pneumatic control valves that automatically feed the ingredients. Little operator attention is required.

Suspension Mixers: Type of mixer is quite important in making suspensions because shear forces must be applied to a certain degree in order to develop good suspension properties. Pump recirculation has been widely used. Mixers of the helical ribbon and turbine type have been developed that are claimed to give superior results.

Developments in Handling and Application

There have been few developments in the handling of liquids. Pipeline transport of nitrogen solutions has been suggested but so far the only significant pipeline practice is in the anhydrous ammonia field. Storage of phosphoric acid in lined pits and in collapsible rubber containers, both relatively old techniques, has continued to increase. A typical pit is 40 x 100 x 6 feet, lined with 30-mil polyvinyl chloride sheet. A drain line under the plastic leading to an outside sump is normally included as a leak detector. Such pits have also been used in storage of urea-ammonium nitrate solution and liquid mixes. A typical "pillow" storage vessel is 45 x 53 x 4 feet, containing 50,000 gallons. They are installed in the open on flat ground.

Broadcast Applicators

The main developments have been in application, especially for the broadcast type. The industry has tried to take full advantage of the economy afforded by the liquid form in allowing high speed, high volume application with a minimum of handling difficulty and a maximum of labor saving. Larger applicator loads have been made possible by use of high-flotation equipment such as that shown in Figure 8. With the very large tires, up to 43 inches wide and 66 inches in diameter, the compaction force on the soil has been reduced to as low as one-third of that exerted by the normal type of truck application equipment, thereby allowing much heavier loads during normal soil conditions and also the possibility of operating when soil conditions are adverse. Several types of high-flotation equipment are available including special wheels and tires for converting an ordinary truck to the flotation type.

(Figure 8)

Application equipment has continued to increase in size in other ways. Applicator booms long enough to cover a swath 60 feet wide have become common. As much as 60 acres can be covered per hour, and applicator tank volumes are as high as 1500 gallons.

Advances in applicator design for suspensions have been significant (32), particularly in regard to agitation during transport and application (to ensure uniformity of composition) and to broadcast spray nozzle design. In a TVA development, air is sparged into the bottom of the applicator tank to agitate the suspension and the air pressure developed over the suspension then serves the further function of forcing the material out through a single spray nozzle. Uniform distribution over a swath as wide as 38 feet has been accomplished.

Application During Irrigation

In areas where the rainfall is so low that irrigation is profitable, a convenient way of applying fertiliser is to incorporate it in the irrigation water. Either solid or liquid fertiliser can be used but the convenience of the liquid form has led to widespread use. Both surface type (furrow) and sprinkler irrigation are involved. Subsurface irrigation with plastic tubing has also been attempted but the problem of orifice plugging does not appear to have been solved (33).

One of the problems has been development of accurate meters for controlling the flow of the liquid fertiliser into the irrigation water. In the past few years there has been a trend to use of piston-type metering pumps.

These are accurate and relatively unaffected by solid impurities carried in the liquid fertiliser. They are usually driven electrically but sometimes by a small water turbine.

Mixing is a problem also, but can usually be accomplished by introducing the fertiliser at a point where there is turbulence in the water flow.

Phosphates have given trouble by causing precipitation when the irrigation water contains appreciable quantities of calcium and/or magnesium. These precipitates can cause clogging of strainers and plugging of water nozzles. Liquid fertilisers in which the phosphate is mainly in the polyphosphate form are less likely to cause difficulty because of the sequestering effect. In addition, tests at TVA (13) have shown that reducing the pH of ammonium polyphosphate solutions (to a level on the order of 2.5-4.5) before introduction into the irrigation water is helpful. Phosphoric acid was used as the acidulant.

The practice of using nitrogen solutions in sprinkler irrigation units is gaining popularity rapidly. It is referred to as "spoon feeding the crop" because small quantities of nitrogen are fed to the crop throughout the growing season at the rate the crop needs it, thus providing a means for reducing the proportion of nitrogen lost by leaching. It is common practice, for example, to add urea-ammonium nitrate solution through sprinkler irrigation units in those parts of Nebraska and Kansas where irrigation is required. Moreover, if the water hardness is less than 200 parts per million (as calcium carbonate), an N-P liquid can be added as ammonium polyphosphate solution (10-34-0, 11-37-0, or 12-44-0) without problems.

Aerial Application

In areas of the United States where farms are quite large--on the order of 2000-6000 acres--application of liquid fertilisers by airplane has been carried out on a limited scale. In a typical situation, the airplane carries about a ton of fertiliser and takes off from a pasture or road. The application requires only a few minutes and can be carried out when the soil is too wet for surface applicators. The fertiliser is sprayed from nozzles under the lower wing. Pressure on the nozzles is developed in some systems with a pump driven by a propeller turned by the slip stream.

Application of liquids in this way is quite limited because of the high cost and because use of high-flotation equipment has greatly reduced the problem of applying on wet ground. Some attempts have been made to apply liquids to forests by airplane but granular solids are preferred because of less drift and less sticking to foliage. There has also been some air application on flooded rice fields.

Status of the Liquid Fertiliser Industry

The rapid growth in use over the past few years has brought liquid fertilisers into a position of some prominence, not only in the United States where the practice has received the most emphasis but also in other parts of the world. Many factors have contributed to this (34). For nitrogen solutions, the lower price--as compared with solid fertilisers--is the main driving force;

for liquid mixes the price is usually higher than for solids, so the reasons for growth in consumption are found among such factors as convenience, ease and uniformity of application, high speed of application, and amenability to combining such farm practices as fertilising and pesticide application. Various other considerations have entered also, including cost reduction by use of suspensions, relatively low pollution during production, and the claim by some that liquid fertilisers have superior agronomic value.

Consumption

One indication of the rate of growth in the United States is the number of production plants (Fig. 9). The very large current number, over 3000, indicates the degree to which the industry has spread over the country. (It must be noted, however, that this includes many small "satellite" installations that have only storage tanks and a meter.)

(Figure 9)

Consumption of liquid fertilisers in the U.S. has been reported recently by Achorn and Balay (18); published data plus estimates are assembled in Table II to show the relative growth rates of solid fertilisers, anhydrous ammonia, nitrogen solutions, and liquid mixed fertilisers. The table shows that in 1971 fertilisers in the fluid form (including anhydrous ammonia) made up about 27% of the total tonnage and about 58% of the total nitrogen.

(Table II)

Thus liquids have moved forward at a rapid pace since their beginnings in the early 1950's. This is expected to continue because the factors that have caused the growth up to the present are likely to become even more important in the future. Farm labor becomes less available and more expensive every year, and thus pushes the farming industry in the direction of laborsaving practices. Moreover, the production developments discussed earlier in this paper are improving liquid fertilisers in regard to their main drawbacks--relatively high raw material cost and low concentration as compared with solid fertilisers.

In other countries the growth has not been nearly as rapid. The situation has been reviewed by Stangel (35), who lists the following factors as the main ones involved.

1. For rapid liquid fertiliser adoption, the economy must be well along in the shift of labor from farm to industry.

2. In many countries, the government has more control over the economy than in the United States. Consequently the decision to produce and market liquid fertilisers often is a government decision rather than one resulting directly from economic pressures.

