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PROSPECTS FOR NEW FERTILIZERS, FERTILIZATION CONCEPTS, AND BULK BLENDING IN ASIA, AFRICA, AND LATIN AMERICA

by Dr. Paul J. Stangel*

Fertilizer use has increased dramatically the world over during the past 10 years, particularly in the developing regions of Asia, Africa, and Latin America. About 7.83 million metric tons (mt) of plant nutrients were added to the agricultural soils of these regions during 1969, as compared to only 2.75 million mt just a decade ago. This growth will continue, possibly at a slightly reduced but nevertheless substantial rate, to where by 1980 it is estimated that nutrient consumption will reach 24.03 million mt of plant nutrients for the developing portion of Asia, 3.48 million mt for a similar region of Africa, and 7.41 million mt for Latin America (1). Cumulatively, predictions for these three regions are for 34.9 million mt of plant nutrients to be used by 1980 or over four times the level used in 1969 (table 1).

To ensure continued growth in fertilizer use, new fertilizer materials, improved methods of handling fertilizers, and new fertilization concepts must be considered. This paper is designed to examine on both short- and long-term bases, the types of new fertilizers one might expect to see in Asia, Africa, and Latin America, shifts in handling techniques that might be expected, and new concepts of fertilization with special emphasis directed toward the rice, maize, and wheat systems of these three regions.

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Table 1. Estimated Fertilizer Consumption by Region for Developing Countries, Million mt of plant nutrients (1)

	Region											
	Latin America[a]				Africa[b]				Asia[c]			
Year	N	P_2O_5	K_2O	Total	N	P_2O_5	K_2O	Total	N	P_2O_5	K_2O	Total
1965	0.74	0.45	0.28	1.47	0.51	0.25	0.16	0.92	1.36	0.50	0.23	2.09
1966	.76	.46	.31	1.53	.56	.37	.17	1.10	1.48	.51	.30	2.29
1967	.86	.54	.34	1.74	.55	.40	.20	1.15	1.96	.71	.39	3.06
1968	.96	.63	.39	1.98	.62	.47	.21	1.30	2.53	.98	.53	4.04
1969	1.09	.78	.58	2.45	.68	.52	.24	1.44	2.89	.95	.53	4.37
1970	1.31	.94	.66	2.91	.78	.56	.29	1.63	3.34	1.19	.64	5.17
1975	2.44	1.70	1.03	5.16	1.29	.75	.51	2.55	5.63	2.35	1.17	9.15
1980	3.56	2.45	1.40	7.41	1.79	.95	.74	3.48	7.91	3.51	1.71	13.13

[a] Includes Mexico, Central America, South America, Caribbean Islands, but excludes Cuba.
[b] Includes all countries on the continent of Africa.
[c] Excluding Japan and Communist Asia.

PART I
NEW FERTILIZERS FOR ASIA, AFRICA, AND LATIN AMERICA

The more progressive farmers of Asia, Africa, and Latin America have already begun a shift to new fertilizers, some with strange sounding names. Shifts from sodium nitrate and ammonium sulfate to urea and ammoniated phosphates have been particularly significant. Some areas already have shifted or are considering a shift to nitrogen solutions and even anhydrous ammonia, although in most areas these products are of minor importance or in the discussion stage awaiting introduction sometime in the future. New phosphate products such as monoammonium phosphate, diammonium phosphate, triple or double superphosphate are becoming common in a number of countries. Even more advanced materials, such as liquid fertilizers, suspensions, and ammonium polyphosphates, will soon be making their appearance.

In short, a major renascence is taking place in the developing world. It is being spearheaded by the rapid incorporation of technology borrowed from the developed world and adapted to new fertilizer production facilities now being built in Asia, Africa, and Latin America. The purpose of this part is to provide a broad assessment of the changes that are or soon will take place in fertilizer technology and provide an opinion as to the applicability of these changes to the developing countries of Asia, Africa, and Latin America.

Fertilizer Products Having Broad Immediate As Well As Long-Term Potential

The straight nitrogen and nitrogen-phosphate fertilizers are experiencing and will continue to experience the greatest acceptance and offer the greatest growth potential of all the new fertilizers on the market today.

Although special local situations may dictate otherwise, the materials in decreasing order of immediate potential in Asia, Africa, and Latin America are as follows:

Urea

(46% N, solid, prilled or crystalline, usually white, formula NH_2CONH_2, molecular weight 60.06, melting point 132.7° C, heat of solution 57.8 cal/g, specific heat 0.320 cal/g 20° C, solubility 119 g/100 ml H_2O at 25° C, specific gravity 1.335) (2).

Urea is the highest N-containing solid fertilizer material commercially available. Its high analysis permits considerable savings in shipping and distribution costs. Because of this, plus the fact that solid fertilizers have better worldwide growth potential than liquids due mainly to the simplicity of shipping and handling dry materials in areas lacking widespread availability of sophisticated equipment, urea has proven very attractive to a very large number of farmers and fertilizer manufacturers of Asia, Africa, and Latin America.

When properly applied, urea has been shown to be equal or nearly equal to ammonium sulfate as a source of N to a wide variety of crops, including maize, wheat, and rice (3). In those instances where response to urea was less than to ammonium sulfate, the differences have been attributed to either the sulfur component of ammonium sulfate or to the improper use of urea. For these reasons, no other single-nutrient fertilizer has captured the attention of agricultural and fertilizer production specialists. In most areas, it already has become or is rapidly becoming the leading fertilizer used in the developing world.

In spite of this potential and current rate of acceptance, urea has certain inherent problems that must be overcome if it is to continue to enjoy this current flush of growth. This is particularly true in those regions

lacking sophisticated capabilities in handling fertilizer and modern methods of tilling soil. The more significant of these problems are: (a) Its hygroscopic nature which often results in poor handling properties--either as straight material or in blends, particularly under hot, humid conditions. Unless corrected, this disadvantage could restrict its use to reduce costs by bulk blending, bulk transport, and mechanical bulk spreading; and (b) nitrogen losses through volatilization as ammonia when urea is surface-applied to soils, especially in warm climates. This is a major problem when the product is not incorporated into the soil after application (4, 5, 6). As much as 60% of the N applied as urea may be lost through this mechanism. Even on flooded rice soils urea has occasionally been shown to be vastly inferior to ammonium sulfate as a source of N to the crop (7). These problems are real and will become more apparent as fertilizers become more available and farmers have an opportunity to compare various nitrogen sources in supplying the needs of the crop.

Although it has been suggested by some that the biuret content in all urea produced should be less than 0.3%, it is now believed that this is important primarily for citrus crops in situations where urea is applied as a foliar spray. Extensive tests on other crops suggest that biuret levels in foliar-applied urea can approach 0.75% and not be harmful, 3% biuret is acceptable if the urea is applied to the soil (8, 9, 10).

Ammoniated Phosphates

(11-48-0, 18-46-0, 21-53-0, 16-20-0, 16-48-0, 13-29-0).

Product	Analysis	Formula	Molecular weight	Color	Specific gravity	Solubility (cold water)
Monoammonium phosphate	11-48-0	$NH_4N_2PO_4$	115.0	white-gray	1.803	58.2 g/100 ml
Diammonium phosphate	18-46-0	$(NH_4)_2HPO_4$	132.06	white-gray	1.619	22.7 g/100 ml
Ammonium sulfate phosphate	16-20-0	-	-	-	-	-

The term "ammonium phosphates" encompasses a wide variety of fertilizers produced by the ammoniation of phosphoric acid, often in admixture with other materials. The most popular of these materials are monoammonium phosphate (11-48-0), diammonium phosphate (18-46-0) and in some areas ammonium phosphate sulfate (16-20-0). The materials listed above are used for direct application to soil or as an intermediate in the production of compound fertilizers. They can be used, as is now the case in the United States, in bulk blends.

Second only to urea in growth potential, the ammoniated phosphates are experiencing and will continue to experience a substantial increase in use (11). This may not be apparent because of the phenomenal growth in urea consumption in many of the developing countries and the current major emphasis in many areas on N fertilization. Nevertheless, ammonium phosphates--because of their binutrient content, overall high analysis, excellent handling qualities, 100% water solubility of their nitrogen and near 100% solubility of their phosphate--offer considerable advantages not only in savings accrued in transport and application but also agronomically because of their quick acting effect on crops. The consumption of ammonium phosphates has increased rapidly in the United States in relative as well as absolute terms of total fertilizer used and will probably follow the same trend in Asia, Africa, and Latin America. However, the true direction of this growth is dependent upon whether bulk blends or compound N-P-K fertilizers become popular. In the United States, growth in use of DAP and MAP has been very significant during the past 10 years (figure 1). This is probably due to the rapid acceptance of bulk blending and the flexibility these materials offer under that system of marketing.

Ammoniated phosphates are particularly suited for direct application in situations where substantial amounts of basal or band-applied phosphorus and small amounts of nitrogen are required. As more sophisticated application equipment

is developed, they will be banded rather than broadcast at time of planting for such crops as wheat, maize, and sorghum. Where conditions permit, these materials will more and more be supplied to rice soils during seedbed preparation. Since all of the nitrogen in the ammoniated phosphates is in the ammonium form, they are particularly well suited for rice (3).

In contrast to urea, there are few physical or chemical problems associated with the use of ammoniated phosphates in the humid tropics. They have good handling characteristics, can be shipped in bulk in hot, humid regions with little or no difficulty, are compatible with a wide range of other fertilizers, and can be safely applied to the surface of the soil with less danger of either N or P loss. There is at least one problem, however, usually associated with diammonium phosphate; when banded at high rates in contact with or close to the seed under dry conditions, it can release free ammonia in sufficient quantities to retard seed germination or young seedling growth (13). This can be easily avoided through proper placement of fertilizer either by hand or with special banding equipment to ensure that at no time it is closer than 1-2 inches to the side and below the seed.

Chemically- or Physically-Combined High-Analysis N-P-K Fertilizers

Granular, solid, color variable but generally grayish, usually in excess of 30 units of plant food, available in a number of ratios, chemical or physical combinations of two or three major nutrients, 100% water-soluble N, and 50%-100% water-soluble P depending upon the choice of phosphate materials and production processes.

Next to straight urea and one or more of the ammoniated phosphates, complete high-analysis N-P-K grades of fertilizer are just beginning and in the near future will receive major consumer acceptance in Asia, Africa, and possibly Latin America (11).

This, however, will not occur at nearly the rate of acceptance for either of the other products discussed because under current cropping practices, the need for a complete N-P-K fertilizer is not as widespread. The frequency of potash deficiency, particularly for rice, is less than 1/10 that for nitrogen and 1/3 that observed for phosphates. But with intensification of farming, including use of new and higher yielding varieties, responses to potash will become more frequent, particularly on the organic sandy and laterite soils; thus N-P-K compounds or mixtures will be in demand. As already discussed in the section on ammoniated phosphates, the acceptance of N-P-K grades is dependent upon the potential of bulk blends. Where bulk blends have good potential (probably in Latin America), physically-mixed N-P-K grades which include ammoniated phosphates will probably increase in demand. In regions where bulk blends do not have great potential, such as in much of Asia and Africa, the chemically-combined compound fertilizer will grow in acceptance.

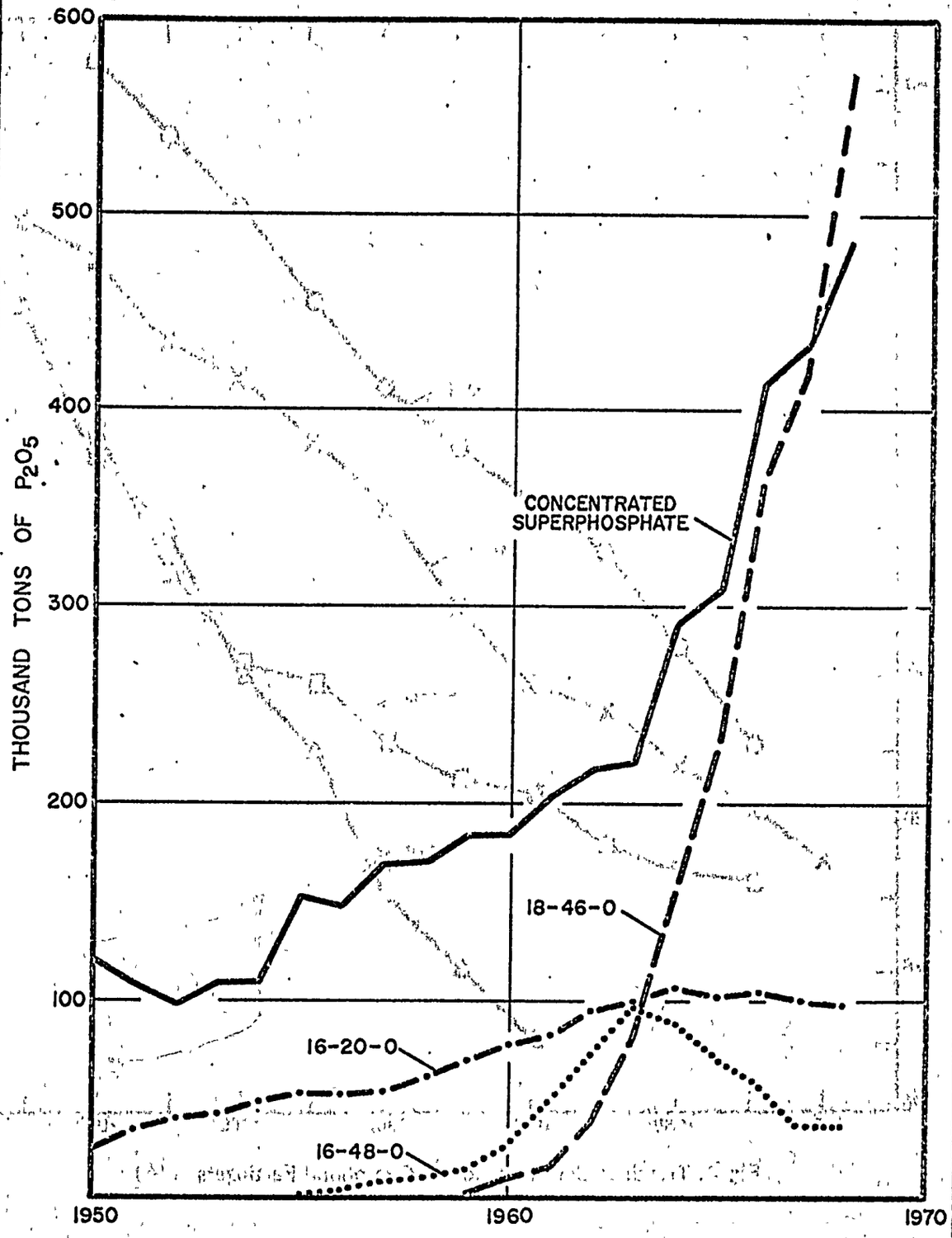
Regardless of whether as a blend or compound, N-P-K grades will be of high analysis. Products are now available to make complete fertilizers in either form with at least 40 units of plant food.

The trend toward high analysis has been evident in many of the developed countries for at least the past ten years (figures 2 & 3). There is every reason to believe this will also prove to be the pattern in most of the developing countries.

Fertilizers Currently or Soon to be Available But of More Limited Potential

There are other fertilizers that are or soon will be available to the farmers but represent a more limited potential, often only in special areas. No attempt is made to list them in order of importance for their acceptance will depend upon a specific set of conditions.

Figure 1. CONSUMPTION OF PHOSPHATE FERTILIZERS AS STRAIGHT MATERIALS
UNITED STATES (12)



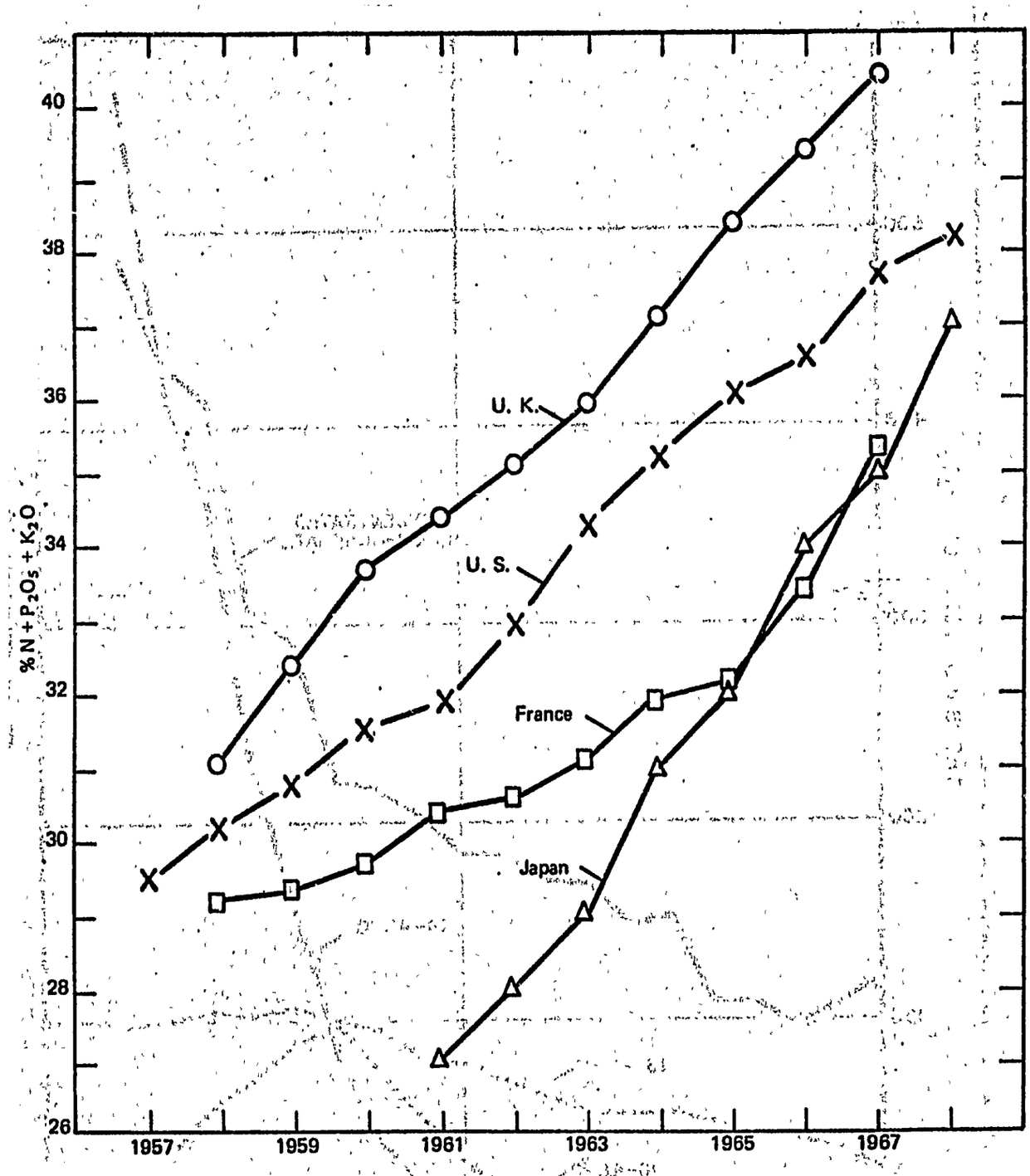


Fig. 2. Trends in Concentration of Compound Fertilizers (14)

