

SOME ASPECTS OF LIQUID MIXED FERTILIZER TECHNOLOGY IN THE UNITED STATES OF AMERICA

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Introduction

Any review of liquid fertilizer technology must be concerned very largely with developments in the United States of America, where liquid fertilizers are finding increasing application and where the usage of liquid nitrogen sources in particular has increased quite spectacularly in recent years. Growth in consumption of liquid mixed fertilizers was unremarkable in the years before 1965 but has since shown a marked upward trend. Consumption of liquid direct-application materials (consisting almost entirely of anhydrous ammonia, aqua ammonia and nitrogen solutions) and liquid mixtures over the past 15 years is shown in Fig. 1 on page 40. To lend perspective, the approximate consumption of liquids relative to solids during 1967 is shown in Table 1.

TABLE 1 — Fertilizer consumption in USA 1967

	Total tons	Plant nutrient content—tons		
		N	P	K
Liquids — direct application	5 850 000	2 930 000	13 000	0
Liquids — mixtures	1 830 000	137 000	128 000	93 000
Liquids — total	7 680 000	3 067 000	141 000	93 000
Solids — all types	2 765 000	3 130 000	1 839 000	3 287 000
Total — all fertilizers	35 333 000	6 197 000	1 980 000	3 380 000

Data sources 1 USDA, quoted by Comm. Fert., 1968, 20, 19-22

2 USDA, quoted by Farm Chem., June 1968, 38-39

Thus liquid mixed fertilizers, with which this review is concerned, supplied 3 per cent of the total plant nutrients (N+P+K) consumed during 1967. It is interesting to note that the average analysis of all American liquid mixtures was not far removed from the average analysis of all solid mixtures consumed in South Africa during the same year:

	Average analysis (NPK) %	Total pfu %
US liquid mixtures 1967	7.5 : 7.0 : 5.1	19.6
SA solid mixtures 1967	7.6 : 7.1 : 7.2	21.9

It seems probable that most of the material referred to above as liquid mixtures consisted of true solutions or suspensions containing little solid matter, and that slurries (ie. suspensions containing substantial proportions of suspended solids) are not yet marketed on any significant scale.

Almost all liquid mixtures produced at present — whether solutions, suspensions or slurries — are based on solutions of ammonium phosphate or ammonium polyphosphate, produced in turn from phosphoric or superphosphoric acid and ammonia. For purpose of discussion it is convenient to classify liquid mixtures in terms of the origin of the phosphoric acid or superphosphoric acid utilised in their production — i.e. furnace-grade or wet-process. In the fertilizer industry wet-process acid is by far the more important source of phosphorus.

Discussion

Mixed fertilizer solutions based on furnace-grade ortho-phosphoric acid

Raw materials for the production of solutions include furnace-grade phosphoric acid (usually 22-23% P), ammonia, supplemental nitrogen (urea, ammonium nitrate or nitrogen solutions) and potassium chloride.

Two basically different types of production process are used. (The same distinction can be made in all solution or suspension fertilizer operations, irrespective of the source or type of phosphoric acid used)

Hot-mix processes Ammonia and phosphoric acid are reacted to yield ammonium phosphate solution as part of the process. The heat evolved in the reaction gives rise to the term 'hot-mix' and necessitates cooling of the reaction products.

Cold-mix processes Ammonium phosphate solution (8.0:10.4:0 NPK) is obtained elsewhere as a base solution, and the process consists simply of adding supplemental nitrogen and potash. No appreciable heat evolution occurs, and the plant is simpler and cheaper than that required for the hot-mix process.

Whichever type of process is used, phosphoric acid is normally ammoniated to an N/P mol ratio of about 1.7, corresponding with the mono-ammonium-diammonium phosphat mixture of maximum solubility. Solutions of N/P ratio substantially lower than 1.7 are corrosive, while at N/P ratios higher than 1.7 ammonia losses become excessive. Ammoniation to an N/P mol ratio of about 1.7, together with the dilution necessary to ensure a solution stable at 0°C, yields an ammonium phosphate base solution of analysis 8.0:10.4:0 (NPK). In consequence, solutions with N/P mol ratios substantially below 1.7 (corresponding with an N/P weight ratio of 0.76) are impracticable, and solutions with higher N/P ratios require supplemental nitrogen. Higher NPK grades are attainable with urea as supplemental nitrogen source than with ammonium nitrate because of the relatively low solubility of potassium nitrate (Slack, 1955).