3. The initial experience usually indicates a need to alter the production and distribution program in order to fit it into local conditions. Thus several years may be required to develop an acceptable system.

Most areas other than northern Europe, North America, and a few countries in Latin America and Asia are ruled out by the first of these factors. However, agricultural technology is changing generally and the new patterns tend to favor liquids. This is particularly true for nitrogen solutions, where the relatively low production cost is added to the other advantages of the liquid form. Moreover, where herbicides are already being applied the amenability of nitrogen solutions to joint application makes it relatively easy to move into solution application.

Hignett (36) has also commented on the reasons for slow liquid fertiliser growth in some countries. A major one is lack of raw materials at acceptable cost; these no doubt would be supplied by native industry if a demand were demonstrated but in the absence of such demand it is difficult to get started. In the United States, in contrast, the organization of the solid fertiliser industry was such that raw materials suitable for liquid fertiliser production were already available.

Another factor is the attitude of the farmer--whether he is educated and progressive or the opposite. Much of the impetus to liquid fertilisers in the United States has come from large-farm areas where the farmers are highly progressive in all farm practices. In the less developed countries this may be a major factor.

The availability of relatively pure phosphoric acid (furnace type) at an acceptable price was a major factor in getting liquid fertilisers started in the United States. This has not been available in many countries, but the new method for making high-poly base solution should solve this problem.

Data assembled from various sources have been assembled in Table III to indicate the consumption situation. Many of the figures shown are very rough estimates but they are adequate for perspective. France, the United Kingdom, and Canada are the main areas outside the United States in which liquids have made significant headway. There is some indication of significance in Eastern Europe but good data are not available.

(Table III)

Clear Solutions Versus Suspensions

One of the important considerations in future growth of fluid fertilisers is the role of suspensions, which make it possible to attain very high concentration and to use the lowest cost raw materials. The rate of growth in use of suspensions has been quite rapid in the United States, faster than for the clear liquids. About half of the fluid fertiliser producers now make suspensions (9), although most of these (about two-thirds) also produce clear solutions. In 1971 about one-third of the total fluid fertiliser tonnage reported in a survey conducted by TVA and the National Fertilizer Solutions Association (NFSA) was in the form of suspensions (about 682,000 tons from the total of 2,037,000 tons). The survey also showed that in some states, notably Iowa, Illinois, Indiana, and Georgia, suspensions were more popular than clear liquids.

Most of the suspension producers (about 70% as reported in the survey) make the product from ammonium polyphosphate base solution. However, a growing number (about 20% of the total in 1971) use wet-process phosphoric acid and thus get the advantage of lower raw material cost. This trend is expected to continue.

One of the advantages of suspensions is practicality of high-potash suspensions. The leading current grades include 4-12-24, 3-10-30, and 5-15-30. Such ratios give very low total nutrient content in clear solutions.

Consumers look on high analysis and compatibility with additives (pesticides and micronutrients) as the main attractive features of suspensions. Economy, grade flexibility, and absence of salt-out problems in cold weather are also regarded as advantages. Handling problems and high investment are the main drawbacks. The net balance seems to favor the suspension route, however, and further displacement of clear liquids by suspensions is expected.

Use of suspensions in other countries is quite limited. In Belgium, Prayon makes a 3-10-30 base suspension and combines it with urea-ammonium nitrate solution in small mixing plants. No use appears to have been reported elsewhere.

Pollution

Another factor that probably will improve the position of fluid fertilisers in the future is the relatively low air and water pollution during manufacture. Ammonia loss to the atmosphere in hot-mix plants is the only significant source of pollution, and this can be easily controlled by a simple scrubber (37). In contrast, solid fertiliser production involves some difficult pollution problems that are expensive to cure. In ammoniation-granulation plants, for example, ammonium chloride fume formation, ammonia loss, and dust emission (both to the air and in waste water) are serious pollution problems.

To the extent that solid fertilisers increase in price because of the expense of pollution control, the competitive position of liquid fertilisers should improve. In the United States the tightening regulations may make this factor more important in the near future.

Agronomic Considerations

Some producers have claimed an agronomic advantage for liquids over solids which, if demonstrable, should give liquids a major further advantage and improve the competitive situation. As Hignett has pointed out (36), there are several factors in regard to composition and placement that should be considered in comparing the two forms. The consensus among agronomists seems to be that there is no particular benefit or drawback from the presence of water, which is the only difference between liquids and solids if everything else is equal. However, as a practical matter there are differences between commercial solids and commercial liquids (and in the ways they are used) that could have an effect. The phosphate in liquids is almost always completely water soluble whereas that in solids often is not; liquids can be applied more precisely in bands as starter fertiliser; and liquids because of their homogeneity and more uniform ground coverage are less subject to nutrient maldistribution during application than are solids. Whether these advantages give any significantly better performance in actual practice is a question difficult to answer.

A considerable amount of data have been published supporting the claims of better performance for liquids. Much of this is associated with the use of polyphosphate, which can be in the solid form, of course, but is mainly supplied in liquid fertilisers; thus the comparison is really between the poly and ortho forms of phosphate rather than between liquid and solid.

It has been postulated that polyphosphate is superior because its reactions with soil chemicals are quite different from those of orthophosphate, especially in regard to sequestration of metal compounds and resistance to precipitation in an immobile form. Some investigators have reported superior performance for polyphosphate; others have found no difference or, in cases such as application during cold weather, impaired performance because of slow hydrolysis (38). It appears that no significant difference in agronomic performance between polyphosphate and orthophosphate has been established.

Nonfertiliser Uses

Uses are developing that move liquid fertiliser into fields other than fertiliser. Although this does not directly affect the fertiliser field, the broadened market could have some impact on overall economics.

Some 3000 tons of liquid fertiliser were used in the United States in 1970 as a fire retardant for forest and range fires (39). Most of this was applied by airplanes, usually flying relatively high as compared with farmland application and dropping the load as a "blob" rather than a spray. Since the phosphate is the active component, 10-34-0 (diluted with about four parts water) is the material normally applied. Bomber-type airplanes are often used, carrying as much as 1000 gallons per trip.

While the fertiliser value from the practice is incidental and usually disregarded, it is nevertheless an advantage for the liquid fertiliser as compared with other fire retardants.

Some liquid fertiliser, probably a very small tonnage, is used in northern areas for melting snow and ice from traveled areas in the winter. Sizeable amounts of common salt have been used for this purpose in the past but the resulting corrosion and pollution are major drawbacks. The liquid fertiliser has the advantage that some fertiliser value is obtained from the runoff.

Animal feed supplements are made in liquid form by some liquid fertiliser producers. The components are usually urea, phosphoric acid (or 10-34-0 or 11-37-0) and molasses, plus small quantities of vitamins and trace elements (40). About 23% of the cattle feeders in the United States are reported to have used liquid feed supplements in 1970. Information on the tonnage is not available.