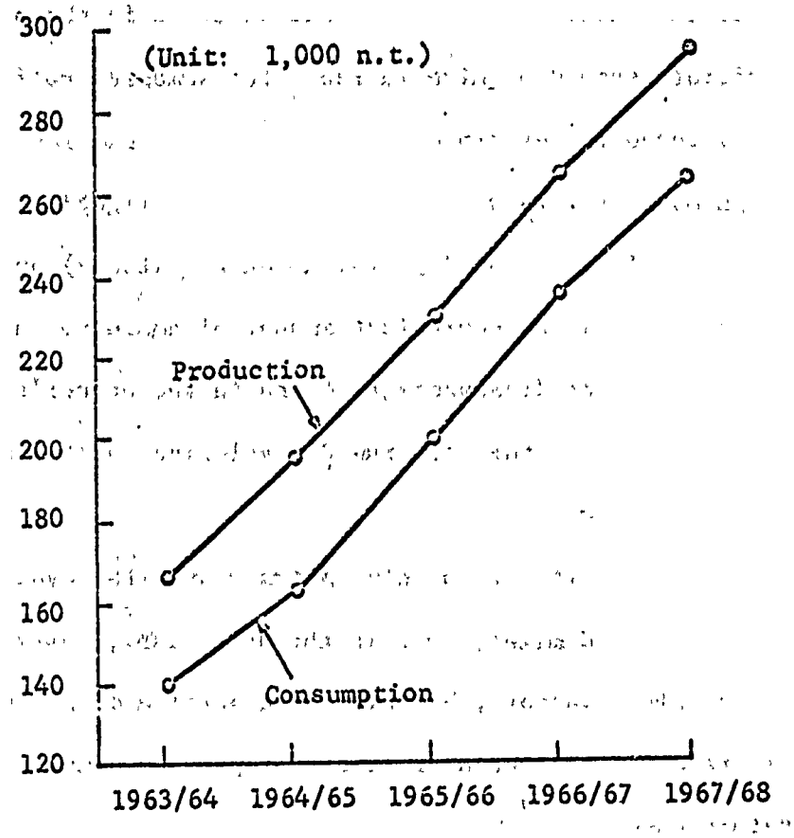


Figure 3. Production and Consumption Trend of High-Analysis Compound Fertilizers--Japan (15)

Ammonium Nitrate

(26%-33½% N; formula NH_4NO_3; molecular weight 80.05; melting point 170.4° C; density 20°/4° C 1.725; solubility 0° C 118 g/100 g H_2O, 100° C 843 g/100 g H_2O; white crystalline or prilled; specific gravity 1.29) (2).

Prior to the major breakthrough that occurred in the production of urea, ammonium nitrate showed promise in replacing ammonium sulfate as the major source of nitrogen in certain developing regions, particularly in Latin America. Although most of this was attributed to its slightly higher N content (21% N for ammonium sulfate versus 33½% for ammonium nitrate) and tendency to be less acid forming than an equivalent amount of ammonium sulfate, this product has certain distinct disadvantages which in the author's opinion limit its use particularly in the hot, humid developing countries. The major disadvantages are as follows.

1. The extreme hygroscopicity of ammonium nitrate and its resultant incompatibility with urea in blends and mixes, even in the same plant, severely restrict its suitability in bulk transport, blending or general use in the humid tropics. Even in temperate regions the hygroscopic property becomes a problem when the temperature exceeds 25° C.
2. The explosive tendency of ammonium nitrate when mishandled has in a number of countries prompted laws requiring that it be diluted with other products to reduce this hazard. As a result, in many countries the N content of the finished product has been lowered to 24%-27% thus eliminating some of the cost savings that could be generated by shipping the 33½% N product.
3. Fifty percent of the nitrogen is in the nitrate form. Many rice researchers and educators feel that most of the N should be supplied to the rice crop in the ammoniacal form; if nitrate nitrogen is used, it should be applied

usually in the later stages of growth. Research work has shown ammonium nitrate to be inferior to either urea or ammonium sulfate as a source of N on rice (3). Thus, a vast rice market in Asia and significant markets in Africa and Latin America as well appear to be closed to this product. For these reasons, we see ammonium nitrate as having very limited potential in the hot, humid areas of the tropics. [illegible] these limitati[illegible] ammonium

Insspite of these limitations, ammonium nitrate will probably be available in large quantities primarily because of advantages in production. This will be more apparent as the nitrogen industry in many of the developing countries begins to mature and producers look for new markets.

Nitrogen Solutions (Including Aqua Ammonia)

(20-0-0, 28-0-0, 32-0-0, 37-0-0, 41-0-0, and 44-0-0.) The rapid expansion in the number of NH_3 plants that has occurred both in the developed and developing world has prompted many companies to produce a variety of nitrogen compounds as a means of disposing of nitrogen production and satisfying the various agronomic and marketing needs. Not only does this provide additional market outlets for nitrogen, but the cost of storing some of these nitrogen materials is considerably less than for storing NH_3, which requires pressurized vessels or refrigeration.

One group of new nitrogen materials is those classed as nitrogen solutions. They have had wide acceptance in the United States and Europe and are just now being introduced into Japan as well as certain developing nations. For purposes of discussion and to afford clarity in the following paragraphs, a brief statement is made as to the properties and classes of materials.

Nitrogen solutions are be classed according to composition, as follows: (a) aqua ammonia; (b) solutions containing ammonia and ammonium nitrate; (c) solutions containing ammonia and urea; (d) solutions containing ammonia, ammonium nitrate, and urea; and (e) solutions containing ammonium nitrate alone or with urea but without ammonia (16).

Aqua Ammonia. Usually 20% N, the production of aqua ammonia involves the addition of anhydrous ammonia to water, a relatively simple operation that can be carried out independently of an ammonia synthesis plant, thereby saving the expense of transporting water. The operation requires facilities for proportioning the flows of water and ammonia, cooling freshly formed aqua ammonia to remove the heat of absorption, and measuring the concentration of aqua ammonia.

Cast-iron or mild-steel equipment is suitable for handling aqua ammonia. Storage and applicator tanks should be designed for a working pressure of at least 7 kilograms per square centimeter (kg/cm^2). Equipment for handling aqua ammonia is not necessarily suitable for handling other nitrogen solutions, which are generally more corrosive.

Aqua ammonia is used primarily as a direct-application fertilizer. A considerable amount of experience and success with this product has been gained in the United States, Europe, and Japan. When used properly, it is an effective source of N (ammonium form) for a wide variety of crops. Application should be subsurface; otherwise, gaseous loss will occur. Aqua ammonia can be prepared in the field by injecting anhydrous ammonia into irrigation water.

Ammonia-Ammonium Nitrate Solutions. (37-0-0, 41-0-0, and 44-0-0.) Solutions containing ammonia and ammonium nitrate are produced by injecting ammonia into ammonium nitrate solutions. Although such solutions are usually produced at an ammonia plant, they can also be produced from transported ammonia.

Ammonia-ammonium nitrate solutions are used both for manufacture of mixed fertilizers and for direct application to the soil. Ammonia-ammonium

nitrate solutions cannot be economically handled in ordinary steel equipment because of corrosion. Equipment made of aluminum or stainless steel is satisfactory.

Ammonia-Urea, Ammonia-Ammonium Nitrate-Urea Solutions. (37-0-0, 41-0-0, and 44-0-0.) Aqueous urea-ammonia solutions and ammonia-ammonium nitrate-urea solutions are designed for use by the manufacturer of mixed fertilizers, the latter type solution usually being added to improve condition of finished product. A tracing of the development of this type of solution in the United States may help illustrate the manner in which it could develop in many of the countries of Asia, Latin America, and Africa.

The original use of nitrogen solutions was in the manufacture of solid mixed fertilizers in the United States. Some of the solutions found their way into the direct field application market. A large potential market for nitrogen solutions as direct-application materials soon became evident--a situation promoted by the growing market for liquid mixed fertilizers, anhydrous ammonia and aqua ammonia. Manufacturers of solid mixed fertilizers recognized this potential and found that some of their ammoniating solutions purchased for manufacturing could also be sold locally as liquid fertilizer. The ammoniating solutions could be diluted with water as desired to lower the gauge pressure and salting out temperature. This permitted the solutions to be handled in nonpressure applicators, but the prescence of small amounts of free ammonia in all these solutions resulted in losses of ammonia to the atmosphere during application unless the solutions were injected beneath the soil surface. Thus, surface application of this product was not entirely suitable. Furthermore, the presence of ammonia increased the corrosiveness of the solutions.

Non-Ammoniacal Solutions of Ammonium Nitrate and Urea. (16%-32% N, typical grades 28-0-0 and 32-0-0.) This type of nitrogen solution offers its greatest potential in many of the developing countries.

To satisfy the market for nonpressure nitrogen solutions suitable for surface application, aqueous solutions containing ammonium nitrate alone or with urea or other sales were produced. The compositions and properties appear in table 2.

As with ammoniacal solutions, the manufacture of nonammoniacals is usually integrated with an ammonium nitrate plant. These solutions are not as corrosive as ammoniacal solutions and can be handled in plain steel equipment if corrosion inhibitors are added.

These products have the same agronomic effectiveness as similar amounts of dry urea or ammonium nitrate. This may prove to be a very effective way to market ammonium nitrate in the tropics.

Anhydrous Ammonia

(82-1/5% N, gas at atmospheric pressure; liquid when compressed and cooled; colorless; molecular weight 17.03; critical temperature 1.33° C; critical pressure 1,657 psig; latent heat vaporization at 28° F 589 BTU/lb; liquid density at 60° F 38.50 lb/ft^3; vapor density at 1 atm, 60° F 0.0456 lb/ft^3; vapor specific gravity (1 atm, 60° F, air = 1), 0.597; vapor volume (1 atm, 60° F) 22.0 ft^3/lb; boiling point at 1 atm -28° F; freezing point at 1 atm -107.9° F) (2).

Anhydrous ammonia is by far the highest analysis N product commercially available anywhere in the world. Because of its high analysis, it can be shipped great distances to its point of use at competitive prices. Anhydrous ammonia has one major disadvantage--high vapor pressure at ordinary temperatures. It must be transported and stored in pressure containers, generally with a minimum working pressure of 265 psig. Unless injected into irrigation water, anhydrous ammonia must be injected as a liquid into the soil with special equipment where, beneath the soil surface, it vaporizes, reacts with the soil water, clay or organic fractions, changes to the ammonium form and is retained by the system.

Table 2. Selected Commercial Noncommercial Solutions of Ammonium Nitrate Alone and With Urea for Direct Application (17, 18)

Solution	Total N	Percentage			Salt out temp. (Centigrade)
		Ammonium nitrate	Urea	Water	
160(0-46-0)	16.0	45.7		54.3	-12
170(0-31-0-36)[a]	17.0	30.9		32.9	0
175(0-50-0)	17.5	50.0		50.0	- 6
190(0-54-0)	19.0	54.3		45.7	1
200(0-48-0-20)[b]	20.0	47.5		32.0	14
200(0-57-0)	20.0	57.3		42.7	6
210(0-60-0)	21.0	60.0		40.0	11
227(0-65-0)	22.7	65.0		35.0	-
245(0-70-0)	24.5	70.0		30.0	-
280(0-40-30)	28.0	39.5	30.5	30.0	-17
300(0-42-33)	30.0	42.2	32.7	25.1	- 9
320(0-44-35)	32.0	44.3	35.4	20.3	0

[a] Contains 36.2% calcium nitrate.
[b] Contains 20.5% sodium nitrate.

When properly used, anhydrous ammonia is equal to any other form of ammonium nitrogen and is occasionally superior to urea or nitrate forms, but does require special management or its agronomic performance can be affected (3). Ammonia applied either as pre- or post-plant should never be placed in close proximity to the seed or young roots; otherwise, as in the case with diammonium phosphate, germination or growth can be retarded. Depending upon the amount injected, losses of ammonia can result if the ammonia is injected at too shallow a depth in soils low in moisture, clay content or organic matter or when tracks left by the injector knife fail to close because of insufficient or excessive moisture. In general, anhydrous ammonia requires special equipment for handling.

Prospects for Use of Nitrogen Solutions and Ammonia in Developing Countries

It is generally accepted that dry fertilizers offer the greatest potential in the developing countries of the world. Many believe the immediate potential for ammonia and nitrogen solutions is quite limited.

These assumptions are probably correct based primarily on the general acceptance of dry fertilizers. Their simplicity of handling, compared to the more sophisticated system required for liquid materials, makes them more readily accepted in a country which lacks mechanization. However, to stop here would be an oversimplification of the situation and would not reflect the true potential for nitrogen solutions and ammonia.

Although dry fertilizers, particularly urea, ammoniated phosphates, and complete N-P-K compounds will be the dominant force in the developing country market for some time, ammonia and nitrogen solutions, particularly aqua ammonia and nonpressure, could very well make substantial advances in the next few years. This will occur for at least four reasons. These are: (1) Labor shortages are developing in certain regions, thus placing a premium on increasing efficiency of handling agricultural inputs, (2) adaptation to nonpressure aqua ammonia or nonpressure solutions requires only a very limited amount of sophisticated equipment, (3) because of the tendency for ammonia producers to look for additional markets for excess ammonia, they will actively push to develop these markets, and (4) increasing evidence indicating the seriousness of N losses from surface-applied urea will pressure producers to look toward alternate ways of marketing this product and alleviate losses.

Under these four conditions, prospects are good for acceptance of one or more of these materials as agriculture becomes mechanized. The major potential for nitrogen solutions exists mainly in large estate areas that are the major earners of foreign exchange and which produce rubber, oil palm, sugarcane, or where these holdings are old, must be rejuvenated, and are converted to such crops as rice, maize, or wheat. Potential also exists in certain areas of smaller land holdings. Of particular promise are areas where farmers are willing to pool equipment and cooperatively farm their land. Under these circumstances, nitrogen solutions can offer both labor saving and low cost per unit N advantages. An additional potential, its success dependent upon government policy and development of regional projects, is aerial application of nitrogen solutions. There are vast areas of India, Pakistan, and Indonesia where much of the rice and wheat is grown under uncertain moisture conditions. In these areas, farmers often use only a very minimum of fertilizer. Where optimum rainfall occurs, usually

well into the growth cycle of the crop, additional nitrogen could prove to be profitable. Under these conditions, it would prove to be profitable to apply possibly by airplane a small amount of nitrogen, 12-30 kg/ha to quickly take advantage of the more favorable water supply.

Low pressure solutions and high pressure anhydrous ammonia, although widely accepted in the United States and Europe, offer limited potential for direct application in Asia, Africa, and Latin America. Considering that these materials are of high analysis, particularly anhydrous ammonia, the special equipment needed to take advantage of this offsets any advantage accrued in labor saving or low-cost nitrogen. The exceptions to this are areas where landholdings are substantial and individual fields are sufficiently large to allow for the economic use of this relatively sophisticated equipment.

This is particularly true where labor is short in supply and/or nitrogen losses are occurring where urea is currently applied to the surface soils. Under those circumstances, urea solutions and anhydrous ammonia in particular seem attractive.

Triple Superphosphate

(0-46-0, solid, nonhygroscopic, 85%-100% of phosphate in water soluble form.) Triple superphosphate containing 46%-47% P_2O_5 is a high-analysis phosphatic fertilizer that has become significantly more important in the last twenty years, but is expected to increase only slightly from its current 20% share of the total phosphate market in much of Asia, Africa, and Latin America (11). The fact that ammoniated phosphates are experiencing good acceptance precludes any additional growth as a major source of phosphorus at the consumer level.

The most economical production of triple superphosphate is close to the source of phosphate rock, and the phosphoric acid is produced in large and continuously operating plants. The P_2O_5 content of triple superphosphate is almost entirely water soluble and is readily available to most crops under a wide range of conditions. Its low sulfur content (3% or less) relative to that of normal superphosphate is easily overcome by including sulfur-containing material somewhere else in the fertilization program. This fertilizer is nonhygroscopic and free flowing in either run-of-pile or granular form and lends itself readily to ammoniation. This is a particularly important characteristic for those countries that must import phosphate but have their own ammonia facilities. Finally, it is a relatively low cost source of P_2O_5, and its high analysis permits additional economies in handling, shipping, and distribution. In spite of all these apparent advantages, most if not all, are equalled or surpassed by ammoniated phosphates, particularly DAP. This coupled with its incompatibility with DAP or urea in blends limits its future growth potential as a material to be used directly by the farmer.

Nitric Phosphates (Nitrophosphates)

Solid, more hygroscopic than urea or ammoniated phosphates, typical analysis 29-29-0, 26-26-0, 20-20-0, 14-14-0, water solubility ranges from less than 10% to more than 80%, depending upon the process. Nitrate nitrogen comprises 30%-50% of the total N, again depending upon the process.

In contrast to the dominant role of ammoniated phosphates in the U.S. phosphate industry, nitric phosphates (called nitrophosphates in Europe) have been almost equally dominant in Europe. By the late 1960s, European plants accounted for over 5 million mt, a major portion of the phosphate produced in Europe (11).

Nitric phosphates have a low sulfur requirement and as a result recently gained in popularity when sulfur was expensive or in short supply. Several plants to produce nitric phosphates were built in developed and developing countries as a result of the tight sulfur supply situation. With sulfur now in more plentiful supply, however, this route has lost much of its attractiveness.

Nitric phosphates do not offer a great potential for growthiin Asia, Africa, and Latin America for at least two basic reasons. First, and dominant in rice-growing Asia, is the fact that from 30%-50% of the total nitrogen in nitric phosphates is in the nitrate form, a form not recommended by many rice specialists. Those rice specialists who do feel there is a place for nitrates restrict use of fertilizers containing nitrate nitrogen to one of the later top dressings. The second drawback to the use of nitric phosphates is the limited water solubility of phosphorus. Depending upon the researcher, the acceptable range of water-soluble phosphorus for use on upland crops appears to be from 35%-80%. Depending upon the process, the water solubility of nitric phosphates is usually under 50% and frequently below the 35% minimum (19, 20, 21, 22).

Further research may offset much of the objection raised regarding water solubility. Even so, other economic drawbacks, plus the fact that it is unacceptable to many as a source of nitrogen for rice, leads one to conclude that nitric phosphates will not be widely used in many of the developing countries.