Solutions based on furnace-grade phosphoric acid are of little direct interest, but they must be considered so that maximum grades likely to be attainable in solutions based on wet-process acid can be estimated later. The grades of a selection of solid mixtures presently marketed in South Africa are shown in Table 2 together with the maximum grades, at corresponding NPK ratios, of solutions made with potassium chloride as potassium source and urea as supplemental nitrogen. Potassium chloride solubility is clearly a limiting factor with respect to the grade of these solutions. Higher-grade solutions are attainable if potassium hydroxide is used as the potassium source, but this is almost invariably uneconomic (Potts, 1961).

TABLE 2. Maximum grades attainable in true solution produced from furnace-grade phosphoric acid

Maximum grade of solutions	Present South African granular products
2:1:2(19)	2:1:2(26)
2:3:0(18)	2:3:0(15)
2:3:2(18)	2:3:2(22)
2:3:4(15)	2:3:4(24)
3:2:1(20)	3:2:1(22)
4:1:6(14)	4:1:6(31)

Data Source Langguth, 1955

Mixed fertilizer solutions based on furnace-grade superphosphoric acid

These solutions are produced from furnace-grade superphosphoric acid (33-35% P), in which a substantial proportion of the phosphorus is present as polyphosphate. Either hot-mix or cold-mix production processes may be employed. Ammonium polyphosphates are more soluble than ammonium orthophosphate, and the ammoniated base solutions used in the cold-mix process are of correspondingly higher grade (up to 11:16:0 NPK, with 45-65% of phosphorus present as polyphosphate). The maximum attainable grades of a selection of solutions produced with potassium chloride as potassium source and urea as supplemental nitrogen are given in Table 3 together with the grades of corresponding orthophosphoric acid-based solutions and current South African solid mixtures.

TABLE 3. Maximum grades attainable in true solutions produced from furnace-grade superphosphoric acid

Maximum grade of solutions based on superphosphoric acid	Maximum grade of solutions based on orthophosphoric acid	Present South African granular products
2:1:2(22)	2:1:2(19)	2:1:2(26)
2:3:0(25)	2:3:0(18)	2:3:0(15)
2:3:2(21)	2:3:2(18)	2:3:2(22)
2:3:4(18)	2:3:4(15)	2:3:4(24)
3:2:1(25)	3:2:1(20)	3:2:1(22)
4:1:6(17)	4:1:6(14)	4:1:6(31)

Data Source Slack, 1964.

Superphosphoric acid-based NP solutions of quite high analysis are possible. As in the case of orthophosphoric acid-based solutions, however, maximum grades of NPK mixtures fall off rapidly with increase in potassium chloride content.

Some micronutrients (Zn, Cu, Fe, Mn) are considerably more soluble in ammonium polyphosphate solution than in ammonium orthophosphate solution (Slack, 1965; Kibbel, 1968).

The scale on which furnace-grade superphosphoric acid and the ammoniated acid are used commercially is not clear, but it may be quite small. The Tennessee Valley Authority (TVA) produces the ammoniated base solution 11:16:0 (NPK) from furnace-grade superphosphoric acid in a 15 ton/hr plant, the product being made available to industry (Scott, 1965. TVA, 1968). In general; however furnace-grade phosphoric acid cannot compete

economically with wet-process acid.

Liquid mixed fertilizers based on wet-process phosphoric acid

Ammoniation of wet-process phosphoric acid invariably results in the precipitation of solids, mainly iron and aluminium phosphates, sometimes followed by the slow crystallisation of struvite ($MgNH_4PO_4 \cdot 6H_2O$) (Slack, 1961). Solids may be precipitated in substantial quantities — the ammoniation of Foskorite phosphoric acid for example, to a nominal composition of 8:10.4:0 (NPK) has been observed to yield a fairly stable opaque suspension containing 7 per cent of suspended solids.

Liquid mixed fertilizers based on wet-process phosphoric acid must thus be handled as suspensions rather than solutions. Precipitated solids can be a nuisance in storage tanks, can lead to loss of plant nutrients and can cause blockages in pipelines and spray nozzles. Four methods of overcoming these problems are practised (Walstadt, 1961).