Summary

The use of fluid fertilisers in significant quantities is less than 20 years old. Nevertheless, growth has been so rapid that in the United States the consumption of mixed liquid fertiliser is now over 4.5 million tons per year (about 12% of the total fertiliser tonnage), and all fluid fertilisers (including nitrogen solutions and anhydrous ammonia) supply about 30% of the total tonnage.

Liquids have not been accepted as rapidly in other parts of the world, for several reasons. The main usage is in France and the United Kingdom.

The main problems in mixed liquid fertiliser production and use are raw material cost, nutrient concentration, and product quality. All three areas have been improved by the introduction of polyphosphates, which reduce cost by allowing use of wet process phosphoric acid, increase concentration because of the high solubility of ammonium polyphosphates, and improve quality by sequestering impurities and holding them in solution. The new form of phosphate has been adopted widely, to the extent that about 70% of the liquid fertiliser produced in the United States now contains part or all of the phosphate in the poly form.

The basic production method for polyphosphate-based liquid fertiliser is a two-step process in which polyphosphoric acid ("super acid") is first made by dehydrating wet process orthophosphoric acid and the super acid is then ammoniated to give a 10-34-0 base solution. There is a growing trend, however, to a direct process in which the ortho acid is dehydrated and ammoniated in a single operation.

The suspension method, in which fluid fertiliser is made by adjusting composition to give a slurry of crystals in saturated solution and the suspension is then stabilized by addition of clay, is another way of reducing raw material cost and increasing nutrient concentration. Wet process acid can be used because the impurities remain suspended with the salt crystals, and the grade can be as high as most of those available as solid mixed fertilisers.

One of the major advantages of fluid fertilisers is the uniformity of composition and absence of segregation when small amounts of micronutrient sources are mixed with the major materials. This is also true for pesticide-fertiliser mixtures, with the added advantage that the complete and uniform ground coverage afforded by liquid fertilisers is quite desirable in pesticide application. Such advantages are pushing consumption of fluid fertilisers to higher levels.

Developments in application are keeping pace with advances in manufacturing procedures. The intrinsic laborsaving advantage in application of liquid fertilisers is being exploited by use of high-flotation application equipment, large applicator tanks, and applicator booms covering a swath up to 60 feet wide. Application rates of up to 60 acres per hour are becoming common.

The basic advantages that have pushed liquid fertilisers to the present level of consumption seem likely to continue their effect. At the same time, research developments are reducing the drawbacks of high raw material cost, low nutrient concentration, and low product quality--problems that have plagued liquid fertiliser producers in the past. As a result it is expected that fertilisers in the fluid form will occupy a position of continually increasing importance in the future.

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TABLE I[a]

Distribution of Acid Species in Superphosphoric Acid[b]

Total P_2O_5, %	$(P_2O_5)/(H_2O)$	Ortho	Pyro	Tripoly	Tetrapoly	5	6	7	8	9	10	11	12	13	14
67.4	0.263	100.0													
68.7	0.279	99.7	0.33												
70.4	0.302	96.2	3.85												
71.7	0.321	91.0	8.86	Trace											
73.5	0.352	77.1	22.1	0.79											
73.9	0.360	73.6	25.1	1.34											
75.7	0.394	53.9	40.7	4.86	0.46										
77.5	0.438	33.5	50.6	11.5	2.68	0.74	Trace								
79.1	0.481	22.1	46.3	20.3	7.82	2.26	1.02	0.34							
80.5	0.523	13.8	38.2	23.0	13.0	6.86	3.38	1.67	1.03	0.22					
81.0	0.542	12.2	34.0	22.7	14.6	8.42	4.36	2.27	1.41	0.56	Trace				
81.2	0.549	10.9	32.9	22.3	15.0	9.36	5.41	2.85	1.75	0.97	0.36	0.05			
82.4	0.594	7.32	23.0	19.3	15.9	12.3	8.21	5.73	3.89	2.52	1.36	0.91	0.14		
84.0	0.667	3.92	11.8	12.7	12.0	10.5	8.97	7.99	6.62	5.63	4.54	3.72	3.03	2.46	1.68

[a] Phosphoric Acid, Vol. 1, Part II, Chapter 13, p. 993 (A. V. Slack, editor), Marcel Dekker, Inc., New York (1968).

[b] Percent of total P_2O_5 as species of indicated chain length; 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 refer to penta, hexa, hepta, and so on. Data given are for pure phosphoric acid.

TABLE II

Consumption of Fertilisers in the United States

Type	Millions of short tons			
	1955	1960	1965	1971
Solid[a]	21.8	22.4	26.1	28.5
Anhydrous ammonia[a,b]	0.4	0.8	1.8	4.1
Nitrogen solutions[a]	0.1	0.7	1.9	3.5
Liquid mixed fertiliser[c]	-	0.6	1.0	4.5

[a] Data from U.S. Department of Agriculture (USDA).

[b] Includes aqua ammonia.

[c] Clear liquids and suspensions; data from USDA plus TVA-NFSA survey data.

[d] Projected from TVA-NFSA 1971 survey.

TABLE III

Liquid Fertiliser Consumption in Major Consuming Areas[a]

	Thousands of metric tons 1965	Thousands of metric tons 1970[b]	Rate of growth over 5 years, %/yr.	Major producers
France	-	414[c]	-	APC
Spain	0.4	21	-	Ammoniaco Espanol
U.K.	95	219	18	J. W. Chafer
Yugoslavia	-	140[d]	-	State
New Zealand	-	2	-	Kempthorne Prosser
Japan	5.7	13.2	18	Sumitomo; Mitsui Toatsu
Canada	36	74	15.5	Various
U.S.	2635	6090	18	Various

[a] Includes nitrogen solutions but not aqua or anhydrous ammonia.

[b] In some cases data for 1971 are used.

[c] In 1970-71, 192,000 tons of liquid mixed fertiliser. All liquids (mixes plus N solutions) supplied 7.2% of total N consumed, 2.4% of P_2O_5, and 0.4% of K_2O.

[d] Planned; may not be all in production.