Polyphosphates

A very significant breakthrough in phosphoric acid, a basic ingredient of many phosphate fertilizers, has led to the development of a new family of polyphosphate fertilizers, many of which are now being tested by TVA and others.

Ordinary phosphoric acid (54% P_2O_5) may be concentrated to super acid which, depending upon whether the electric or wet process is used, ranges from 68%-80% in P_2O_5 content. To our knowledge, neither super acid nor products made from it are available commercially in the developing world. Nevertheless, some offer immediate potential in selected areas and will be discussed in brief.

Superphosphoric Acid. More than 10 years ago, TVA developed a method for producing concentrated phosphoric acid, usually referred to as "superphosphoric acid." This new product contains over half of its phosphorus in the pyro and more condensed forms; the remainder is as the standard ortho form. When made by the standard electric-furnace process, P_2O_5 content is 76% or more. Table 3 illustrates the difference between furnace acids of ordinary and superphosphoric concentrations.

The main advantages of super acid are its high analysis (almost 50% more P_2O_5 than ordinary acid), its low corrosion rate (less than half as rapid as ordinary acid), and ability to sequester impurities often found in wet-process acid, an advantage in making liquid fertilizers.

Ammonium Polyphosphate. (Liquid 10-34-0, 11-37-0; solid 15-62-0, 12-57-0). The term "ammonium polyphosphate" refers to material containing condensed phosphates either as solutions or solids and produced by ammoniation of superphosphoric acid. These have proved to be favorite intermediates for making liquid fertilizer. Typical compositions of these have been described by Hignett (23) and appear in table 4.

The solutions 10-34-0 and 11-37-0 are produced by ammoniation of superphosphoric acid with the addition of water (24).

The more concentrated the acid, the larger the portion of total phosphate as pyro and/or tripolyphosphate. Usually the same proportion of these species exists in the 10-34-0 or 11-37-0 as in the super acid.

Ammonium polyphosphate can also be produced as a solid by ammoniation under pressure (25). The distribution of polyphosphates made under this process, however, is different and not necessarily related to the content of the super acid. Usually there is a tendency to form more pyrophosphate and less of the more condensed phosphates.

The proportion and species of polyphosphate present in ammonium polyphosphate are important because to some extent they determine the chemical and agronomic properties of the end product.

Ammonium polyphosphates (liquid or solid) can sequester considerable amounts of impurities usually found in wet-process acid, thus producing a more trouble-free liquid fertilizer. In addition, considerably larger quantities of certain micronutrients can be sequestered in polyphosphates than with standard ortho sources, a decided advantage when liquid fertilizers are to be used as a carrier of micronutrients (table 5).

There is some evidence to suggest that polyphosphates are a superior source of phosphorus to a number of crops, but this is by no means conclusive. Work in the United States has been summarized (26) and has led to the conclusion that no clear-cut superiority exists between monoammonium phosphate and ammonium polyphosphate (APP), although both were

Table 3. Comparison in Properties Between Ordinary and Superphosphoric Acid Made With Electric-Furnace Acid (23)

Parameter	Type of acid: Ordinary	Type of acid: Super
Acid concentration (% P_2O_5)	54	76
H_3PO_4 equivalent (percentage)	75	105
Lb P2O5/gal	7.1	12.2
Percentage of P_2O_5 as poly acids	0	51
Viscosity (Centipoises)		
at 40° C	12	400
at 100° C	4	45
Corrosion rate (mils/yr)		
Mild steel at room temperature	523	230
Type 316 stainless steel at 110° C	5	0.5

Table 4. Phosphate Composition of Various Polyphosphates (24)

Species	Phosphate species in ammonium polyphosphate % of total P_2O_5: 10-34-0 solution	11-37-0 solution	15-62-0 solid
Ortho	55	27	41
Pyro	39	42	54
Tripoly	5	20	4
Tetrapoly and higher	1	11	1

Table 5. Comparative Abilities of Liquid Ammonium Polyphosphate and Standard Orthophosphates To Carry Micronutrients (23)

Material added	Solubility, % by wt. of element (Zn, Cu, Fe, Mn, B, Mo) In 11-37-0 base solution (Ammonium poly)	In 8-24-0 base solution (Standard ortho)
ZnO	3.0	0.05
$ZnSO_4 \cdot H_2O$	3.0[a]	-
$ZnCO_3$	3.0	-
Mn_3O_4	0.2	< 0.02
MnO	0.2[b]	< 0.02
$MnSO_4 \cdot H_2O$	0.2[b]	< 0.02
CuO	0.7	0.03
$CuSO_4 \cdot 5H_2O$	1.5	0.13
$Fe_2(SO_4)_3 \cdot 9H_2O$	1.0	0.08
$Na_2MoO_4 \cdot 2H_2O$	0.5[c]	0.5[c]
$Na_2B_4O_7 \cdot 10H_2O$	0.9	0.9

[a] pH of 6 was maintained by addition of ammonia.
[b] Precipitates formed after several days.
[c] Largest amount tested.

Solid ammonium polyphosphate (15-62-0 or 12-57-0) of the materials in this family offers the greatest potential for use in developing countries. This is because (a) it is a high-analysis, binutrient fertilizer (77 units of plant food) second only to anhydrous ammonia in plant food content, and (b) it can be shipped in the solid form to intermediate points where it in turn can be readily converted to a liquid (11-37-0) if and when the situation should warrant.

For these reasons, solid APP has good potential in the same regions offering good opportunities for nitrogen solutions and bulk blends. The solid APP (imported) together with the locally-produced nitrogen solution could serve as the nucleus of developing a low-cost liquid industry. It could also serve as a high-analysis, binutrient component of a bulk blend.

Urea-Ammonium Polyphosphate. (Solid; 30-30-0, 39-13-0, 19-19-19 or varying grades; all nitrogen in urea or ammonium form; phosphate 100% water solubility and 50% in the nonortho form.) Agronomically, this product is as good as MAP or DAP. This coupled with its high analysis, simplicity of production and low production costs makes it a product with good potential in Latin America, Asia, and Africa.

Suspension Fertilizers (Fluid; 12-40-0, 14-44-0, or other grades; requires superphosphoric acid. Nitrogen in ammonium form, 50% of phosphate in condensed (nonortho) form, all phosphorus 100% water solubility.) Only in very special cases will suspension fertilizers have a place in Asia, Africa

and Latin America, the major limitations being a readily available source of super acid and the need for highly-specialized equipment. Nevertheless, the next ten years will see the appearance of this product in areas of Africa and Latin America where large, uniform fields exist, mechanization of equipment is possible and the desire exists to save labor through the applications of high-analysis N-P-K micronutrient-pesticide combinations--all possible with suspensions. However, this is a very sophisticated, service-oriented market; the frequency of its occurrence in most of the developing world is rather limited at the present time.

Potash Fertilizers

Potash ranks third in major nutrients consumed in the developing countries. The relative importance of this nutrient in relation to nitrogen and phosphorus varies significantly among the various regions under consideration. Using potash as a base and assigning it a value of one, the $N:P_2O_5:K_2O$ consumption ratio between the three major nutrients was 1.88:1.34:1 for Latin America, 2.84:2.17:1 for Africa, and 5.45:1.79:1 for Asia (table 1). Clearly in relation to potash by far more nitrogen and phosphorus is used in Asia than is the case in Africa and Latin America. This most probably is due to the types of crops grown in these regions. Rice, the dominant crop in Asia historically has responded much more readily to nitrogen and phosphorus than to potassium. Although this relative emphasis has changed in Japan, Korea, and Taiwan and is now changing in India and a few other countries, the major emphasis for some time to come will be on nitrogen and to a lesser extent phosphorus as long as rice is the dominant crop of the area.

The probable reason there is a narrower ratio between potash and the other prime nutrients in Africa and Latin America is the relative importance of maize and wheat relative to rice. Both maize and wheat are good users of potash as well as of nitrogen and phosphate.

Based on this relative difference in crop and regional requirement, the author is of the opinion that the majority of the potash needs by the farmer in Asia will be satisfied via chemically- or physically-combined N-P-K fertilizers. Very few straight potash materials as such will be sold directly at the retail market. Thus, increased use in potash for the area will be very closely related to the growth of N-P-K grades. To a lesser extent, this analysis may also apply for Africa; for although the consumption ratio of K to P_2O_5 and K_2O is somewhat narrower, the absolute amounts consumed are quite small.

The potential for use of straight potash materials in Latin America is good. This is based primarily on relatively high demand for potash by the crops grown in the area. There are several potash-containing materials that can be used either for direct application or as part of N-P-K fertilizers.

<u>Muriate of Potash.</u> Commercial agricultural muriate of potash products contain from 96%-99% KCl, equivalent to approximately 60%-62.5% K_2O. Muriate of potash products made from the flotation recovery processes are usually of varying pink to red hues, reflecting the presence of small quantities of colored impurities. Products made by solution and recrystallization methods are white in color, the principal impurity being colorless NaCl.

The potash is 100% water soluble, readily available to the crop, and accounts for over 90% of all of the potassium consumed in the world. KCl is readily acceptable as a source of K for most crops which are not affected by the chlorides associated with the product.

Sulfate of Potash. Commercial agricultural sulfate of potash contains from 92%-98.5% K_2SO_4, equivalent to about 50%-53.2% K_2O. It also contains over 17% S as the sulfate; thus combined sulfate of potash represents over 67 units of plant food. The potassium and sulfur are readily available to the crop and this material is used widely on vegetables, tobacco, and other crops where low chloride levels are desired. This product constitutes about 6% of the current sales of all potash.

Sulfate of Potash-Magnesia. It contains from 21%-26% K_2O, 7%-11% Mg and 18%-23% S depending upon the process used to produce the product. All three nutrients are readily available to the crop. It is used primarily in N-P-K grades where magnesium and/or sulfur are needed and contains approximately 55 units of plant food.

Potassium Nitrate. Potassium nitrate contains almost 14% N and 46% K_2O making it a fairly high analysis product. The agronomic value of the product is well known with both the potash and nitrogen water soluble and readily available to the crop. It is used mainly on high-value specialty crops and not well suited for rice because all of the N is in the nitrate form.

New Potential For Old Products

Without exception, all of the new fertilizers just discussed are higher in N, P or K than their predecessors and all are either void or extremely low in sulfur. Because of this and the proven beneficial effects of sulfur, particularly on wheat, maize, sorghum, and certain pulses, it would seem appropriate to reassess the potential of some of the so-called low-analysis fertilizers. Two of these are ammonium sulfate and ordinary superphosphate.

Ammonium Sulfate

Because of its low nitrogen content (21%, all ammonium nitrogen), the downward trend in use of ammonium sulfate was predictable. In most

research tests, and in many government fertilizer education programs, it has been replaced by other nitrogen sources, usually urea. Under the circumstances then, now and in most instances in the future, this decision was justified; per pound of N, urea is a more economical choice. Nevertheless, the relative competitive situation for ammonium sulfate is changing. The majority of ammonium sulfate produced today is as a byproduct usually of the steel or caprolactum industries. The loss of domestic and export N markets to urea has been substantial (27). This, coupled with increased emphasis on pollution control, has led to a very substantial supply of ammonium sulfate in recent years. Prospects are good for an even more abundant supply of ammonium sulfate in the coming years. Since it is a byproduct of another industry and since it is in oversupply, recent prices f.o.b. vessel Japan, United States, or Europe have been under $10, often $5/mt, and thus very competitive with urea on a delivered per unit of N cost (27). Although urea will remain the dominant source of N in the developing nations, the pricing of ammonium sulfate will be sufficiently attractive for the next several years to warrant its reconsideration as a significant source of nutrients. Consideration must be given to its 22% sulfur level. In addition, ammonium sulfate has shown a slight but consistent superiority over urea as a source of N for rice. Vegetable producers the world over have shown some favor to ammonium sulfate, presumably because of its sulfur content. The current surplus of ammonium sulfate, coupled with new stress on ways to improve the marketability of the product and recent recognition of sulfur problems on maize and wheat in Brazil, Kenya, India, and elsewhere, has led the author to predict that ammonium sulfate will be reclassified on the basis of its N and S content and be considered as a binutrient fertilizer having 43 units of plant food. On this basis and as the fertilizer market becomes more complex, the developing world fertilizer market will take a new look at ammonium sulfate and use it in increasing quantities possibly at the expense of urea.

Ordinary Superphosphate

Like ammonium sulfate, ordinary superphosphate was by far the leading phosphate fertilizer in most of the developing countries of the world. This has changed, the decline being caused mainly by the acceptance of concentrated phosphates, so that it now comprises less than 20% of the world's phosphate and possibly even less in the developing areas of the world. The primary reasons for this decline were high production and transportation costs both directly related to its low P_2O_5 content (11). Despite these negative factors, the rate of decline in normal superphosphate is expected to decrease. Depending upon availability of alternate sources of sulfur in fertilizers, such as ammonium sulfate, ordinary superphosphate could actually grow in acceptance in certain regions. Like ammonium sulfate, it contains a significant amount of sulfur. The maize growers of Kenya have already recognized this and have returned to its use after having tried the more concentrated phosphates. As sulfur needs become more apparent and as granulation of N-P-K fertilizers becomes more common, the use of ordinary superphosphate should continue to be significant particularly in compound fertilizers unless, of course, an alternate and cheap source of sulfur is available.

Fertilizers in the Future--Ultrahigh-Analysis Forms of Phosphorus and Their Agronomic Value

The long efforts toward new product development in the fertilizer industry has for the most part been geared toward ever increasing concentration of the primary plant nutrients. Ammonium polyphosphate (APP) (15-62-0) is the most concentrated fertilizer currently available--and it on a limited basis. It generally consists of 41% orthophosphate and 59% polyphosphate of

varying chain lengths. Research amounts of very long-chain APP and ammonium tetrametaphosphate of approximately 14-73-0 grade have been prepared and tested. It now appears the 14-73-0 grade is close to the limit of high-analysis with orthophosphates or condensed phosphates. On this basis, further development of ultrahigh-analysis P or NP sources must, of necessity, be concerned with new forms of P with covalent N-P bonding and little or no oxygen in the molecule.

Although the actual chemistry of these products has not been worked out in various systems, in theory, products of this type may react with soil water through chemical or biological action to yield conventional forms of P and N in the soil.

Ultrahigh-analysis fertilizers have been defined as those compounds that contain more than 100% plant food on an oxide basis (usually N-P basis although more emphasis will be placed on N-P-S systems). There are four basic groups under study: vapor phase reaction products, phosphonitrilics, cyclic metaphosphimates, and linear polyamides (28, 29, 30).

Vapor Phase Reaction Products

(NH_3 - P - O.) One of the more promising routes to ultrahigh-analysis P sources is the direct reaction of NH_3 and P in the presence of air. By controlling reaction conditions, high-analysis products varying in content of water-soluble P and N may be prepared. Results obtained thus far are encouraging, particularly from a production standpoint. Greenhouse tests have revealed that these products are 30%-50% as effective as conventional N-P sources. Under the present level of technology, at least 50% of the reaction products are inert--usually very long-chain polyphosphates. Modification of the process might offer a combined quick- and slow-release action sought in slow-release fertilizers. The interest in this product is

for use as an intermediate which probably would be converted to solutions at the point of distribution.

Phosphonitrilic Hexaamide Compounds

One of the highest nitrogen component N-P compounds that shows some promise is phosphonitrilic hexaamide (55-92-0), an N-P ring compound. It contains no oxygen and very little hydrogen. Greenhouse tests suggest that the unsaturated phosphonitrilic ring apparently yields available P at rates sufficient for optimum growth. The nitrogen component appears to be completely available to the crop.

The following proposed reaction scheme may be indicative of the fate of hexaamide in soil (28):

$$[PN(NH_2)_2]_3 + 3H_2O \longrightarrow 3\ PO(NH_2)_3 + 9H_2O \longrightarrow 3(NH_4)_2HPO_4 + 3NH_3$$

Certain amidophosphates that are presumed to form as intermediates between $PO(NH_2)_3$ and $(NH_4)_2HPO_4$ have been evaluated and found to be fully effective sources of P and N for corn. On this basis, the major conclusion from the above may be that hexaamide reacts with soil water to form conventional forms of P and N in the soil. Thus, the ultimate in high-analysis has almost been reached by eliminating chemically bound water from fertilizer salts.

Cyclic Metaphosphimate

(27-60-0.) In contrast to the phosphonitrilic compounds, cyclic metaphosphimate ring structures are not subject to microbial attack, and do not readily release their N and P and thus must be considered very stable in soil systems. Further processing, such as breaking the ring by chemical or thermal action, is necessary before this material proves attractive for use as a fertilizer.

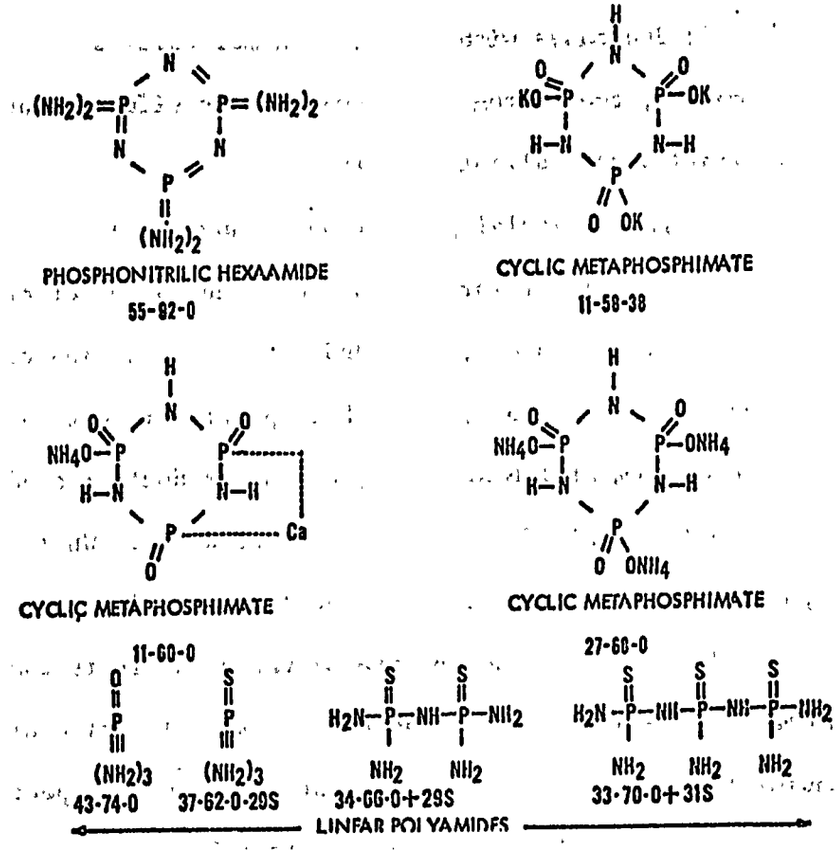
Linear Polyamides

Another potential route to ultrahigh-analysis sources of P is the synthesis of linear polyamides and thiopolyamides.