- (i) The product is distributed immediately after production. This appears to be a common procedure, liquids which are to be stored for any period usually being made from furnace-grade acid.
- (ii) Particle size of precipitated solids depends upon reaction conditions during ammoniation. By suitable control of reaction conditions, an ammoniated base solution (8.0:10.4:0 NPK) is obtained in which suspended solids settle very slow and are too fine to cause blockage in spray nozzles. In NPK solutions produced from the 8:10.4:0 base, however rate of settling may be objectionable high (Slack, 1961).
- (iii) Polyphosphates, in the form of either furnace-grade or wet-process superphosphoric acid or ammoniated superphosphoric acid, are added as sequestrants to prevent precipitation of impurities. Substantial quantities of polyphosphate, supplying up to about 40 per cent of the product phosphorus content, are required (Wilbanks, 1961; Scott, 1968).
- (iv) Ammoniation is effected in the presence of suspending agents, particularly certain types of clay (attapulgite, sodium bentonite). In the presence of 1—2 per cent of clay, impurities apparently precipitate as very fine particles and products may be stored for some time without much settling. Products are of high viscosity. The method is effective but may be costly.

Maximum grades attainable would certainly be no higher, and might be significantly lower, than those listed in Table 2 for true solutions based on furnace-grade phosphoric acid.

Mixed fertilizer solutions based on wet-process superphosphoric acid

Wet process superphosphoric acid

The term superphosphoric acid refers loosely to acids of phosphorus content close to 31.6 per cent, the value corresponding with pure orthophosphoric acid (H_3PO_4). The expression was originally applied to acid containing about 33 per cent P, equivalent to 104 per cent H_3PO_4 , but it has since been extended (less justifiably) to acids with phosphorus contents in the range 30—31 per cent (95—98 per cent H_3PO_4).

The production of superphosphoric acid from wet-process phosphoric acid (by a submerged combustion

process) was first investigated on pilot scale by TVA (Scott, 1961). The product acids contained about 30 per cent P, with about 45 per cent of the phosphorus present as polyphosphate. For liquid fertilizer production the product shared the same advantages as furnace-grade superphosphoric acid, the polyphosphate acting as a sequestrant both in the acid itself and in the ammoniated acid. Similarly, the acid was an effective sequestrant in the production of liquid fertilizers from normal (ortho) wet-process acid. Ammoniation of the superphosphoric acid yielded an NP solution of analysis 10:15:0 (NPK).

Recent work at AE and CI on Foskorite superphosphoric acid has yielded results in line with those reported in the literature for American products. Thus, the proportion of phosphorus present as polyphosphate in Foskorite superphosphoric acid was found to be about 50 per cent at a total phosphorus content of 31 per cent P (Kaplan, 1969).

The marked increase in growth of liquid mixed fertilizer usage which occurred in America in 1965 was undoubtedly triggered by the increasing availability of wet-process superphosphoric acid and its ammoniated product (Hignett, 1968). The acid is being produced on a commercial scale in at least five plants, the largest of which appears to be that of Texas Gulf Sulphur at Lee Creek, North Carolina, with a design capacity of 280 tons P_2O_5 /day (Caldwell, 1968). Total superphosphoric acid capacity now exceeds 1000 tons P_2O_5 /day. (Hignett, 1968).

Superphosphoric acid may be transported as such from the production site to the consumer for conversion into liquid fertilizers, but its high viscosity necessitates special handling — e.g. the use of heated and lagged rail cars (Anon., 1967) — and it is more usually converted to the ammoniated base solution 10:15:0 (NPK) before shipment. The slow precipitation of magnesium ammonium phosphate or other magnesium compounds from the 10:15:0 base can cause trouble in handling (Hignett, 1968; Luke, 1969).

The cost of converting normal (22%P) phosphoric acid to superphosphoric acid is stated by Hignett to be \$10/ton P_2O_5 . Superphosphoric acid currently sells in Florida at \$15/ton P_2O_5 above the cost of normal (22%P) acid (Luke, 1969).

Wet-process superphosphoric acid-based solutions

As before, solutions are produced by one of two processes:

"Hot-mix", in which superphosphoric acid is ammoniated before the addition of potassium chloride and supplemental nitrogen, and Cold-mix, in which the ammoniated superphosphoric acid base solution 10:15:0 (NPK) is brought in as a raw material.

The maximum grades of solution attainable would depend upon the detailed chemical composition of the superphosphoric acid used. Although early TVA reports stated that the wet-process acid was an effective sequestrant, more recent sources report that the presence of potassium salts in solution tends to nullify the action of polyphosphates as sequestrants (Scott, 1966; Anon, 1966). Maximum grades would thus lie somewhere between (at worst) those attainable with normal wet process orthophosphoric acid and (at best) those attainable with furnace-grade superphosphoric acid (Table 3).

Direct production of ammonium polyphosphate from normal wet-process phosphoric acid

All the preceding discussion has been concerned with the production of liquid fertilizers in three succes-

sive processes — the production of normal (22% P) wet-process phosphoric acid, its concentration to the superphosphoric (30—33% P) range and, finally, ammoniation of the superphosphoric acid to yield ammonium polyphosphate solution followed by the addition of potassium and supplemental nitrogen sources.