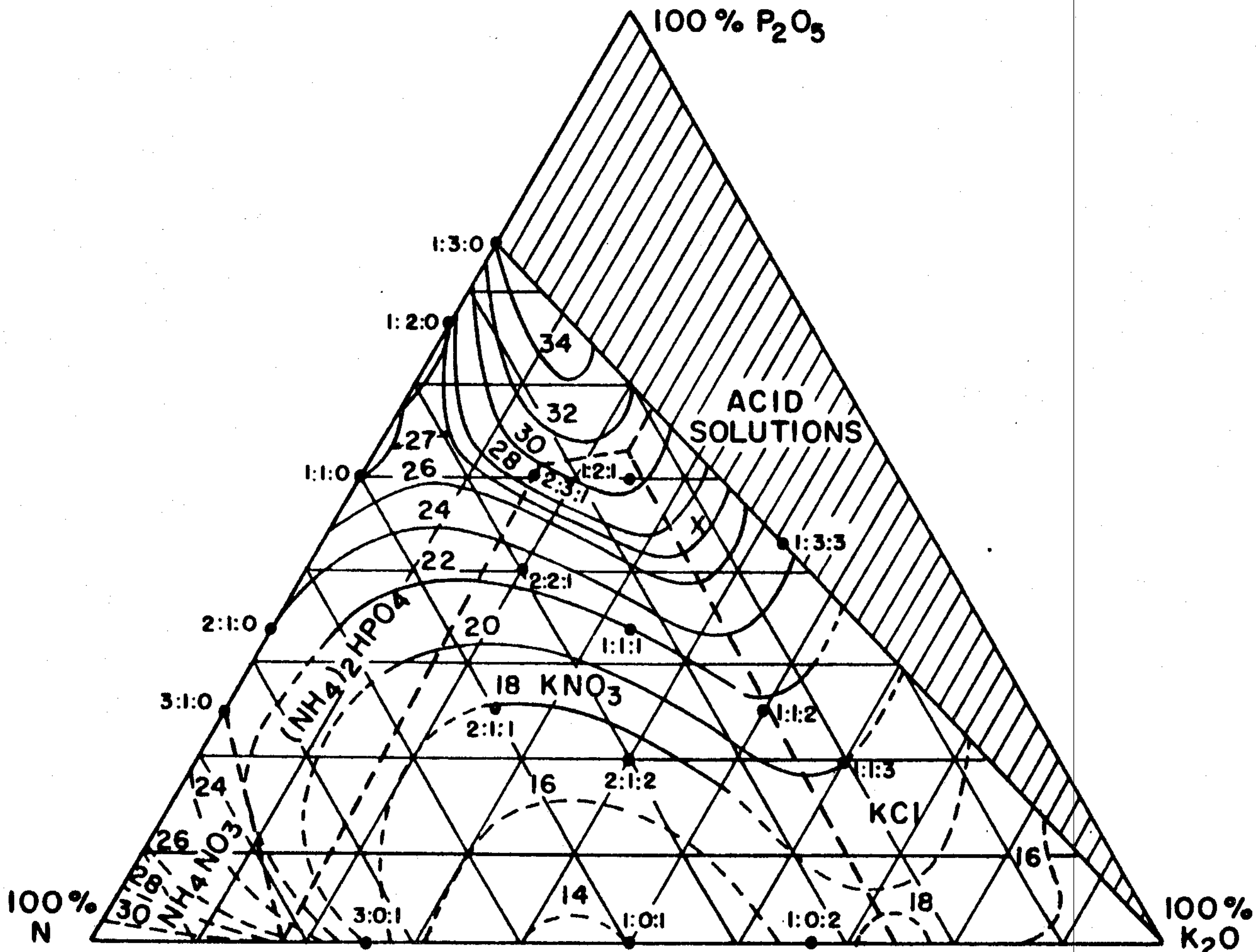
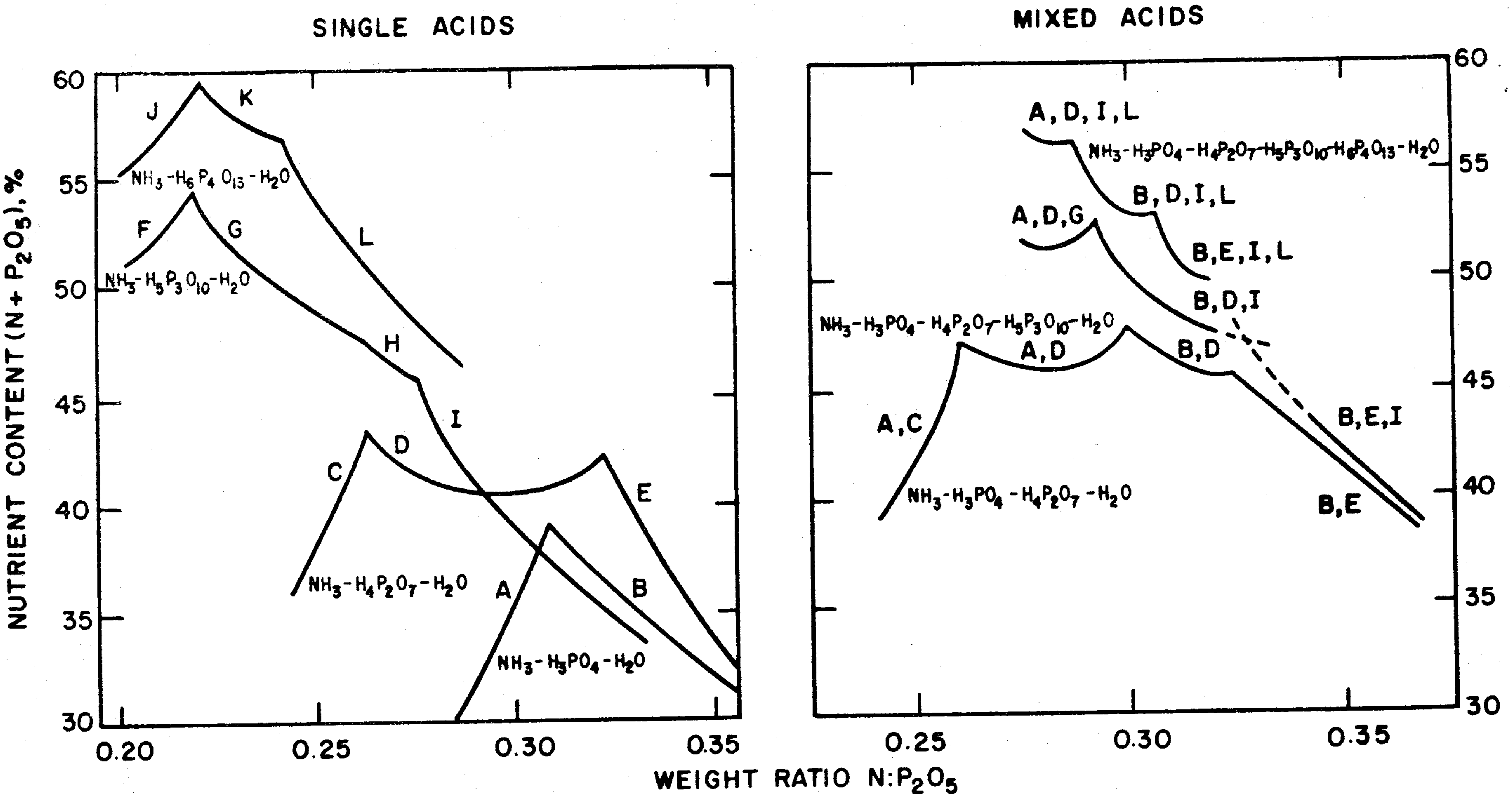


FIGURE I
SYSTEM UREA – AMMONIUM NITRATE – AMMONIA – PHOSPHORIC ACID – POTASSIUM CHLORIDE – WATER AT 0°C.

The compounds listed are those that crystallize from solution in the particular composition area indicated. Typical grade ratios are indicated, e.g., 1:1:1, and the numbers on the curves indicate total nutrient that can be held in solution at 0°C. For example, at a 1:1:1 ratio, 22% nutrient will stay in solution, giving a nearest whole number grade of 7-7-7.