Three of the four compounds shown in figure 5 include substantial amounts of sulfur. All contain little or no oxygen. This plus the S results in a much higher content of plant nutrients. The phosphate availability of these compounds decreases with increase in molecular size. With the exception of thiopolyamides, the nitrogen sources were as effective as ammonium nitrate. The thiopolyamides were slightly toxic.

Although commercial production of any one of these ultrahigh-analysis products is probably 10 or more years away, they do offer promise of becoming the fertilizers of the future, provided certain technological difficulties can be overcome. Furthermore, when their plant-nutrient contents are expressed on an elemental basis, many of the products tested approach the theoretical (100%) limit for high-analysis products. While initial agronomic tests appear very promising, a very concentrated effort on methods of synthesis will have to be made before ultrahigh-analysis compounds, particularly polyamides, can be produced at reasonable cost. In spite of these restrictions, the fundamental chemistry is being investigated and prospects are good for the appearance of new ultrahigh-analysis fertilizers within the next 20 years.

Figure 5. **Structural formulas and analyses ultra high analysis fertilizers.** (28, 29, 30)



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PART II
CONTROLLED AVAILABILITY OF FERTILIZERS

Many fertilizers are readily water soluble, hence under optimum soil moisture conditions, release their nutrients to the crop at a very rapid rate. In numerous instances, this release is at a rate faster than needed by the crop, and efficient nutrient use may not occur. On the other hand, if the nutrients are not absorbed by the plant but left in the soil system, they may be lost through leaching or volatilization. Various biological, physical, and chemical forces may render the nutrients unavailable and thus reduce crop utilization. Agronomists, horticulturists, farmers, and fertilizer manufacturers alike have long desired a fertilizer that releases nutrients at exactly the rate needed by the crop. Should it be possible to achieve this goal, much labor would be saved and many of the obstacles to efficient nutrient utilization would be eliminated

The objective of this part of the paper is to examine the basic concepts justifying the efforts to gain controlled availability of fertilizers, the approaches tried or being considered thus far in developing these specialty fertilizers, and to provide a general discussion of the materials used and the successes obtained thus far.

Basic Concepts and Objectives Employed in Developing Controlled Availability of Fertilizers

It is well known that crops utilize only a fraction of the fertilizer nutrients applied to the soil. Recovery rates of from 40%-80% are common for fertilizer nitrogen or potassium (1, 2). Even lower recoveries have been reported for phosphorus, with values of 20%-30% very common;

certain conditions, recovery values as low as 10% are not unexpected (3). Crops are notoriously inefficient users of micronutrients, with only 1%-3% of a given nutrient recovered by any given crop (4).

Thus, almost without exception, the basic objective of most researchers working with fertilizers is to improve the plants' efficiency in utilizing a given amount of fertilizer. Workers are attempting to accomplish this by developing products that will release or keep in available form plant nutrients in sufficient amounts to sustain maximum yields but minimize the nutrient-immobilizing physical, biological, and chemical forces in the soil system.

These forces can reduce availability in a number of ways. Among the more prevalent are losses through leaching, denitrification, volatilization, and fixation. Although immobilization can be temporary, most of the losses described are permanent and thus cannot be considered potential sources of nutrients for future crops.

Agronomists have recognized these mechanisms of loss or immobilization and have developed fertility programs to keep them at a minimum. Such practices as multiple applications of fertilizer (nitrogen) during the growth cycle, banding or deep placement of fertilizer, or foliar sprays all are ways to counter these nutrient-immobilizing forces and still provide optimum nutrient availability to the crop. This, however, has not been accomplished without some disadvantage. Almost all of these practices have increased the cost of supplying fertilizer to the crop. In many cases, it has been due to an increased labor requirement. Thus, farmers are a long way from achieving the ideal fertilizer program of being able to apply fertilizer once during the life cycle of the crop, at most annually, and still supply nutrients at the level needed to ensure maximum yields.

Although scientists have worked for almost three-fourths of a century on ways to increase the efficiency in nutrient utilization by crops, it has been only within the last 10-15 years that a major effort has been made to develop specific fertilizer compounds that would provide controlled availability of nutrients and still achieve the goal of one application per crop cycle. These efforts have come primarily from scientists in the fertilizer industries of the United States, Japan, and Europe.

In recent years, research to achieve controlled availability has centered in two major areas. One is through controlled release, either with the use of slowly-soluble compounds or by covering soluble compounds with an insoluble or impervious material that will deteriorate and release the contents when the crop needs them. A second is through protected availability designed to keep the nutrient in a form readily available to the crop but at least partially protected from the immobilizing forces present in the system. Nitrification inhibitors and chelates fall into this category.

Controlled Release

The controlled-release approach has seemed to offer the greatest opportunity for achieving objectives of controlled availability. Some very encouraging progress has been made through either the development of slowly-soluble materials or the coating of soluble conventional compounds. Work in this area has already led to the first large-scale commercial application (100,000 tons annually) of the controlled-availability concept.

Advantages of Controlled Release

There are several potential advantages to controlling the release of nutrients to a crop. The relative merits of each vary according to the specific set of conditions being considered. These can generally be placed in three broad categories--labor saving, reduced fertilizer burn, and reduction in nutrient losses.

Saves Labor. Ideally, one application of fertilizer should last the crop for the entire season; however, under current conditions, and particularly in many of the high rainfall areas of the tropics, this is not possible. In many of the developing countries, crops such as rice, wheat, maize, sugarcane, and vegetables are being managed at a very intensive level--so much so that the current practice necessitates multiple applications of certain fertilizer nutrients. Nitrogen, for example, sometimes must be applied as many as three, four, and in some cases five times during the growth cycle.

Rising costs of agricultural labor, particularly in the labor-scarce countries of North America and Europe, and now to an increasing extent in Japan, Korea, and Taiwan have stimulated research in exploring ways to make most efficient use of a diminishing labor supply. To a varying extent, farmers in these areas are willing to pay the price for specialty fertilizers if they will extend the limited supply of labor. Thus, in areas where agricultural labor is scarce and cash returns for the crop high, and in situations where a single application of conventional fertilizer will not maintain optimum yields, there is a place for controlled-release fertilizers. The degree to which controlled-release fertilizers will be accepted will depend in part on the level they can economically substitute for labor.

Less Fertilizer Burn. Another advantage to controlled release, one that is probably more applicable to the developing rather than the developed countries, is that of reduced possibility of fertilizer burn. As cropping practices become more intensive and rates of application of fertilizer increase, there is always a possibility that soluble conventional sources of nitrogen may be placed too close to the seed or young plant, thus preventing germination or stunting seedling growth.

It is well known that urea and/or diammonium phosphate under certain conditions release free ammonia and, when in close proximity to the seed or plant, greatly restrict growth (5). Fertilizers having a high salt index can through their osmotic effect also hinder growth. Controlled-release fertilizers, either coated soluble materials or compounds which have a low solubility, do not pose these hazards. In general, these materials can be placed at high rates in close proximity with the seed or young plant with little or no deleterious effects. However, the real advantage gained from controlled release is dependent upon the level of mechnization in fertilizer application; in many countries, fertilizer burn problems have been minimized through effective placement (banding) with special equipment or by shifting the time of application to a stage when the crop is less sensitive. As a result, it appears these problems can be solved with existing technology; therefore, this reputed advantage for controlled-release fertilizers in some areas may be marginal.

Reduces Nutrient Losses Through Metered Release. A third advantage, one that agronomists, horticulturists, farmers, and fertilizer manufacturers alike have ascribed as the major reason for developing a controlled-release fertilizer, has been the ability to meter the release of nutrients, particularly

nitrogen, at rates corresponding very closely to the needs of the crop, thereby minimizing the exposure of nitrogen to losses through leaching, denitrification, or volatilization. This is extremely difficult to do, and to date, researchers have met with very limited success in this area. Nevertheless, the ultimate acceptance of controlled-release fertilizers is at least partially dependent upon whether the researchers achieve this goal. The following examples will illustrate the types of problems facing these researchers.

For many crops, the demand for the major portion of their nutrients, particularly nitrogen, occurs at a specific time during their life cycle. Crops such as rice, maize, and wheat are examples of this. They require very little nitrogen during the early stages; this, however, increases significantly somewhere between 30 and 60 days after emergence with major peaks of demand slightly before or during flowering and then diminishes thereafter (6, 7).

Under this type of demand curve, nitrogen needs for certain varieties of maize, rice, cotton, and lettuce can be as high as 3-4 kilograms of N per hectare per day. Work reported by Allen (8) and which appears in figures 1-5 suggests that demand curves for very high yielding crops place substantial demands on the system on a per day basis. Based on these earlier findings, it does not seem unreasonable to expect the daily demands for nitrogen by some of the new high-yielding varieties of rice, wheat, and maize to be double and triple those reported by Allen. Failure of the crop to absorb nitrogen at the required rate will result in a reduction in yield, provided other growing conditions are at or near optimum. Conversely, fertilizers applied to the soil must release nutrients rapidly enough to staisfy this peak period.

Some crops, such as many of the forages as well as sugarcane, (figure 5) have demand curves that although substantial in total do not have the intense peak demands as found in the case of rice or maize. The demands

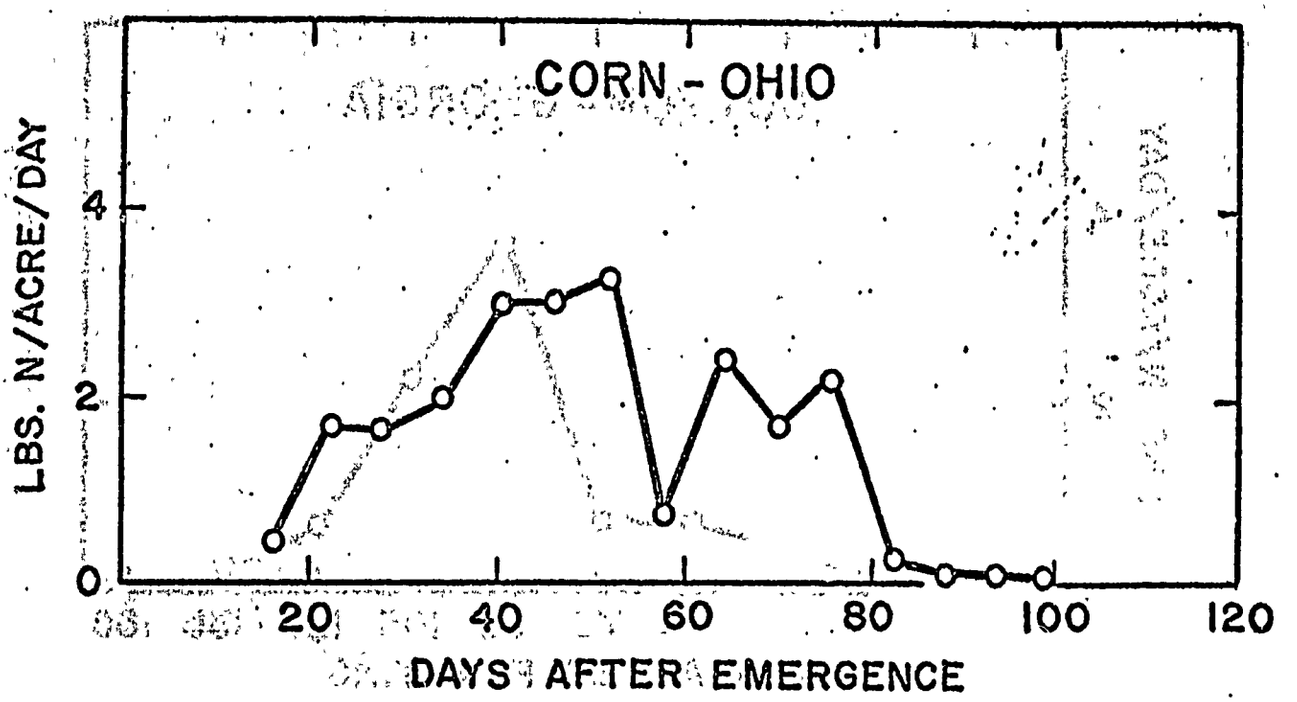


Figure 1. Nitrogen uptake rate by maize in Ohio (8)

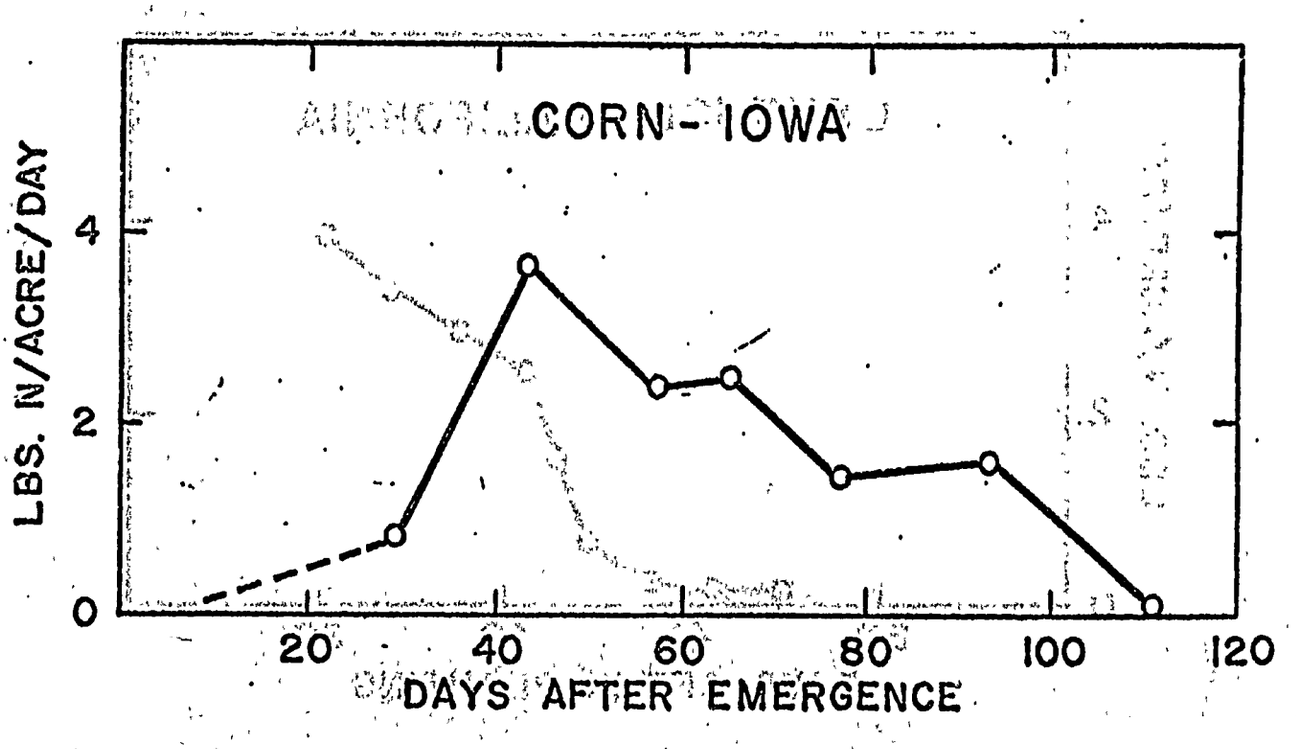


Figure 2. Nitrogen uptake rate by maize in Iowa (8)

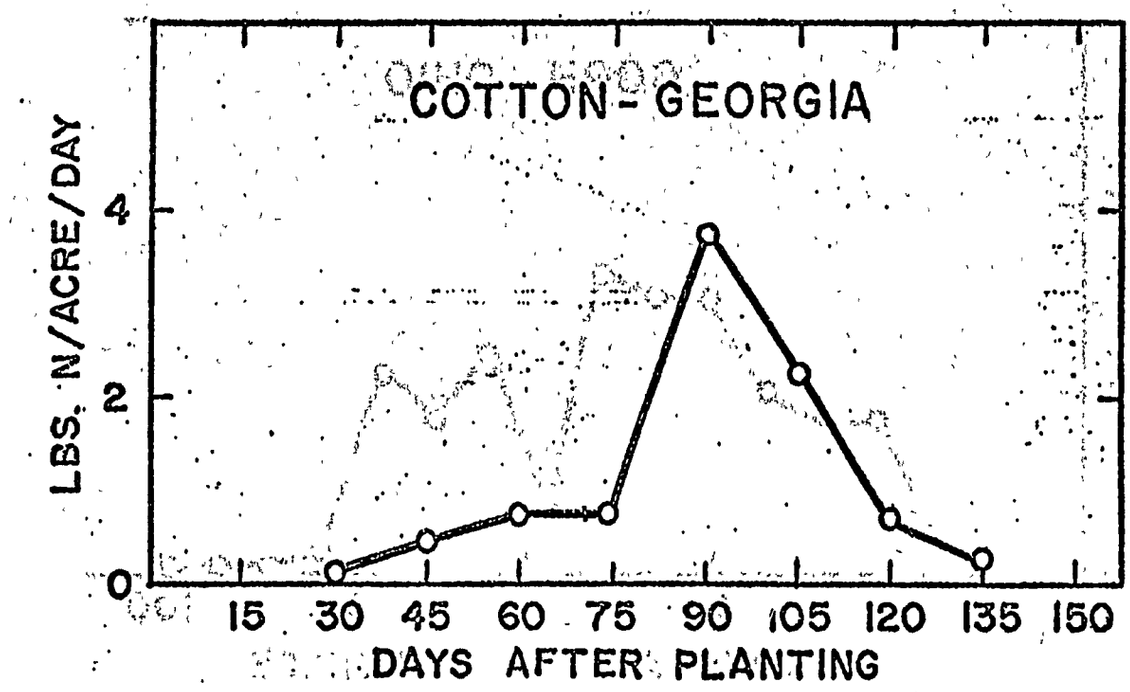


Figure 3. Nitrogen uptake rate by cotton in Georgia (8)