In a process developed on pilot scale at TVA, ammonium polyphosphate (or ammonium polyphosphate solution) is produced in one step from normal (22% P) wet-process phosphoric acid and ammonia (TVA, 1968). In this process, the heat of reaction between ammonia and phosphoric acid is utilised in removing water from the system. The process can be operated to yield either a solid ammonium polyphosphate, 12:25:0 (NPK), a 10:15:0 (NPK) solution or a 11:16:0 (NPK) suspension.

A second and very similar process, apparently developed independently, has recently been announced by an industrial concern (Ferguson, 1968).

Neither of these processes is yet in commercial operation.

Suspension and slurry fertilizers

General

There is no clear distinction between suspensions and slurries, and the terms will be used interchangeably. One authority prefers to distinguish between slurries (containing solids that settle rapidly and tend to pack) and suspensions (containing solids that settle only slowly and are easily re-dispersed) (Silverberg, 1966).

The scale of production of suspensions is not clear but appears at present to be fairly small. The estimated production of suspensions during 1967 was only 10 per cent of the total production of liquid mixed fertilizers, but a survey suggested that production was likely to double in 1968 (Hignett, 1968). Although there appear to be differences of opinion on the future of suspension, the general feeling among TVA officials and equipment manufacturers is that suspensions will be the fastest-growing segment of the fertilizer industry during the next few years (Luke, 1969). As with solutions, this growth in consumption is associated with the increasing availability of ammoniated superphosphoric acid as a raw material of manufacture.

The products under discussion are suspensions of solids, which may consist of water-soluble and water-insoluble materials, in a saturated solution of salts. Since solubility is not a limiting factor they permit higher grades, particularly of high-potash mixtures, than are attainable in clear solutions. Micronutrients can be incorporated without difficulty. The major process problem is the production of suspensions which can be handled without separation of the solid phases and which can be distributed without difficulty through spray nozzles. Apart from obvious measures such as the use of finely-divided solids, the provision of agitation in storage tanks and speedy distribution after production, the commonest aid in this difficulty appears to be the incorporation of suspending agents. The usual additive is a gelling-type attapulgite clay which, upon gelling increases the viscosity of the system, delays solids setting and hinders crystal growth. The impression given by the literature, however, is that even when clay is used for this purpose some form of agitation (mechanical agitation, circulation by pumping, or air agitation) is invariably necessary in storage tanks and is very desirable in field distribution tanks.

Production of suspensions

Most plants now being built appear to be of the cold-mix type, the commonest phosphatic raw material being

10:15:0 (NPK) ammonium polyphosphate solution. Other materials include nitrogen solutions, potassium chloride and clay. The production process is essentially a straight-forward mixing operation, and the average plant output is 10-15 tons/hr.

In areas where it is cheaper to rail in superphosphoric acid and ammonia than the 10:15:0 (NPK) base solution, hot-mix plants are favoured economically. The first stage in the production process is then the production of the 10:15:0 (NPK) base.

One or two plants produce nitric phosphate suspensions by dissolving phosphate rock in nitric acid, partially neutralising with ammonia and adding supplemental nitrogen and potash. Products are particularly corrosive and of low-water soluble phosphorus availability. The process may offer raw material cost advantages under particular circumstances, but capital requirements are high.

Double superphosphate can be used as a cheap form of phosphorus in suspensions made by mixing screened superphosphate, aqua ammonia, nitrogen solutions and potash. Double superphosphate-based suspensions have been investigated in some detail by International Mineral and Chemicals Corporation (Barry, 1966), but they do not appear to be produced on a commercial scale.

Maximum grade of suspensions

Maximum grades attainable in suspensions clearly cannot be specified with any precision. In general, quite high-grade mixtures can be produced, comparable in concentration with current American granular or bulk-blended products and of considerably higher grade than existing South African solid mixtures. Some examples are shown in Table 4. The data source for Table 4 (Polom, 1968) lists a large number of examples of suspension fertilizer, including suspensions containing a variety of micronutrients.

TABLE 4. Some examples of suspension fertilizers produced commercially

Suspension	Total pfu	Nearest existing SA mixture
NPK %	(N+P+K) %	
15.0: 6.5:12.5	34.0	2:1:2(26)
9.0:11.8:15.0	35.8	2:3:4(24)
7.0: 9.1:17.5	33.6	2:3:4(24)
10.0:13.0: 8.3	31.3	2:3:2(22)

Data Source Polom, 1968.