SATURATING SOLIDS:

A = $NH_4H_2PO_4$
B = $(NH_4)_2HPO_4$
C = $(NH_4)_2H_2P_2O_7$
D = $(NH_4)_3HP_2O_7 \cdot H_2O$
E = $(NH_4)_4P_2O_7 \cdot H_2O$
F = $(NH_4)_3H_2P_3O_{10} \cdot H_2O$
G = $(NH_4)_4HP_3O_{10}$
H = $(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O$
I = $(NH_4)_5P_3O_{10} \cdot 2H_2O$
J = $(NH_4)_4H_2P_4O_{13}$
K = $(NH_4)_5HP_4O_{13} \cdot H_2O$
L = $(NH_4)_6P_4O_{13} \cdot 2H_2O$

FIGURE 2
SOLUBILITY OF AMMONIATED POLYPHOSPHORIC ACIDS AT 0°C.

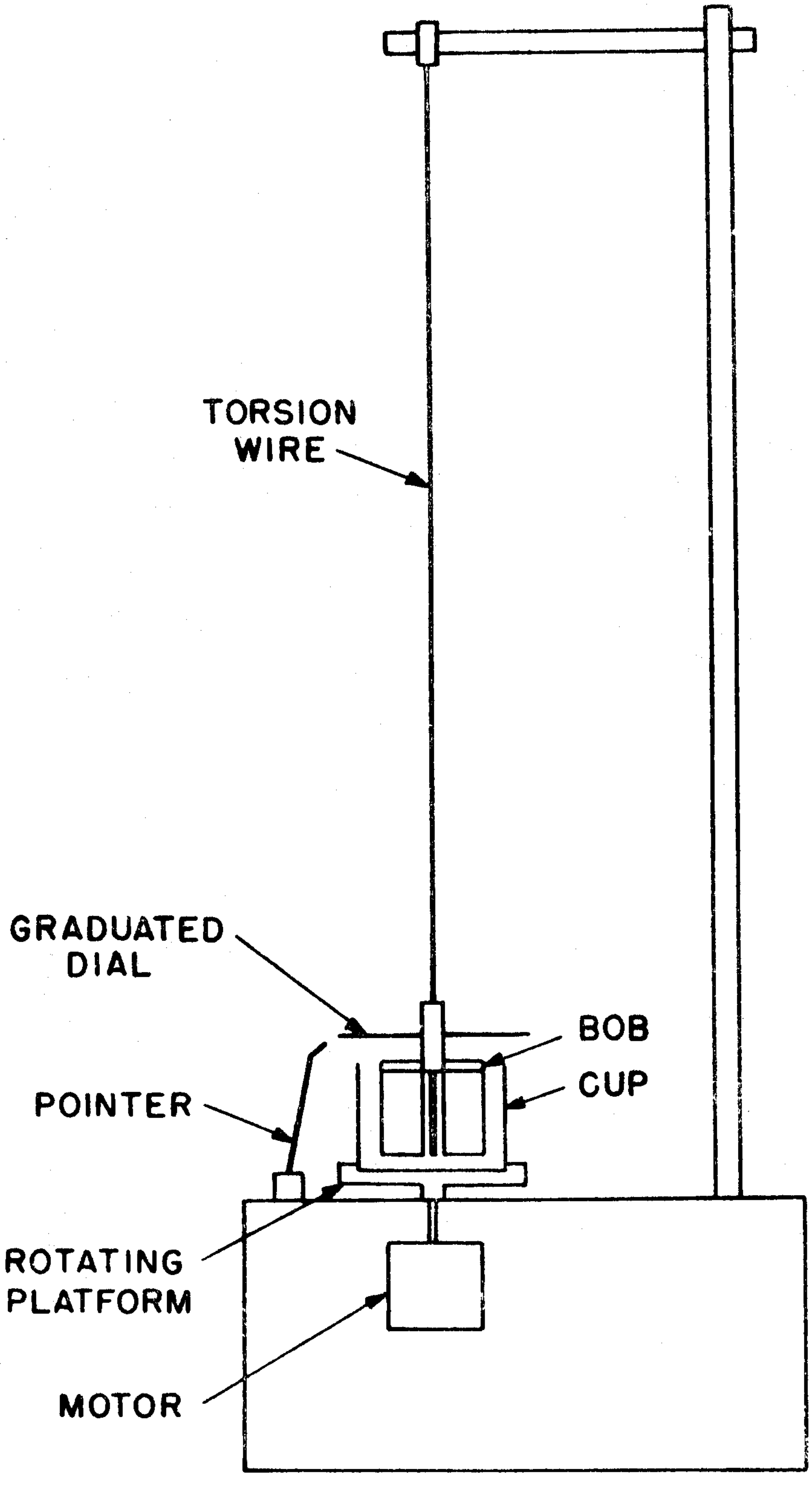


FIGURE 3
TORSION WIRE GELOMETER

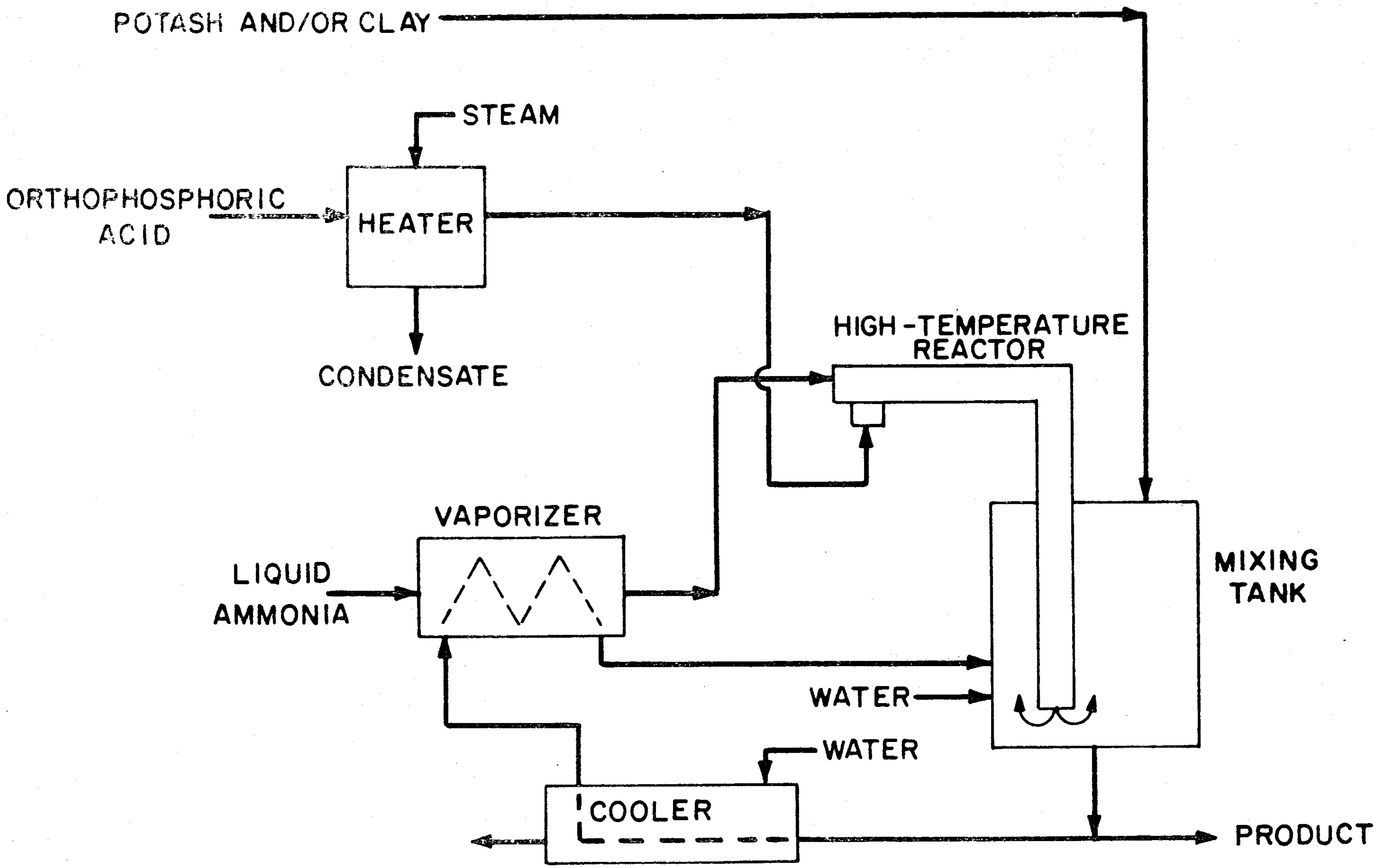


FIGURE 4
SWIFT PROCESS FOR PRODUCING 10-34-0 FROM
WET PROCESS PHOSPHORIC ACID

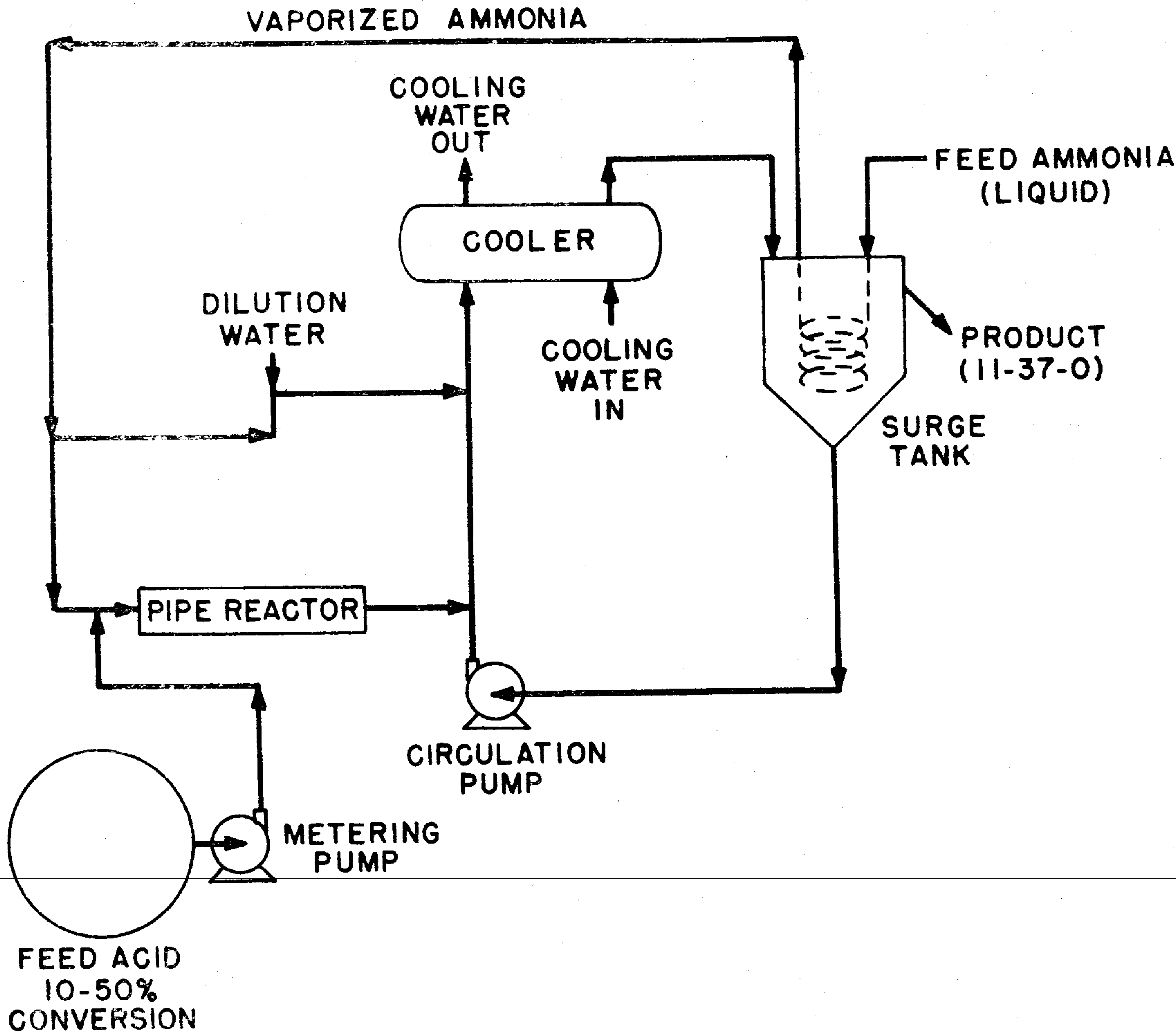