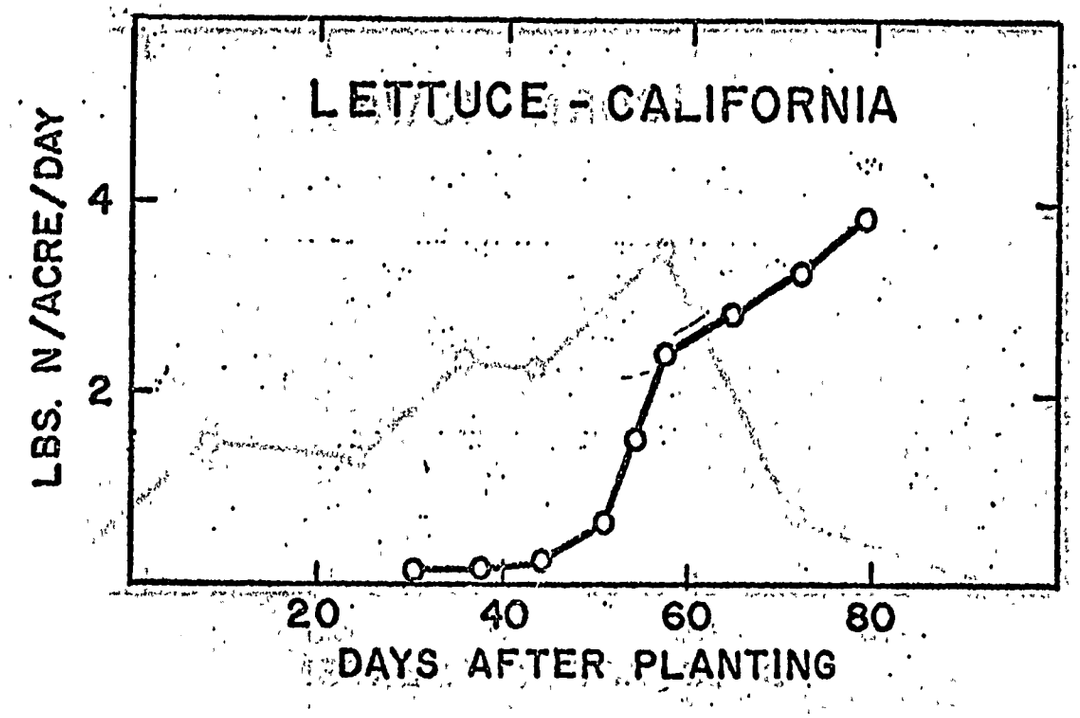


Figure 4. Nitrogen uptake rate by lettuce in California (8)

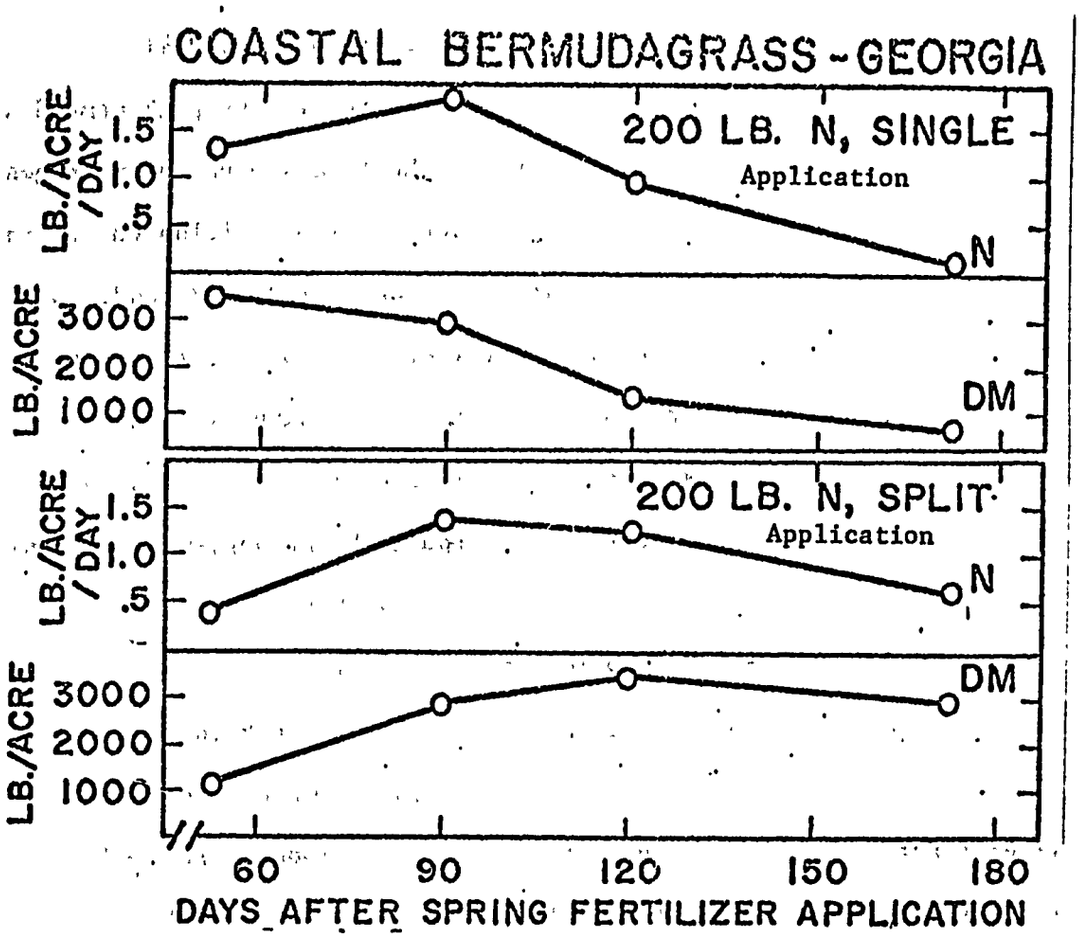


Figure 5. Nitrogen uptake rate by coastal bermudagrass in Georgia (8)

are less per day but more constant over the entire growing season. Thus a controlled release fertilizer for these crops must have a distinctly different release pattern. Under these conditions, the nitrogen needs of the crop can be satisfied by using a nitrogen compound having a low solubility; in the previous illustration, a different material is needed, preferably a highly-soluble nitrogen source coated with a material designed to release the majority of the soluble N at or slightly before the peak demand period.

The goal is not only to supply the total amount of nitrogen needed beyond that derived from the soil to produce maximum yields but to ensure that at no time, particularly during its peak period of demand, is growth limited by an inadequate supply of nutrient. Obviously, the release pattern must fit the demand curves for the crop, taking into account that derived from the soil. Excesses in available nitrogen must also be avoided because of possible exposure to loss through the mechanisms of leaching, volatilization, or denitrification--or luxury consumption resulting in increased incidence of disease--all of which reduce the efficiency by which the crop uses nitrogen. To achieve this goal is no simple task for the nitrogen demand curves even among crop varieties, for example rice (9), vary significantly. This is complicated further in flooded, reduced systems. It is one thing to develop a fertilizer that will release nutrients at a rate to meet nutrient demands for upland crops such as maize, wheat, cotton, etc. It is quite another thing to do this for rice grown in the flooded state (figure 6).

Proper placement of fertilizer within the flooded system is of extreme importance. As can be seen in figure 6, there are two distinct zones within the soil penetrated by the root system of a crop such as rice. These are: the thin, oxidized layer at the soil-water interface and usually a few centimeters deep (depending upon percolation of water through the profile) and a much deeper reduced layer.

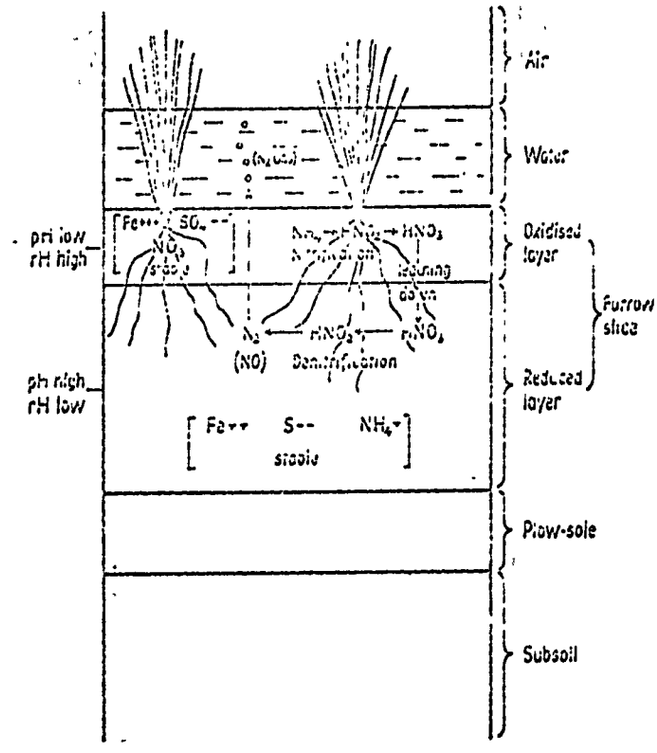
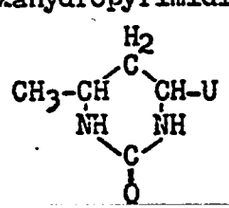
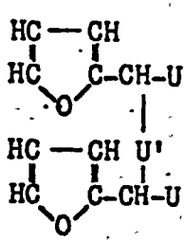
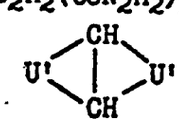


Figure 6. Diagrammatic representation of the soil profile under flooded conditions--showing the chemical changes involved, denitrification in particular.

Table 1. Slowly Available Organic Nitrogen Fertilizers (12)

Name	Materials	Chemical formula or composition	Nitrogen content (%)	Solubility in water
Ureaform*	Urea, formaldehyde	Mixtures of methylene ureas	ca. 40	
	Urea	NH_2CONH_2	46.65	100
	Methylene diurea	$U-CH_2-U$	42.41	2.18
	2 methylene 3 urea	$U-CH_2-U'-CH_2-U$	41.16	0.14
	3 methylene 4 urea	$U-CH_2-U'-CH_2-U'-CH_2-U$	40.56	0.01
	4 methylene 5 urea	$U-CH_2-U'-CH_2-U'-CH_2-U'-CH_2-U$	40.21	trace
Urea-Z	Urea, acetaldehyde	Mixtures of ethylene ureas	31-35	ca. 4
	Ethylene diurea	$U-C_2H_4-U$	38.34	
	2 ethylene 3 urea	$U-C_2H_4-U'-C_2H_4-U$	36.19	
CDU* (Cyclodiurea)	Urea, acetaldehyde	2 oxo- 4 methyl- 6 ureido hexahydropyrimidine 	32.54	0.12
IB*	Urea, isobutylaldehyde	Isobutylidene diurea $(CH_3)_2CH-CH(U)_2$	32.16	0.1-0.0
FU*	Urea, furfural	2 furfurilidene 3 urea 	24.99	hardly soluble
Guanylurea Sulfate	Lime nitrogen	$H_2N-C(=NH)-U \cdot 1/2\ H_2SO_4 \cdot 1/2\ H_2O$	34.99	easily soluble
Phosphate		$H_2N-C(=NH)-U \cdot H_3PO_4$	28.00 (35% as P_2O_5)	easily soluble
Glycoluril	Urea, glyoxal	$C_2H_2(CON_2H_2)_2$ 	39.42	hardly soluble
Oxamide		$(NH_2CO)_2$	31.81	0.02

* commercially available

U: NH_2CONH- (ureido group),

Ammonium nitrogen placed in the oxidized layer can be readily converted to nitrate, then leached into the reduced zone and lost to the atmosphere via the denitrification process.

The objective of most fertilizer programs for flooded soils is to apply ammonium nitrogen in the reduced zone where it is stable but still can be used by the rice plant. If nitrate is used, it must be applied in small amounts when the plant is actively feeding and can quickly use the nitrate nitrogen before it is leached to the reduced zone and subject to loss via denitrification.

Slow-Release Fertilizers and Their Properties

Many slowly-soluble nitrogen fertilizers have been developed. Some of the more common materials listed in table 1 have been reported by several researchers (10, 11, 12) to show promise. At present, the major drawback to these compounds is their high cost per unit of nitrogen. Even when in large-scale commercial production, all seem to have a cost of from two to four times greater than an equivalent amount of nitrogen from a conventional source, such as urea or ammonium sulfate. Nevertheless, several do show promise, and depending upon savings through a combination of high analysis and labor savings through minimizing the number of applications, they may soon achieve wide-scale acceptance, particularly for the labor-intensive crops such as rice, sugarcane and vegetables. Much of the work includes urea as the base material because of its high nitrogen content, east of reaction, and low cost per unit of nitrogen. Most of the slowly-available fertilizers are condensation products of urea and aldehydes.

Although many of these products may appear to be similar and have comparable reactions in a clearly-defined chemical system, their reaction in various soil systems and availability to plants are quite different and as yet not clearly described.

Ureaform (Urea-Formaldehyde). N content is variable but usually between 28% and 42% N. Ureaforms are a mixture of compounds, the composition of which is controlled by the mole ratio of urea to formaldehyde and the conditions of manufacture. Increasing the mole ratio increases the amount of water-soluble components. Decreasing the mole ratio increases the average molecular weight and amount of insoluble components. The most common ureaforms sold today generally have mole ratios of 1.25 to 1.4 (11) and a nitrogen content of about 38% of which two-thirds is water insoluble.

The water-insoluble N in these products must test not less than 40% active by the activity index which is defined as (13)

$$\text{Availability index} = \frac{\text{\% cold water insoluble N - \% hot water insoluble N}}{\text{\% cold water insoluble N}} \times 100$$

The methylene ureas constitute the insoluble portion of ureaform, and the agronomic value of the product is related directly to the amount and type of methylene urea in the product and the amount of unreacted urea.

Mono- and dimethyleneurea are usually considered to decompose too rapidly to be effective as a slow-release material, while tetramethyleneurea and higher members of this series were highly resistant to decomposition in soil. Trimethyleneurea appears generally the most effective single component. It is the major component in the hot water-insoluble, cold water-insoluble fraction of ureaforms (11). Japanese workers (14, 15, 16, 17) have concluded, on the basis of extensive laboratory and field tests, that dimethylenetriurea appears to have the greatest agronomic effectiveness. They conclude that the production of ureaform should be controlled so that this compound is the principal component. However, this is very difficult to do on a

commercial basis. Most ureaform fertilizers are made up of several types of methylene urea.

Particle size does not seem to affect the availability of the product. Decomposition is biological with some of the lag in nitrification rate due to the bactericidal effect of free formaldehyde commonly present in some of the ureaforms (11).

First developed in the United States for use on turf grasses and ornamental plants, ureaform has been tested on a number of crops with varying results. Extensive reviews by both Hauck (11) and Prasad (18) have shown ureaform as a good source of slow-release N for turf, ornamentals, potatoes, sugarbeets, and flax. It has been reported inferior to conventional sources of N for cotton, cucumbers, kohlrabi, cabbage, lettuce, tomatoes, wheat, and rice.

A single application of 300 pounds of N as ureaform was sufficient to satisfy the needs of three successive crops of maize and as effective as split doses of conventional applications (18).

CDU (2 oxo - 4 methyl - 6 ureido hexahydro-pyrimidine) other names--CD-urea, Crotodur, Floranid. Nitrogen content 32.5% except Floranid which has 28% N, 10% of which is as nitrate. CDU is prepared by acid catalysis of urea and acetaldehyde or crotonaldehyde yielding a ring-structured compound (11).

CDU was first prepared by the Germans but now is also commercially produced by the Japanese for use in compound fertilizers. Its slow-release pattern makes it suitable for use on grasses and to a much lesser extent annual crops. Japanese tests (12) have revealed CDU is of limited value on rice because release patterns under water-logged or reduced conditions are very slow--too slow to promote optimum growth of rice.

A major advantage for CDU as cited by Hauck (11) is its low but continuous rate of dissolution thus allowing application of large amounts

(up to 750 kg N/ha) without crop injury and its stability in manufacturing compound fertilizers. A disadvantage of CDU is that it is subject to leaching by irrigation (12).

CDU is degraded primarily through biological action; its solution and rate of degradation are related to particle size (19).

Urea-Z (Urea Acetaldehyde). Nitrogen content varies from 31%-38% of which about 15% is initially water-soluble and the remainder slowly soluble. Urea reacts with acetaldehyde to form ethylene diurea or that plus some unreacted urea.

The release rate for urea-Z is more rapid than most slowly-soluble N products. Decomposition is chemical and not greatly affected by temperature or particle size.

This material was first investigated by German research workers in 1956 and, although it has not been extensively field tested, does offer promise for crops grown on nonflooded upland soils. Urea-Z is not well suited as an N source for flooded rice (12).

IBDU (Isobutylidene diurea). Theoretical N content 32%, commercially 30%, has been developed in Japan and now manufactured on a commercial basis. It is used primarily as part of the nitrogen component in compound fertilizers. For a detailed review of IBDU, see Hamamoto (20).

The compound is a condensation product of urea and isobutyraldehyde; the rate of hydrolysis is relatively rapid even in neutral solutions (11), but is pH dependent (six times greater at pH 4 than 7).

Chemical hydrolysis is the prime means of degradation and can be effectively controlled on either upland or waterlogged soils by change in particle size and hardness of granule (20). The rate of mineralization of IBDU nitrogen is controlled substantially by its rate of dissolution.

The rate of mineralization of IBDU is not greatly influenced by changes in microbial flora (aerobic or anaerobic).

Several Japanese workers (11, 20) have demonstrated that IBDU can satisfactorily supply the N needs for flooded rice and for rice, small grain and vegetables grown on upland soils. Unfortunately in most of the situations where IBDU has been tested, the results are confounded by the presence of other nonstandardized amounts of N, P, and K. Under these conditions, the absolute contributions from each variable are not clear. Nevertheless, IBDU seems to be one of the more promising slow-release compounds.

Glycoluril (Acetylene Urea). Nitrogen content 39.4%, prepared from urea and glyoxal in presence of HCl (12); only slightly water soluble. Shows promise for use on forages. Decomposition is biological with major portion of release after a 3- to 4-week lag phase. This product is in the very early stages of development.

Guanylurea (Lime, nitrogen, sulfate, phosphate.) Nitrogen content 35%, made from calcium cyanamide in a lime-nitrogen matrix by direct acid treatment.

This compound and its properties have been known for at least 20 years. Because of the difficulty in producing a pure compound, its usefulness has been limited to compound fertilizers. Furthermore, cost of this form of nitrogen is quite high; thus commercial potential for this product is very limited.

The potential for this product is good should certain technological disadvantages be overcome. Prospects are particularly encouraging for use of this product on rice. Japanese workers (12) have found the decomposition of guanylurea occurs more rapidly in waterlogged soil than in upland soil; furthermore, there is little release during the first month after application.

This property is vastly different from other slowly-soluble nitrogen compounds discussed and more nearly approximates the needs of crops, such as rice, having specific peak demand periods.

The microorganisms which mineralize guanylurea are anaerobes; therefore, their activities are increased as the soil achieves a reduced state by flooding. Furthermore, guanylurea is strongly adsorbed onto clay particles. Therefore, it is relatively safe from leaching forces.

This easy attack by anaerobes and adsorption to soil particles will likely cause varied results depending upon the state of water control and type of soil (21).

The Japanese work has shown several factors that are involved in the mineralization of guanylurea in flooded conditions. These are: (a) mineralization proceeds faster when clay content is low or the major clay is of the 1:1 type, (b) mineralization is fastest in soils containing ferrous iron, (c) the stronger guanylurea is held by the soil, the slower is the rate of mineralization, and (d) mineralization is always accelerated by the addition of readily decomposable organic material, such as glucose. Based upon its sensitivity to redox potential, guanylurea will not be mineralized if placed in the thin oxidized layer at the soil-water interface of a flooded system (figure 6). This is a very important property since the oxidized layer of flooded soils subject to leaching is thicker than for soils where the percolation rate is much less. One might say guanylurea has a built in on-off switch that is controlled by the degree the soil is reduced.