Marketing and Economics

It is not intended in this paper to dwell on commercial aspects of the industry, but even in what is essentially a technical review of production processes, it is impossible to ignore the fact that the liquid products must, be sold and sold profitably.

From the commercial standpoint, it seems clear that liquid fertilizers cannot be treated merely as a minor variant on granular solids. The average solid fertilizer consumer cannot store or handle liquids, and it would be necessary to sell them to him *delivered into his soil*. In comparison with solid fertilizers, the marketing of liquids almost certainly calls for quite a different pattern of raw material and product movement, and the producer in addition is faced with all the problems and

expense involved in the highly seasonal business of custom application.

Under these circumstances no realistic general comparison can be made between the costs of supplying plant nutrients in solid and liquid form. In specific segments of the American fertilizer market liquids obviously compete successfully with the cheapest solid forms, and detailed cost comparisons for such cases are to be found in the literature (see for example, Hignett, 1968).

Although custom application is commonly regarded as an essential feature of the liquid fertilizer industry, it is interesting to note that farmers in France have been persuaded (on apparently quite a significant scale) to invest in their own storage tanks and distribution equipment (Soubies, 1968).

Conclusion

The production of liquid and suspension mixed fertilizers is firmly established in the United States, and there are indications that the consumption of suspensions in particular will grow rapidly in the future.

There should be interesting developments in this small but expanding segment of the fertilizer industry.

Acknowledgement

The author's thanks are due to the Board of Directors, African Explosives and Chemical Industries Ltd., for permission to publish this paper.

Summary

A brief literature review is presented on the production of solution and suspension fertilizers in the United States, including some discussion on the properties of intermediate and final products.

Opsomming

ENKELE ASPEKTE VAN VLOEIBARE GEMENGDE KUNSMIS TEGNOLOGIE IN DIE VERENIGDE STATE VAN AMERIKA

'n Kort oorsig van geskifte word aangebied oor die vervaardiging van opgeloste en gesuspendeerde kunsmis, insluitende 'n bespreking van die eienskappe van tussen- en finale produkte.

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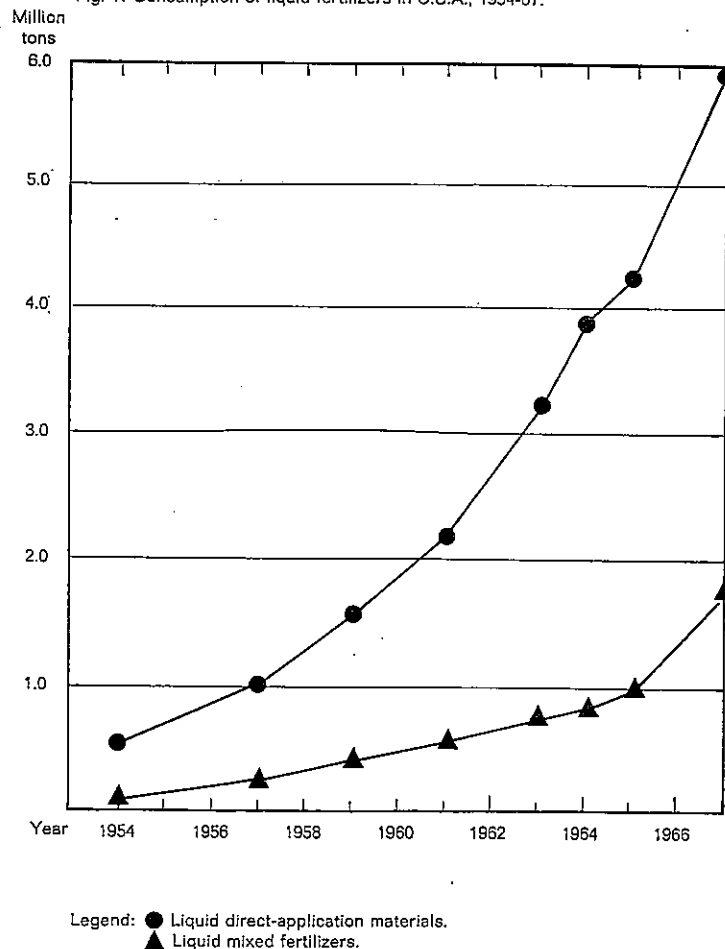
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Fig. 1: Consumption of liquid fertilizers in U.S.A., 1954-67.



Data sources: 1. USDA, 1967, SpCr 7-1 (2-67).
2. USDA, quoted by *Comm. Fert.*, 1968, 20, 19-22.