FIGURE 5

PRODUCTION OF HIGH-POLYPHOSPHATE LIQUID FERTILIZER FROM WET PROCESS SUPERPHOSPHORIC ACID

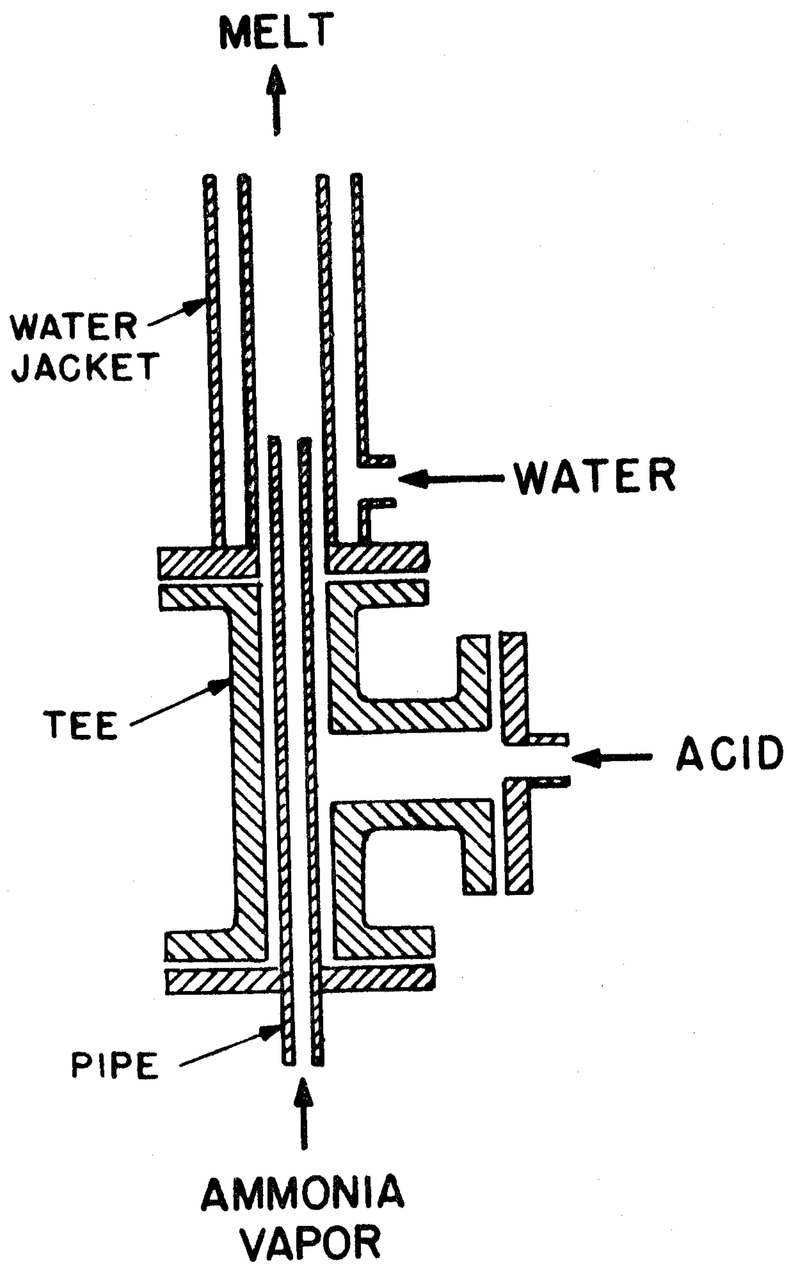


FIGURE 6
PIPE REACTOR FOR
AMMONIUM POLYPHOSPHATE PRODUCTION

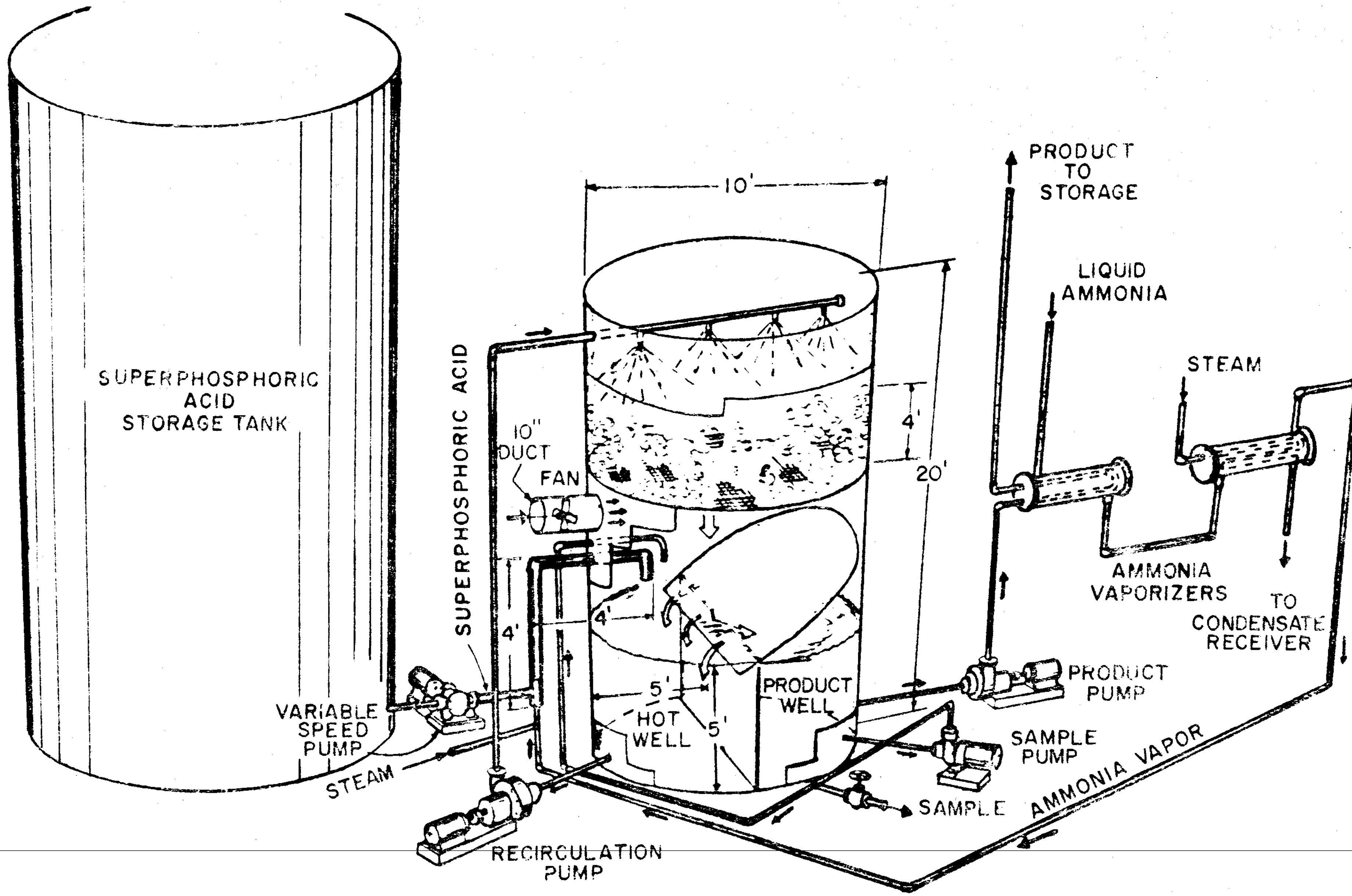


FIGURE 7
LIQUID FERTILIZER PLANT ARRANGEMENT INCORPORATING TVA-TYPE PIPE REACTOR (Farmland Industries, Joplin, Mo.)