Oxamide: Oxamide, 32% N, is a diamide of oxalic acid, has been widely studied but offers limited potential bacause of technological problems in production.

The properties of oxamide are similar to IBDU in that its release rate is governed by particle size. However, in contrast to IBDU, oxamide hydrolysis in soils is biological rather than chemical (11). Fine particles of oxamide nitrify faster than ammonium sulfate and similar to urea in acid soils (11). Oxamide of suitable particle size has proven to be effective as a source of N for maize, grass, rice, and barley (18, 22). Finely divided oxamide is similar to conventional nitrogen fertilizers as a source of N.

Difurfurylidene triureid. N content of 25%, very low water solubility, reaction products are urea and furfural. It has been manufactured commercially on a small scale in Japan. Production on large scale doesn't appear to be feasible at this time. Chemistry somewhat related to urea-Z. Relatively little done regarding agronomic potential of product (11).

Other Compounds. There are several groups of compounds under study most of which are either still in the developmental stage or, because of certain technological problems, lack commercial application.

Triazines (urea pyrolyzates)--Include cyanuric acid, ammelide, ammeline and melamine with corresponding N levels of 32.4%, 43.7%, 49.4%, and 66.5%, respectively. These products are now under study, but because of their very slow N release pattern seem to have potential primarily for grass, shrub, and tree crops (11). Little potential seems to exist for row crops and particularly rice.

Metal ammonium phosphates--(variable N and P levels). For a number of years, researchers in the United States have experimented with metal ammonium phosphates (Mg, Zn, Fe, Mn, Cu) as a nonburning fertilizer with a controlled rate of nitrification. Although effective as a source

of nutrients for lawns, ornamentals, and other specialty crops, metal ammonium phosphates have not shown particular potential for use on such annuals as rice, wheat, or maize (23, 24, 25). As a result, little research activity seems to be centered recently around these compounds.

Coated Fertilizers

The compounds discussed in the previous section all are relatively insoluble when compared to conventional fertilizers (the exceptions being finely-ground oxamide). Their availability is dependent upon a number of factors including microbial activity, soil pH, temperature, oxidative state of the system, etc. Because it is difficult to determine the real effect of each of these factors on the hydrolysis and mineralization of the compound, the release pattern of some of these materials has not always been predictable.

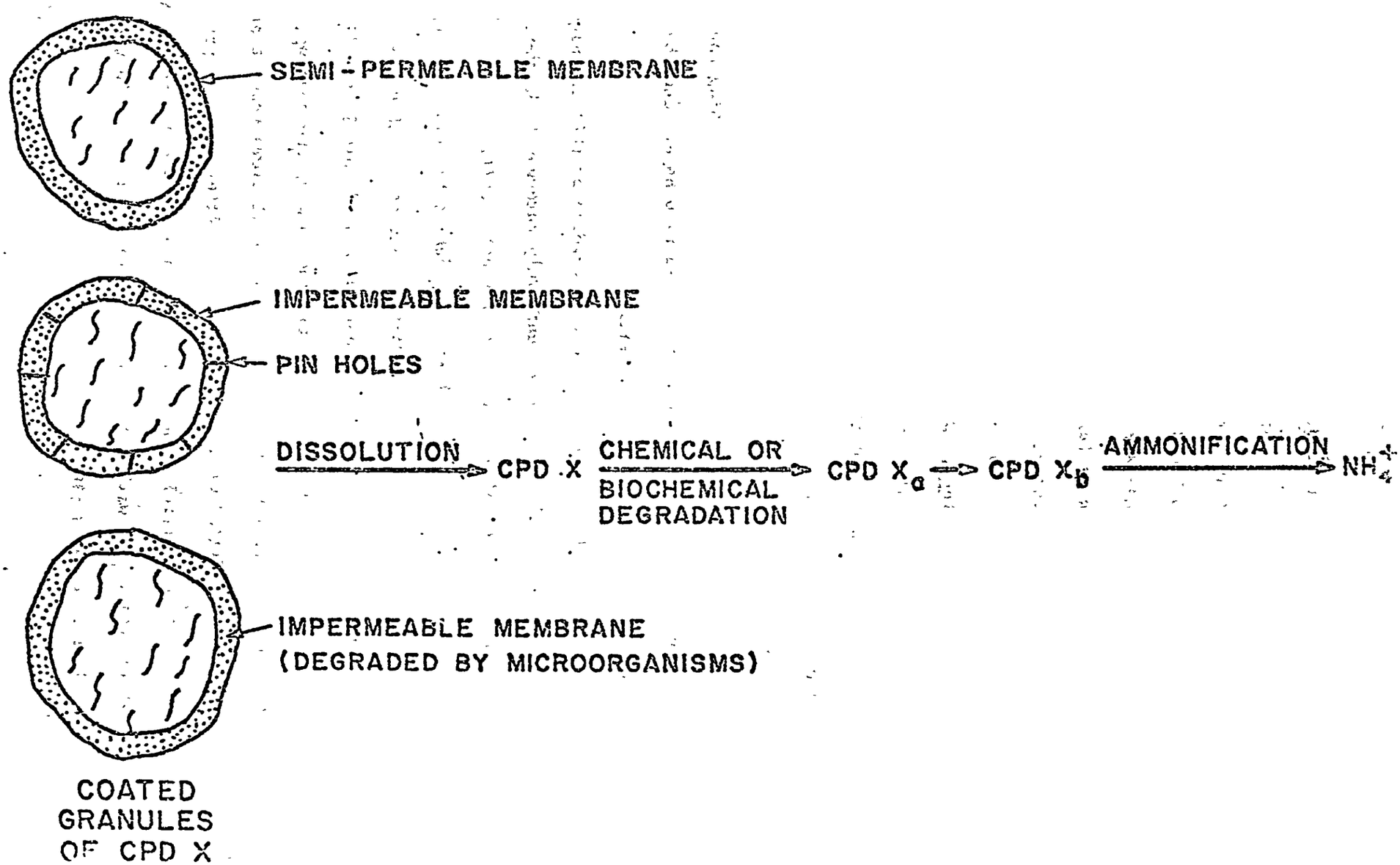
Because of these limitations, coating agents have become the focal point of some intensified research. Metered release has been accomplished with one or more of the three general type coatings (26) (figure 7).

1. Semi-Permeable Membrane--fertilizer is released when the membrane is ruptured following the increase in osmatic pressure which results from water moving across the membrane into the granule.
2. Discontinuous or Perforated Impermeable Membrane--tiny holes through the membrane coating provide the route of release for the fertilizer contained within.
3. The Solid Impermeable Membrane--this is a membrane such that it must be degraded by microorganisms prior to the release of the nutrient.

Materials investigated as coating agents include polyethylene, acrylic resins, vinyl acetate waxes, paraffin compounds, asphaltic mixtures, silicones, and sulfur (27).

Figure 7.

THE COATED GRANULE APPROACH (26)



Coatings (including encapsulation) have certain advantages for altering the physical characteristics of fertilizer compounds. More freedom is obtained in fertilizer formulation and micronutrients or secondary nutrients can be combined with primary nutrients. The major disadvantage of coated fertilizer appears to be in the manufacturing of the product. Coating uniformity around each fertilizer particle is often difficult to obtain in large tonnages. Coatings, although usually cheaper than slowly-soluble materials, are still quite costly.

Wax Coatings. Wax-coated fertilizers are manufactured by dispersing the nutrient material in molten wax, forming the dispersion into small particles in a mold, and allowing the particles to cool below the melting point of wax. The resulting particles are a dispersion of solid fertilizer particles in a solid wax. The water resistance of the fertilizer particles can be increased or decreased by increasing or decreasing the amount of wax employed. Increased water resistance can also be effected by dissolving certain additives in the molten wax.

One of the major problems in developing this technique is to adequately disperse the fertilizer granules uniformly throughout the wax. Nonuniformity and unpredictable release rates are the net result.

Polymer Coatings. Urea-Formaldehyde Solution Coatings, Multilayer Ureaform, Epoxy-Polyester Resin Coated Granules, Urethane, and many other combinations have been tried as coatings around soluble fertilizers with varying success. Whatever the nature and form of the coating, its effectiveness is probably determined by the rate at which it slows vapor transfer into the cavities filled with soluble material. After solution pressure builds up inside the particle, the rate of release is then dependent on the ability of the coating to withstand either rupture or excessive leakage through newly-formed pores (10).

An example of this can be drawn from work done by Ahmed and Attoe of the United States (28). The basic process is the encapsulation of fertilizer granules in polyethylene film. Although strictly speaking not a coating, the actual process is very similar to polymer-coated fertilizers, and the principles governing the release may apply to many of the coated fertilizers, whether wax, polymers, or sulfur. Ahmed (28) achieved controlled release of fertilizers by enclosing or encapsulating water-soluble fertilizers in a small capsule made of thin film, such as polyethylene film, which had several holes having diameters within the 0.05 mm to 2.0 mm range. He successfully grew high yields of maize and maintained satisfactory growth of turf with single applications of this product. He reported the release rate to be determined mainly by:

1. Number and size of holes per capsule.
2. Amount of moisture in the soil.
3. Solubility of fertilizer.
4. Weight of fertilizer in capsule.

This and other processes are being produced commercially but used mainly on specialty crops.

Archer Daniels-Midland Co. has developed a resin-coated urea product that is being sold commercially. It has been used successfully for turf and certain specialty crops.

<u>Sulfur Coatings:</u> Most of the coatings discussed thus far are either inert or are nutrients nonessential to crop growth. In all cases, this has materially increased the cost of the fertilizers.

A way to partially offset this has been to use coatings that have a multiple purpose. Recent research using sulfur as a coating has stemmed from such an interest. There are several reasons for interest in sulfur as a

coating for water-soluble fertilizer ingredients. Along with it providing a product of all-nutrient composition, the material can be applied conveniently as a melt and at a relatively low cost. This method of coating suffers from one serious disadvantage--it has been found that the sulfur coating is too porous and that the leaching rate is about the same as for uncoated fertilizer granules (10).

This problem has been corrected by a process developed by TVA (29) which produces an effective controlled-release urea fertilizer by using sulfur, a microcrystalline, soft wax sealant, and a microbicide. The porous nature of the sulfur coating has been apparently eliminated with a sealant that prevents rapid water transfer through the coating. The microbicide, pentachlorophenol or coal tar oil, acts as a retardant to sealant degradation and possibly sulfur transformation. The release rate of this product is controlled by varying the thickness of sulfur and wax coating and has proven effective in supplying nitrogen to forage crops in a single application (30) and for corn and sugarcane. Sulfur-coated urea (SCU) has also shown promise as a nitrogen source for upland rice or where intermittent flooding prevails. It has not proven superior to conventional sources for rice where water control is good. For a more detailed review of SCU, see Hauck (11).

Protected Availability

The second major approach used to achieve controlled availability is to keep the nutrient in a form which is readily available to the crop but which is protected from the physical, chemical, or biological forces involved in immobilizing the nutrient. Such a process can best be termed "protected availability."

Protected availability is commonly achieved in at least two ways. The more common are: (1) through the use of nitrification inhibitors and (2) through the use of organic chelates.

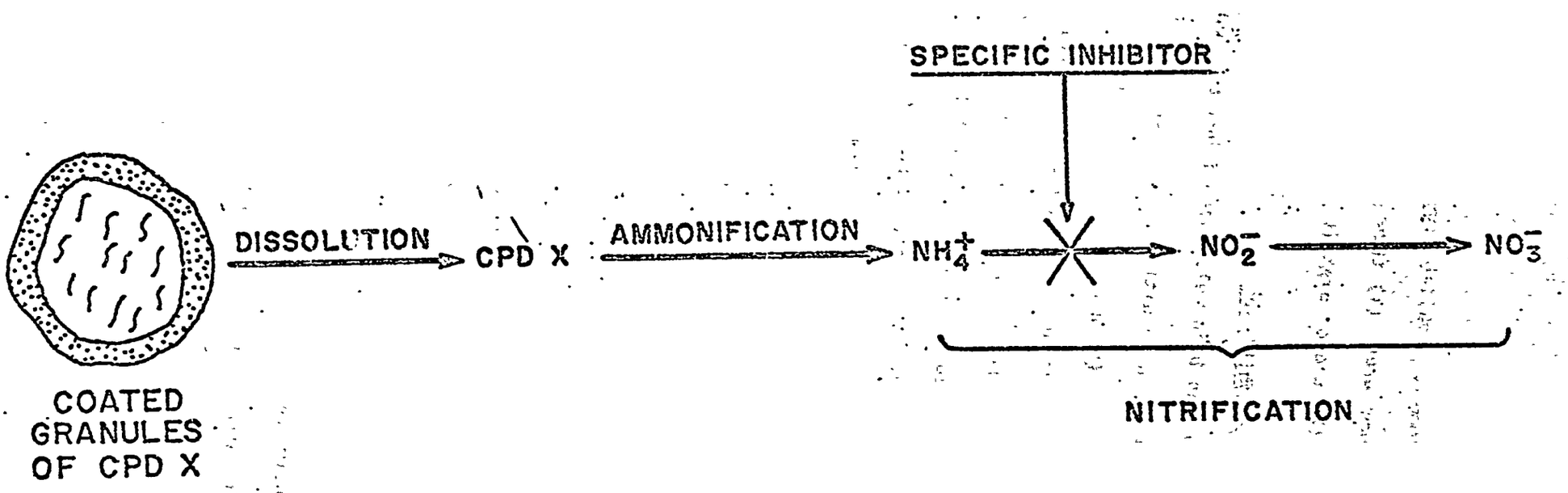
Nitrification Inhibitors

It has been well established that two of the principal mechanisms causing reduction in nitrogen efficiency by the crop are (a) losses due to leaching and (b) gaseous loss through denitrification. In both cases, the nitrogen must be in the nitrate form before these losses can occur. Since most plants can readily use ammonium nitrogen and since ammonium nitrogen is held effectively against leaching on the exchange sites of the clay and organic fractions, it has been shown that keeping the nitrogen in the ammonium form as long as possible before use by the crop will significantly reduce nitrogen losses. This has been accomplished by inhibiting the nitrification process. In almost all cases, the inhibitor blocks the conversion of ammonium nitrogen to nitrate by inhibiting Nitrosomonas growth or activity (figure 8).

There is considerable activity in trying to formulate compounds of this type. To be of practical value, they should effectively and specifically block the nitrification process, be sufficiently mobile to move with fertilizers in the soil solution, persist for a sufficient period of time to protect the ammonium nitrogen from conversion to nitrate until used by the crop, and finally, be nontoxic to the plant and sufficiently low in price to warrant their use. Most of the success to date has been in Japan and the United States. Some of the more promising compounds and their common names and developers have previously

Figure 8

THE COATED GRANULE - INHIBITOR APPROACH (26)



been reported by Hauck (11) and appear in table 2. Only those inhibitors currently available commercially or available for wide testing on an experimental basis will be discussed.

N-Serve 2 - chloro - 6 (trichloromethyl) pyridine. Developed in the United States and possibly the most widely tested of all nitrification inhibitors, N-Serve has proven to effectively control the nitrification process. The properties of this product and its use with anhydrous ammonia, urea and ammonium fertilizers have been described by Goring (31, 32). Reviews by Hauck (11) and Prasad (18, 33) have clearly described the value of N-Serve on various crops. N-Serve persists and is effective in the soil for periods of up to 6 weeks; however, numerous workers have shown the half-life of the compound to be about 15-25 days at 20° C. It is normally more effective when it is applied with banded fertilizers. Effective rates vary from 0.2%-2% of the ammonium nitrogen with the lower rate adequate only when the N is applied in a band.

N-Serve has significantly increased the yields of sugar beets, cotton, sweet maize, spinach, rice, and hybrid maize (11, 18, 33). Considerable loss of effectiveness occurs under field conditions when applied in a flooded system for growing rice. In general, cost of the material limits its use to specialty crops. Effectiveness declines as soil temperature increases.

Dicyandiamide. Sold commercially in Japan, the inhibitory effects of this compound have been clearly demonstrated and known for some time (12). The product is effective over a long period and effectively inhibits nitrification at all rates of nitrogen application (34). Concentrations of 5%-10% (of ammonium N) have been reported effective in restricting nitrification for up to 3 weeks. To maintain effectiveness, the rate of application should increase as organic content of the soil increases. Effectiveness declines with increase in soil temperature.

Table 2. Nitrification Inhibitors Under Test in Japan, 1969.[a]

Chemical	Common Name or Symbol	Developer
Thiourea	Thiourea, Tu	Nitto Ryuso
Dicyandiamide	Dd or Dicyan	Showa Denko
2-mercapto-benzothiazole	MBT	Onodo Chemical Industries
2-benzothiazole-sulfane-morpholine	KN or KNE	Nissan Chemical Industries
2-chloro-6-(trichloromethyl) pyridine	N-SERVE®	Dow Chemical Company (U. S.)
2-amino-4-chloro-6-methyl pyrimidine	AM	Mitsui Toatsu
sulfathiazole	ST	Mitsui Toatsu
2-amino-4-methyl-6-trichloro-methyl triazine	MAST	Mitsubishi Chemical Industries
2, 4-diamino-6-trichloromethlyl triazine	-	American Cyanamid (U. S.)
N-2, 5-dichlorophenyl succinamide	DCS	Sumitomo Chemical Industries
guanylthiourea	ASU	Nitto Chemical Industries
4-amino-1, 2, 4-triazole·HCl	ATC	Ishihara Industries
3-mercapto-1, 2, 4-triazole	MT	Nippon Gas Chemical Industries

[a] Compiled by Hauck (11) from information obtained through the courtesy of the Fertilizer Research Division, National Institute of Agricultural Science, Tokyo. Not included are several materials known only by their code numbers.

Cyanoguanidine. Another compound possessing inhibitory properties provided it is applied at from 5.5%-24% of the ammonium nitrogen present. It has effectively (12) increased the efficiency of N fertilizers applied to wheat as much as 50%. It seems to be most effective on organic or limestone soils which are high in soil nitrates and subject to heavy rainfall at low soil temperatures. It does not show outstanding potential under tropical conditions.

Thiourea. It is sold commercially in Japan and is considered both a slow-release source of N and also one that possesses nitrification inhibition characteristics. Japanese workers have reported thiourea as being effective for a period of up to 4 weeks at concentrations of 14% by weight of applied nitrogen. Often 6%-10% was sufficient for some soils (11). Concentrations above 28 ppm were injurious to barley seedlings. Effectiveness declines with increase in soil temperature.