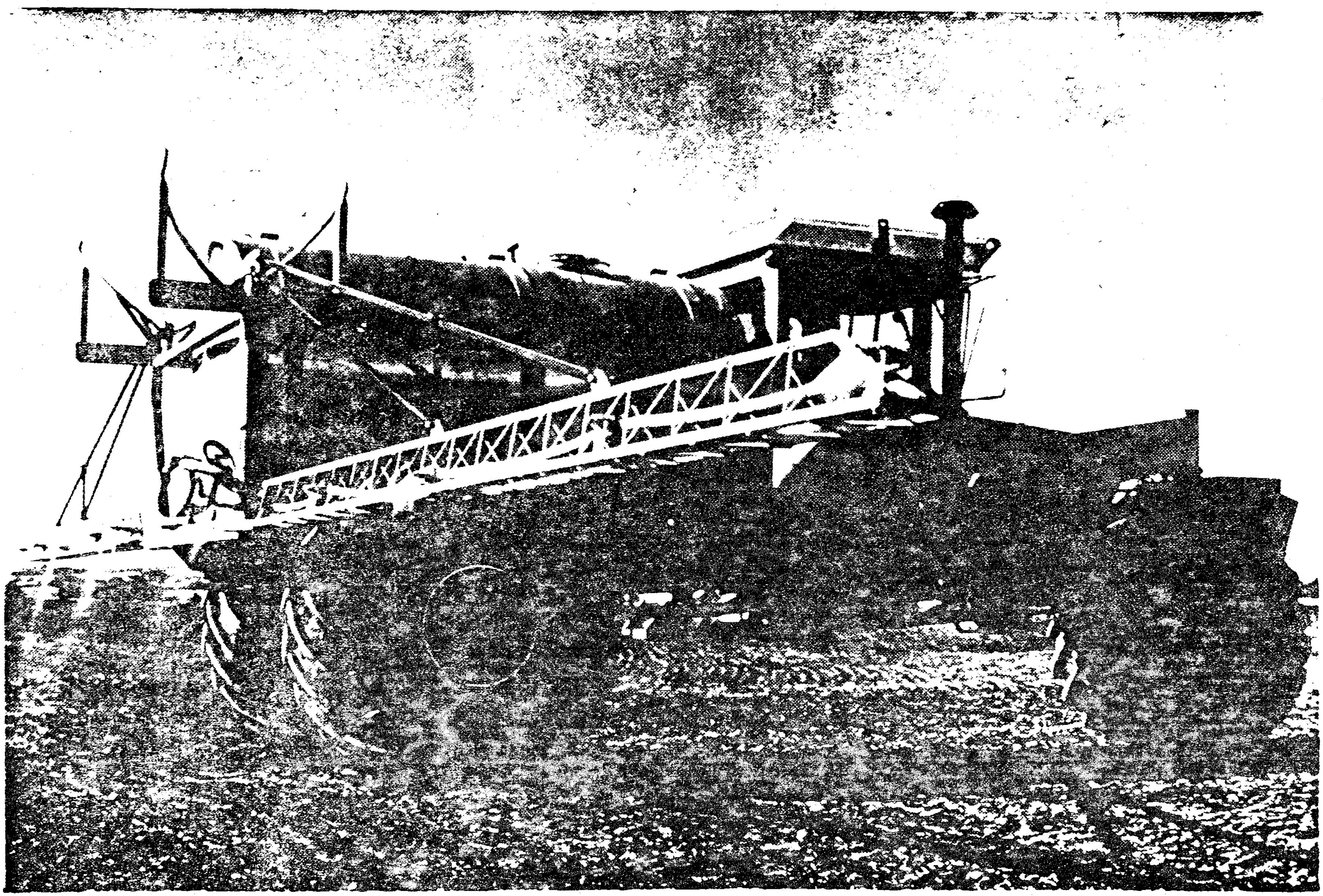


FIGURE 8
TYPICAL HIGH-FLOTATION EQUIPMENT FOR APPLICATION OF FLUIDS

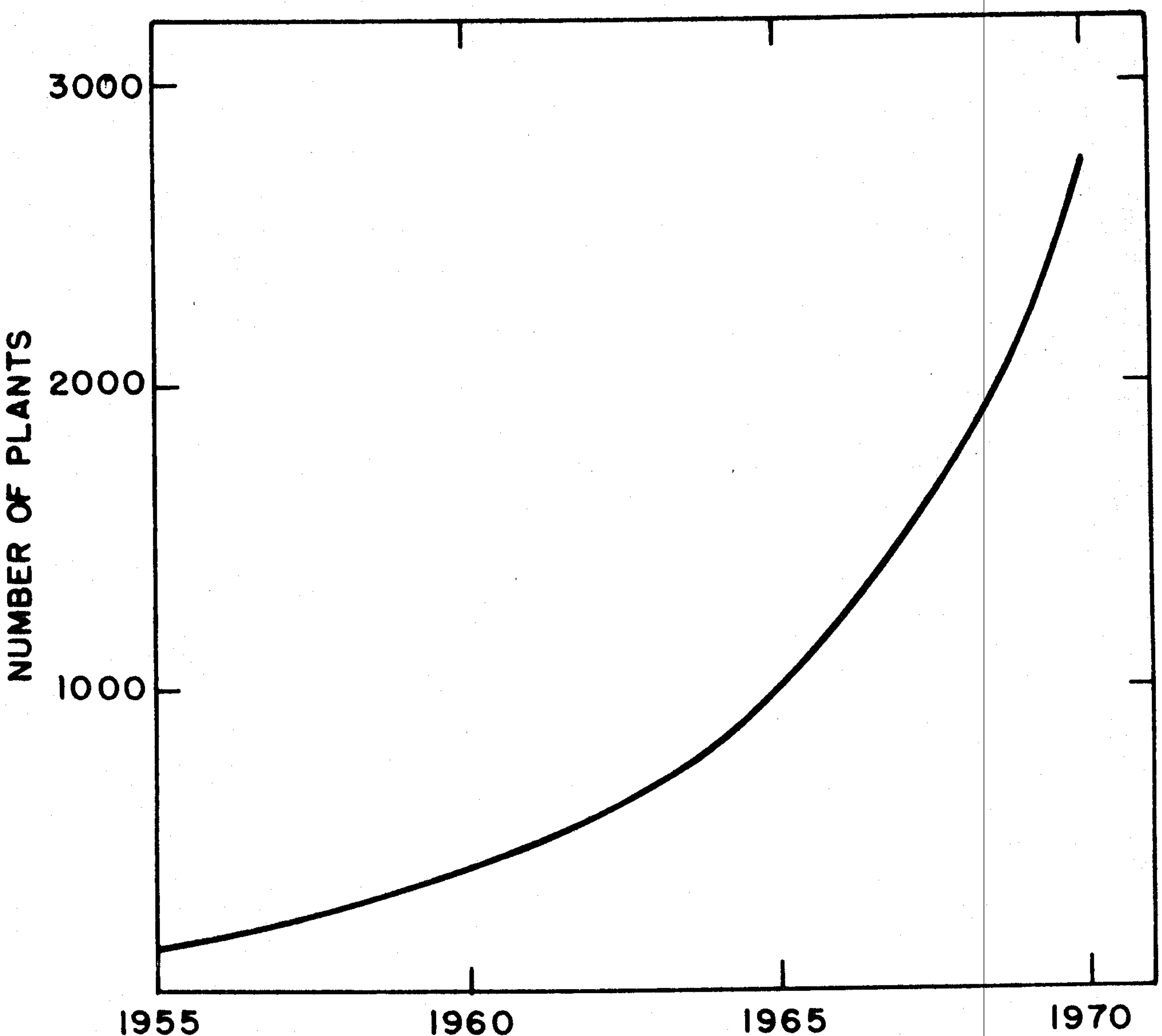


FIGURE 9
GROWTH IN NUMBER OF LIQUID MIXED FERTILIZER PLANTS IN THE UNITED STATES