AM 2 - amino - 4 - chloro - 6 - methyl pyrimidine. Developed by the Japanese, AM has proven to be one of the more popular nitrification inhibitors. Effective concentrations range from 1.5 to 3.5 ppm with 2 ppm the most common. Its average half-life is about 20 days (35) but ranges from 15 to 60 days depending upon the soil conditions and the concentration being tested (36). Increases in temperature greatly decrease the effectiveness of the inhibitor. Therefore, the potential for AM in much of the tropics is limited.

AM has effectively increased the yield of rice, maize, grasses, several types of vegetable crops, and barley.

AM is less volatile than N-Serve, the vapor pressure being 0.002 and 0.005 mm Hg, at 20° and 30° C, respectively. AM cannot be formulated with acid fertilizers such as triple superphosphate. It can, however, be safely formulated and stored with most other forms of fertilizer.

ST 2 - sulfanilamidothiazole (sulfathiazole). Developed by the same Japanese concern that produced AM, it is designed to overcome some of the problems with AM. ST can be mixed with acid fertilizers and can be readily formulated into compound fertilizers (37).

A relatively new compound, it has yet to be extensively field tested. However, preliminary tests show that ST does effectively increase the yield of rice, barley, and spinach (38). Tests are now under way to study this compound over a broader range of conditions. High temperatures reduce the effectiveness of ST.

Synthetic Chelates

One of the best and most successful examples of protected availability has been the development of the synthetic chelate for agricultural purposes. It is well known that when properly used synthetic chelates can keep the essential nutrient it contains in an available form protected from the fixation forces of the system to such an extent that it often is 5-10 times more effective in supplying the nutrient to the crop than a similar amount of a conventional inorganic source.

There are two properties that the chelate must have to achieve the success described above. First, the chelate must have a high resistance to soil microbial degradation, and second, it must also have a high degree of stability with respect to its associated micronutrient. (11)

The fact that researchers have been extremely successful in reaching this goal is illustrated by the large numbers of chelates sold for correcting micronutrient nutrient deficiencies. Some of the more successful are listed in table 3.

Table 3. Abbreviations of Compounds Used to Chelate Micronutrients (40)

Abbreviations	Chemical Names	Commercial Trade Names
EDTA*	Ethylenediamine tetraacetic acid	Sequestrene AA
NaFe EDTA	Mono sodium ferric ethylenediamine tetraacetate	Sequestrene NaFe
Na2Fe EDTA	Disodium ferric ethylenediamine tetraacetate	Versene Iron Chelate
Na2Zn EDTA & Na2Mn EDTA	Disodium zinc and disodium manganese chelates of EDTA	Sequestrene Na2Zn & Sequestrene Na2Mn
DTPA*	Diethylene triamine pentaacetic acid	Chel 330
NaFe DTPA	Mono sodium ferric diethylenetriamine pentaacetate	Sequestrene 330 Fe
HEEDTA*	Hydroxyethyl ethylene diaminetriacetic acid	Versenol (referred to also as EEDTA, HEDTA, and EDTA-OH)
NaFeHEEDTA	Mono sodium ferric hydroxyethylene diaminetriacetate	Versenol Iron Chelate Perma Green Iron 135
CDTA*	Cyclohexane trans 1,2-diamino tetraacetic acid	Chel 600
NaFe CDTA	Mono sodium ferric cyclohexane trans 1,2-diamino tetraacetate	Chel 600 NaFe (Experimental only)
EDDHA* or EHPG	Ethylenediamine (di(o-hydroxyphenyl-acetic acid)	Chel 138 or APCA
HFeEDDHA	Ferric chelate of EDDHA	Chel 138 HFe or Sequestrene 138
RA156 Fe	Ferric phenolic polyamino carboxylic acetate; derivative of Chel 138 HFe	Geigy (Experimental only)
DHEEDDA	Dihydroxyethyl ethylenediamine-diacetic acid	Versendiol
NTA	Nitrilotriacetic acid	
BAETA	Bis[(dicarboxymethyl)aminoethyl]-ether	
BASTA	Bis[(dicarboxymethyl)aminoethyl]-sulfide	
PP	A byproduct fraction of paper pulp	Rayplex

(Sequestrene and Chel are products of Geigy Chemical Company, New York; the Versenes of Dow Chemical Company, Midland, Michigan; Perma Green of Refined Products Corporation, Lyndhurst, New Jersey; Greenz 26 of Crown Zellerbach Corporation, Camas, Washington; NTA of Hampshire Chemical Company, Nashua, New Hampshire. Rayplex is a product of Rayonier Incorporated, Shelton, Washington.)

*The chelating agents are usually available from manufacturers as the pure acids or as sodium salts. The acid form is listed for the sake of simplicity.

For a complete review of this subject, the reader is referred to (39, 40). The purpose of introducing the subject in this paper is merely to provide chelates as another example of how scientists have achieved their goal in developing the controlled-nutrient-availability concept.

Application of the Controlled-Availability Concept in the Developing Countries

It should be clear from the discussions on controlled availability that considerable potential exists for farmers to apply this concept with telling effect in the not-too-distant future. There are obstacles however. Cost has to be listed as number one. With the exception of use on high-value crops (specialty crops), the cost, two to four times that of conventional fertilizer, makes this still too high especially in areas where labor is still quite plentiful.

The second problem, one that should be very clear, is one of knowing how to match the product with the daily nutrient demands of a cropping system. With the exception of Japan and to a lesser extent the United States and Europe, very little has been done to relate these products to specific cropping conditions. This work is just now getting under way in many of the tropical areas. In spite of these limitations, results thus far are promising. The following is the author's opinion as to products that seem to offer greatest potential.

Potential of Slow-Release Materials on Rice

Based upon the review conducted thus far, it would appear that the most comprehensive work done with slow-release materials on rice has been by the Japanese. In the past 4 years, they have extensively tested the following slow-release nitrogen materials: ureaform, isobutylidene diurea (IBDU),

crotonylidene diurea (CDU), guanylurea (GU), urea-acetaldehyde condensate (Urea-Z), difurfurylidene triureido (FU), glycoluril, oxamide, and several others of lesser potential. Based upon the results obtained during the intensive screening, they have concluded that only IBDU and guanylurea offer good potential as fertilizers for paddy rice.

Their tests also revealed that ureaform, CDU, and glycoluril have no potential for paddy rice as the release rate was too slow under the conditions found in Japan. Urea-Z showed promise; however, tests were so erratic, partly because of difficulty in producing a consistently reproducible product and partly for other reasons, that further testing for use on paddy has been abandoned. FU has been discarded because of the high cost of furfural, one of the raw materials for FU. Further testing of oxamide was dropped for a similar reason, it being that cyanide, the probable starting material for synthesis is in great demand elsewhere. It should be remembered, however, should the cost and supply of the base materials needed in the synthesis of FU and oxamide change, further testing should be initiated for they do offer considerable potential.

IBDU consistently provides a 5%-10% increase in yield over conventional sources of nitrogen as split applications. Usually the IBDU is added during seedbed preparation as a complete N-P-K 10-10-10 fertilizer, 5-8 mm granule size, with 80% of the nitrogen as the slow-release compound. It has been shown that IBDU can effectively eliminate at least one, and in some cases two, of the topdressings commonly provided rice. This coupled with its delayed release which prevents an often harmful early flush of growth leads the author to conclude that IBDU does have good potential for use on rice.

Results obtained thus far make guanylurea appear very promising for use on paddy. Properties which warrant this optimism are its relative unreactiveness while in oxidative systems and time lag of 3-4 weeks before rapid hydrolysis occurs in flooded (reduced systems). This product is held on a 2:1 clay complex more lightly than on a 1:1 type.

Sulfur-coated urea offers good potential for use on paddy rice, although some difficulty has been experienced in achieving the proper release rate where good water control exists. At present, SCU seems to offer slightly better potential for use on upland rice soils or rice cultures where intermittent flooding prevails.

Nitrification inhibitors, AM, ST, and N-Serve, all have demonstrated their capability to block the nitrification process. Unfortunately, this has been most effective in laboratory or pot cultures of rice. Under these conditions, water flow, hence leaching of nitrogen, has been more rapid than actually occurs in the field. This might explain the limited positive results with rice under flooded field conditions.

There are at least two reasons for this:

1. Many of the inhibitors are temperature sensitive, being less effective at 30° C than at 20° C.
2. The solubilities of some of the inhibitors differ greatly from that for ammonium, thus they move through the soil system at different rates.

Based upon these findings, we do not find it surprising to find very little evidence in the literature to show that nitrification inhibitors are effective on rice under the hot, humid conditions of the tropics. In spite of this, there are new families of inhibitors and slow-release and coated materials being developed. Numerous tests will be made of these

products. Table 4 lists where in the fertilization system some of the inhibitors and slow-release materials may be tested.

Other Applications of Controlled Availability

As pressures continue to mount on the agriculture of the developing world to produce more food and as stress is placed upon the need to diversify the individual diets of people, farming practices and systems will need to become more intense and at the same time more diversified.

Probably the best examples available anywhere in the world illustrating cropping systems that will utilize land intensely and still produce a wide variety of food are the multiple cropping systems of Taiwan (table 5). Under any one of the six systems described, the demand for fertilizers is very intense and by applying the relay-cropping concept, that of starting a new crop on the land before the last one is harvested, fertilizer demand can be very great and yet remain at a relatively constant level. It would seem that within one or more of these systems the controlled-availability concept is of utmost importance and that there is a place for slow release, coated or chelated fertilizers as well as nitrification inhibitors all within the same cropping sequence.

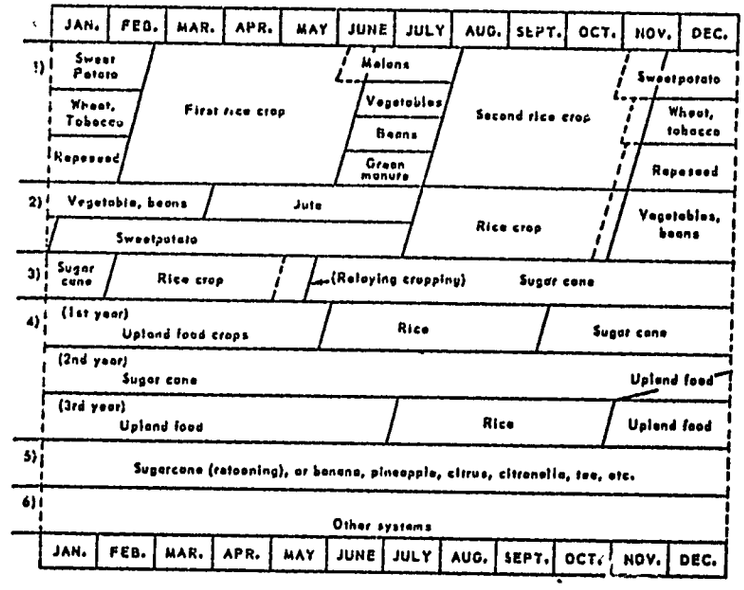
It is when agriculture becomes this intense and a major stress is placed on existing labor that controlled-release fertilizers in particular should come into their own. Possibly more emphasis should be placed upon satisfying the nutrient demands of the total cropping system and less on meeting the demand curve of an individual crop. Under the systems approach, there may be a sufficient number of exotic fertilizers already developed which if properly integrated into the total system will achieve the goal of controlled availability.

Table 4. Possible Methods[a] of Application for Nitrogen Fertilizer on Rice and Possible Uses for Slow-Release or Nitrification Inhibitors

Type of rice system	Parameter		
	Source	Time of application	Type of release rate
Upland rice	Urea, ammonium or nitrate forms	Some applied as basal (as urea or ammonium) with remainder applied as a topdressing (urea, ammonium or nitrate) according to moisture levels	Continuous slow release or coated as basal or topdressing (possible materials IBDU, SCU)
Continuous flooding	Urea or ammonium form preferred, green manure of limited value, nitrate form for late application only	Some applied as preplant, some or all applied as basal or evenly split as topdressing	Nitrification inhibition needed, i.e. SCU, AM, ST, or IBDU or various combinations. Modification in urea or ammonium form only if bulk applied as basal or some as preplant or basal. Guanylurea also of good potential.
Delayed flooding	Same as for continuous	None applied as preplant First application with permanent water. Topdress 2 or 3 times.	Slow release for preplant only. All others in conventional form. Guanylurea, SCU, IBDU, and/or AM and ST all good possibilities.
Intermittent	Same as for continuous	No preplant, very little basal, 2-3 times topdressing	Delayed release controlled by water situation (on-off) possibly SCU and IBDU of greatest potential
Deep water	Urea and ammonium form	Basal only, no topdress	Delayed and slow release. Guanylurea should be tested in this system.

[a]Not to be considered a recommendation.

Table 5. MULTIPLE CROPPING SYSTEMS IN TAIWAN



1) Three or four-crop-a-year system in double-cropping paddy land.
2) Two or three-crop-a-year system in single-cropping paddy land.
3) The sugarcane-rice relaying cropping system.
4) The sugarcane/rice/upland-food-crop rotational system.
5) The year-round-growing system of long-term crops.
6) Besides the above, there are still several other systems such as the six to seven-crop-a-year vegetable farm, and a newly developed 80-20% device for land use of rice-pasture farm--2 rice crops and pasture the rest of the year.

Much is known about how specific fertilizers react within a given environment. Hauck (11) has summarized what is known about certain slow-release nitrogen fertilizers and factors governing their release rate. Based upon his findings, there is no one fertilizer that can be used to achieve the goal of controlled availability. It appears that a combination of materials will have to be used depending upon the cropping and soil systems involved.

Thus, in the developing world, the farmer of the future may well achieve mastery over the food problem by drawing upon a family of fertilizers tailored to a specific multiple cropping system. This may be accomplished through a combination of controlled release fertilizers as a base and supplemented through the use of nitrification inhibitors, chelates, and conventional readily available sources.

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PART III
POSSIBLE EFFECTS OF NEW FERTILIZER TECHNOLOGY ON FUTURE PLANT NUTRITION PROBLEMS

There is no doubt that the trend is toward the use of more fertilizer and of higher analysis. This has been the trend in the United States and Europe for the past quarter of a century, for at least the past 10 years in Japan, and is now becoming an established pattern in many of the developing countries. Although this shift to high analysis in the past has been justified almost solely on the basis of economies generated through reduced transportation and handling costs of nitrogen, phosphate, and potash, these assumptions may not be so straightforward as once thought. This portion of the paper is designed to explore the long-term agronomic effects of using increasing amounts of high-analysis fertilizers.

Increased Nutrient Removal Through The Fertilizer HYV Package

The package approach involving high-yielding varieties and associated inputs has become the message drummed by many, including government and private researchers. They have stressed the importance of using more fertilizers, often of high analysis, to take maximum advantage of the capabilities of the HYV at a minimum cost per unit of primary nutrient. These savings have often generated additional money which could be used for the purchase of additional agricultural inputs.

Often economic analysis reveals that where a limited amount of money is available, it should be spent on nitrogen. The impact and justification of this have been described by Ressel et. al. (1). Their generalized response curves (figures 1-4) for rice, maize, and wheat indicate that the high-yielding varieties require substantially increased N applications.

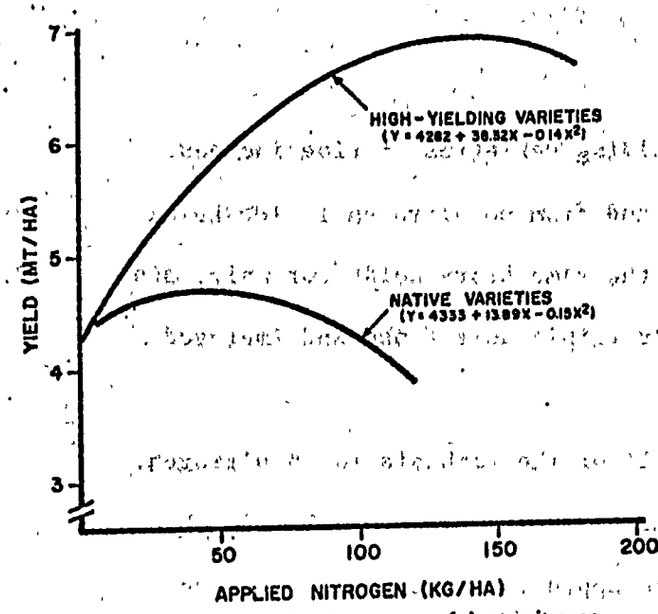

Figure 1. Generalized curve for the response of rice to nitrogen applications in the dry season (1)

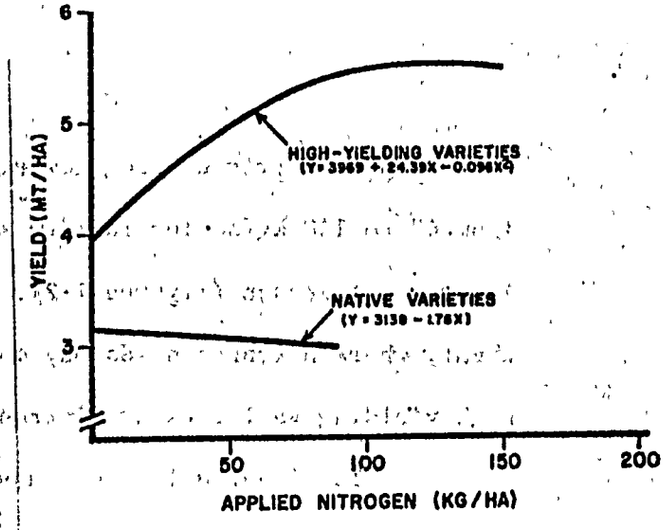

Figure 2. Generalized curve for the response of rice to nitrogen applications in the wet season. (1)

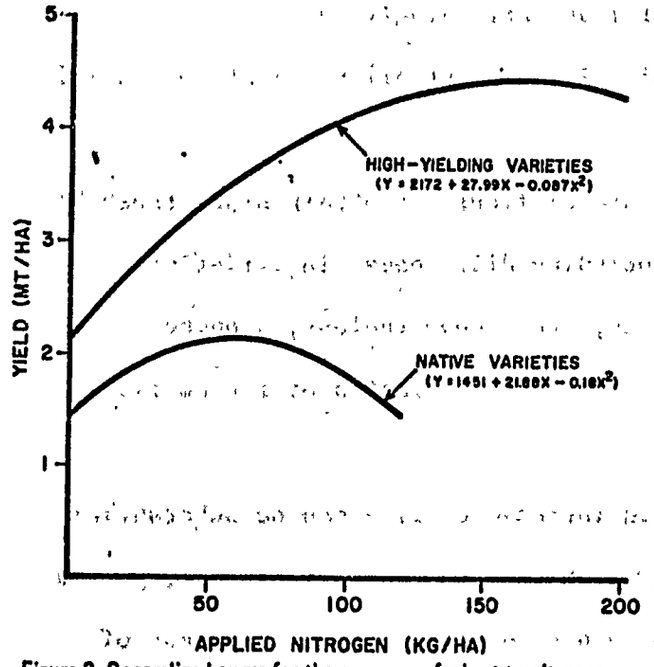

Figure 3. Generalized curve for the response of wheat to nitrogen applications. (1)

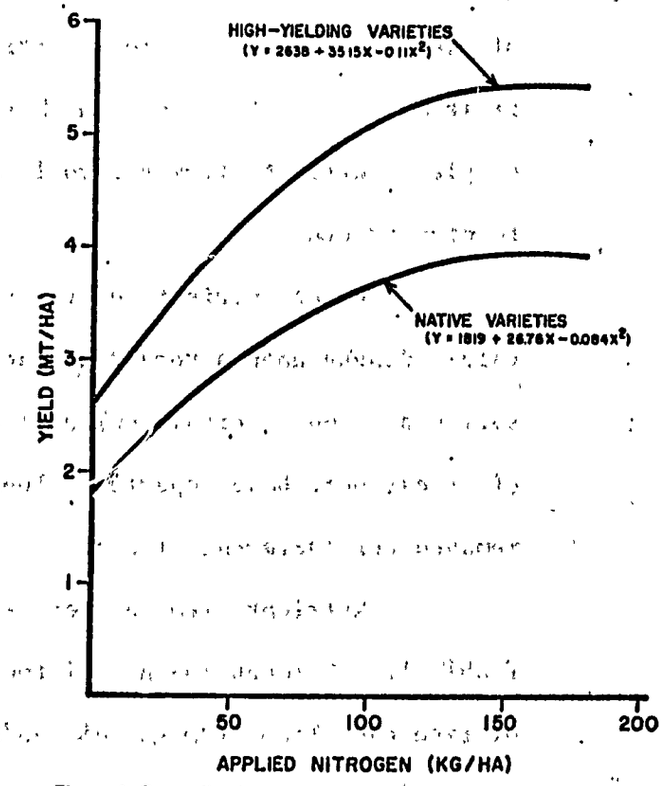

Figure 4. Generalized curve for the response of maize to nitrogen applications (1)

For example, nitrogen needs for high-yielding varieties of rice increase from 40 to 140 kg/ha for the dry season and from no nitrogen to 100 kg/ha for the wet season (figures 1-2). Much the same story holds for maize and wheat, where nitrogen needs may double or triple as the new and improved high-yielding varieties are introduced.

In almost all cases, most or all of the emphasis is on nitrogen. There is no question that where very limited monies are available <u>in the short run</u> this may be the most profitable approach. The positive effect of the high-yielding variety fertilizer package is increased yield. However, it is not without a price. High yields remove increasingly large amounts of plant nutrients from the soil, not only nitrogen but all nutrients essential to crop growth.

Exact nutrient removal figures are difficult to obtain since these values depend upon a number of factors including differences in varieties, soil conditions, certain cultural practices, etc. Nevertheless, a number of researchers have reported values and established estimates of the nutrients removed per increment of crop.

Nutrients removed per metric ton increase of rice can be substantial (table 1). Through the use of the proper high-yielding variety package, yields of rice can climb from the 4½ ton/ha base achieved with proper management of the native varieties to 7 tons or more if favorable weather conditions prevail and the new package is employed (figure 1). This represents a removal of an additional 34 kg/ha of N (rough rice only). However, this is adequately replenished by the additional nitrogen that is recommended for use with the package, but almost 13.2 kg of P_2O_5, 6.8 kg of K_2O, 2.6 of Mg, and 2 kg of S are also removed with the additional 2.5 metric tons of rice produced as a result of the high-yielding variety package. Nutrient removals become even greater when the straw portions of the crop are removed.

Table 1. Kilograms of Plant Nutrients Removed by Various Crops (2)

Crops harvested and portion used for analysis	Increment	Primary plant nutrients			Secondary plant nutrients			Micronutrients				
		N	P_2O_5	K_2O	Ca	Mg	S	B	Cu	Fe	Mn	Zn
Maize												
Grain	1,000 kg	13.1	5.1	3.8	1.4	2.1	1.3	0.011	0.006	0.014	0.009	0.014
Stover	1,000 kg	12.2	4.0	16.0	3.0	2.0	1.2	.005	.005	.010	.17	.030
Wheat												
Grain	1,000 kg	20.8	10.5	6.4	.55	2.5	1.4	.017	.014	.120	.040	.060
Straw	1,000 kg	6.7	1.8	11.8	2.0	1.1	1.8	.040	.040	.43	.05	.018
Rice												
Rough grain	1,000 kg	13.3	5.3	2.7	.89	1.10	.89	-	.002	-	.020	.020
Straw	1,000 kg	6.0	2.0	13.3	1.91	1.0	-	-	-	-	.30	-
Sorghum												
Grain	1,000 kg	16.1	8.9	5.0	1.0	1.11	1.11	-	-	-	.01	.01
Straw	1,000 kg	14.1	4.1	20.8	4.8	3.1	-	-	-	-	-	-

Granted, some of these nutrients return to the soil, often as night soil or other organic residue. Then too, fresh amounts are released from the soil during its normal weathering processes. In spite of all these sources of additions, there is a net loss of nutrients in many of the fertilizer programs now being practiced in the developing countries.

Researchers and policymakers alike have recognized this potential problem. They already have or are in the process of responding by offering a more balanced fertilizer program, first with N-P and now in many areas N-P-K recommendations.

In many cases, this may prove to be adequate, particularly under the levels of management employed. However, in too many cases, little or no attention is directed beyond N-P-K to the total nutrient needs of the crop. The question should be asked: Is the supply of secondary and micronutrients adequate to sustain the continued pressure from the HYV package?

Increased Awareness for Sulfur Needs

As new and higher-analysis fertilizers are introduced, they invariably are higher in content of in nitrogen, phosphorus, or potassium--and by necessity are lower in other elements, some of which are essential to plant growth.

Sulfur is probably the first plant nutrient to be influenced by this shift to high analysis. With decline in popularity of ammonium sulfate and ordinary superphosphate, each containing significant amounts of sulfur (ammonium sulfate--23% S, ordinary superphosphate--12% S) and their eventual replacement by such non- or low-sulfur products as ammonium nitrate, urea, anhydrous ammonia, triple superphosphate, or ammoniated phosphates, it is merely a matter of time before a major sulfur problem occurs in many areas

of the developing world. This will happen unless a major effort is made to identify potential problem areas and add the additional sulfur where needed to sustain plant growth.

Widespread sulfur shortages in some of the developed countries where high-analysis fertilizers are widely used have been slow in coming for a number of reasons. This is true partly because researchers were quick to recognize the possible deleterious side effects of using high-analysis phosphates and nitrogenous products low in sulfur. In many cases, such as in the southeastern United States, laws were enacted necessitating all phosphate and mixed fertilizers sold to contain a minimal amount of sulfur. Then too, the side effects that might have been felt as a result of the shift to high-analysis fertilizers were minimized by the sulfur returned from the atmosphere to the soil in rainwater from accumulations in the air as a result of industrial activity. The impact of low-sulfur high-analysis fertilizers was also minimized because of the large amounts added to the soil in years past via ammonium sulfate, ordinary superphosphate, etc. Finally, this impact was also minimized because much byproduct ammonium sulfate and spent sulfuric acid and other sulfur-containing products from other industries has found its way regularly into agriculture and the fertilizer industry. It must be remembered that in the developed countries these shifts occurred rather slowly, over many years, and were associated with gradually developing industries.

This is not the case in the developing world. New fertilizer technology has been quickly transferred to the LDCs. Associated industry of the type that generated other sources of sulfur is not developing at an equivalent rate; thus the indirect contributions they made through adding sulfur via the air, spent sulfuric acid, etc., are probably not significant factors.

The potential problem of sulfur is recognized by many. The solutions are available provided certain attitudes are changed. The author feels that the value of ammonium sulfate and ordinary superphosphate should be reappraised. The definition of high-analysis fertilizers should be broadene beyond N-P-K and include sulfur, at least where sulfur is potentially limiting crop growth.

Effects of Increased Fertilizer Use on Nutrient Balance

Increased fertilizer use, particularly in high-yielding varieties, will increase yield and profit to the farmer; excessive use can also cause problems of nutritional imbalance. There are three major areas in nutrient balance that should be of concern as new fertilizer technology is introduced. These are: phosphorus-zinc (P/Zn) balance in the plant, potassium-magnesium (K/Mg) balance, and finally, the long-term effect of large amounts of acid-forming nitrogen fertilizers on soil pH.

P/Zn Balance

As new high-analysis phosphate fertilizers are introduced and used at increasing rates per acre, the incidence of zinc deficiency on certain crops and soils increases (3, 4). Although this occurs most frequently on soils inherently low in available zinc and can frequently be explained by increased demand for zinc by high-yielding crops, there is ample evidence that large amounts of phosphorus can interfere directly with the ability of the plant to utilize zinc (5).

Numerous researchers have reported that an inverse relationship exists between concentrations of phosphorus and zinc in the tissue of corn, sorghum, soybeans, and potatoes (figure 5). This type of interaction exists

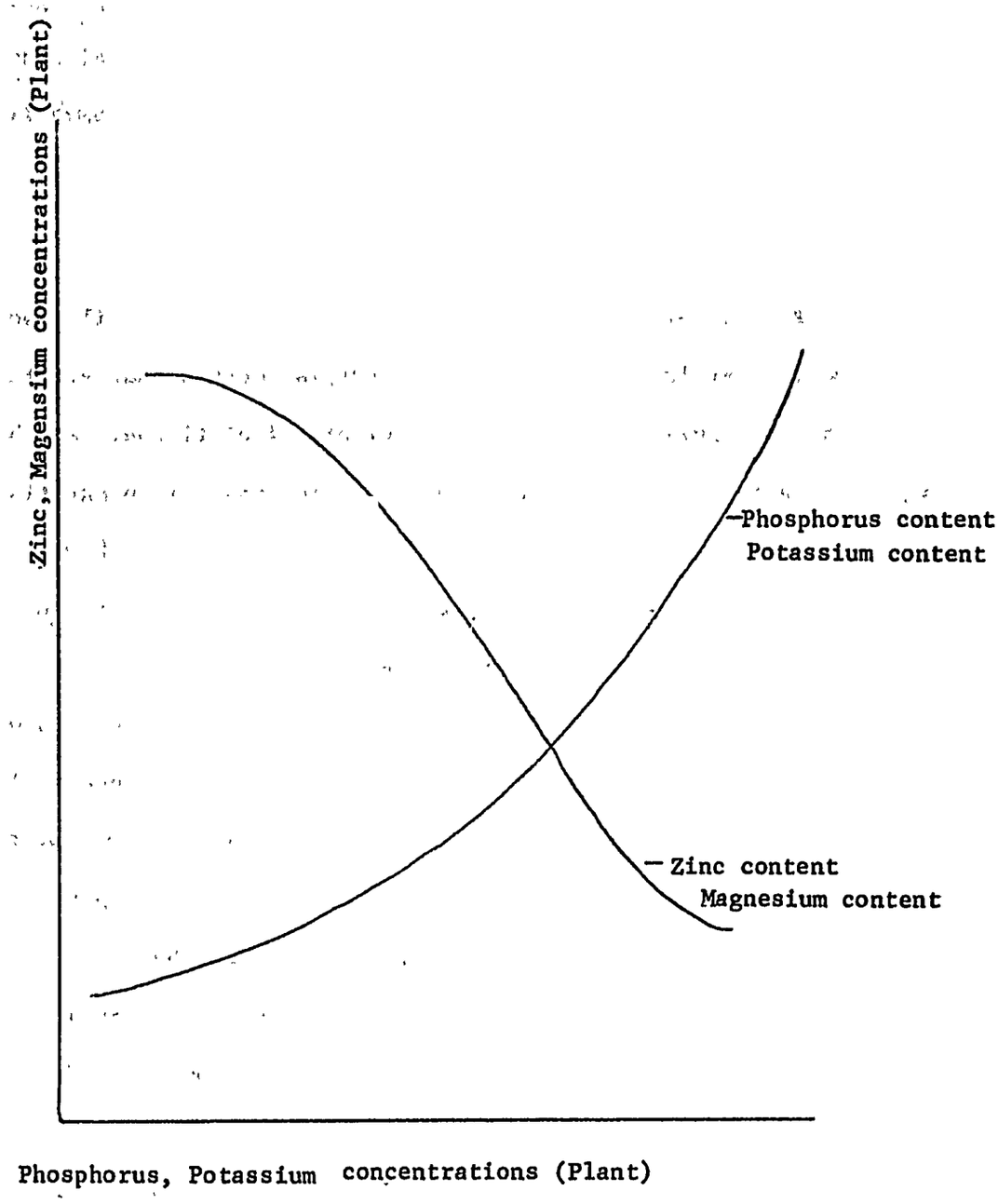

Figure 5. Generalized Effect of P/Zn and K/Mg Balances on Concentrations in Tissue (Corn, Soybeans, Potatoes)

not only in situations where availability of both zinc and phosphorus are marginal but in situations where zinc is adequate under conditions of normal phosphorus availability. In the latter situation, zinc becomes limiting only because soil and plant phosphorus becomes excessively high.

K/Mg Balance

A less serious problem but one that eventually will develop as potassium use levels increase is the interrelationship that exists between potassium and magnesium concentrations within plant tissue. As shown in figure 5, as the concentration of potassium increases in plant tissue, the concentration of magnesium declines (6, 7, 8). Soils that have a high exchange capacity and a reasonable level of exchangeable magnesium are less sensitive to this than soils having a low exchange capacity.

Although potassium use is at a relatively low level in most of the developing countries, its use will increase. When this happens, in some instances, efficient use of the additional potassium will not be possible unless magnesium is also added. In other cases, excessive use of potassium may cause a magnesium deficiency in the manner just described.

Investigators must be aware of these relationships and establish fertilizer programs based upon sound plant and soil analysis data from specific areas

Effects of Continued Use of Large Amounts of N on Soil Acidity

Numerous researchers have expressed concern about the effect high rates of nitrogen, particularly ammonium sulfate and ammonia have on soil pH (9). This is of particular concern on the acid sulfide rice soils where high sulfide levels can and do limit production of rice and other crops. The relative acidifying effect of various nitrogen fertilizers

appears in table 2. Since the effect on soil pH can be considerable, particularly over several years, researchers must work on a solution to this potentially serious problem.

Although acidity in the plow layer can be easily handled by an adequate liming program, it is much more difficult to correct subsoil acidity. Thus, nonacidifying fertilizers may be in more demand under conditions of high fertilization.

Clearly, new fertilizer technology will have a definite impact on future agronomic practices, not all of which are clearly understood at this time.

Table 2. Equivalent Acidity and Basicity of Nitrogenous Fertilizer Materials (9)

Material	% Nitrogen	Lbs. of pure lime; official method for neutralizing fertilizers		
		Per lb of nitrogen	Per 20 lb of nitrogen	Per 100 lb of material
Sulfate of ammonia	20.5	5.35	107	110
Ammo-phos A	11.0	5.00	100	55
Urea	46.6	1.80	36	84
Anhydrous ammonia	82.2	1.80	36	148
Calcium nitrate	15.0	1.35B	27B	20B
Potassium nitrate	13.0	2.00B	40B	26B

B = lime in excess of that required to make neutral salts or neutral fertilizers

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PART IV
THE FUTURE OF BULK BLENDS IN THE DEVELOPING COUNTRIES

The fertilizer industry in much of the developing world is young, formative, and still going through a very rapid, dynamic period of change. As a result, the true character of the industry in many of these developing countries has yet to be established. Fertilizer corporation executives are keenly aware of this and recognize the importance of correctly anticipating the true nature of the market at least 7-10 years in advance. Errors in judgement on their part can result in the committing of large sums of scarce foreign exchange to the building of production, transportation, and marketing systems that may be either obsolete or too sophisticated to effectively service the current needs of the market. There are many decisions facing these executives; however, in recent months, one seems to be receiving major attention. It is: the establishment of true potential for bulk blend fertilizer in the developing countries. Answering this implied question is very fundamental to determining the face of the fertilizer industry in a particular developing country. This portion of the paper is designed to examine the conditions which favored the growth of bulk blends in the United States, suggest which conditions may apply to the developing world, indicate areas of potential, and indicate problems that might be expected where bulk blending is practiced.

Conditions Which Influence the Development of a Bulk Blend Industry

To fully understand the future of bulk blending in a LDC (less developed country), it should be helpful to first analyze the history of this practice in the United States, particularly the circumstances involved in its outstanding acceptance.

It is generally agreed that there is no single clear cut set of circumstances that accounted for the success of bulk blending in the United States. Rather, a multiple set of conditions, each interrelated with the others, prevailed during the early stages of development and apparently accounted for the toehold and eventual establishment of bulk blends in a well-established market. Subsequent growth of bulk blends has been so rapid in the United States that in 1969 it accounted for at least 30% of all of the mixed fertilizer sold (1).

The conditions which prevailed during the early beginning and most commonly cited as responsible for the success of bulk blending in the United States are:

1. Scarcity of labor at the farm level and desire to offset this problem through mechanization.
2. Failure of the existing fertilizer marketing system to try to solve the scarcity of labor problem for the farmer.
3. The existence of large farms (200-500 acres)--often with flat, regular-shaped fields in a centrally-located area--readily conducive to mechanization.
4. The rapidly increasing demand for fertilizer both in total and on a per acre basis and at a rate more rapid than could be <u>efficiently</u> serviced by the existing marketing system.
5. The complacent attitude by a portion of the existing industry, which was characterized by having the questionable concept that chemically-combined fertilizers were superior to bulk blends.
6. The availability of a competent, agressive sales force eager to accept a new approach to selling fertilizers, an approach that would provide a sales edge in effectively penetrating the territories of the established fertilizer industry.

The development of a prescription concept of fertilization on a per field basis primarily through soil testing, which was strongly promoted by the most effective force in fertilizer education at that time--the land grant colleges.

8. The existence of a well-developed transportation system sensitive to the changing needs of the total transport market.

9. The location of a fertilizer market having the characteristics described in 1-7 and at a great distance from the source of supply thus placing major importance on the need to cut transportation costs through the use of high-analysis fertilizers.

10. The rapid development of new capacity capable of producing single or multiple component high-analysis fertilizers at low per unit cost but at a rate of production that exceeded the amount that could be consumed by its captive retail system.

There are other conditions that may have been conducive to the development of bulk blending in the United States, but most agree that those listed above were prime factors. Let's look specifically as to how these were applied in the United States.

Bulk Blending in the United States

Bulk blending as it is known today probably began in the central United States (2), the heart of the Corn Belt, an area which is characterized by large, uniform fields and farms 200-500 acres in size. Furthermore, this market is situated some distance from the basic production points (conditions 3, 9). During the late 1940s and early 1950s, the corn and soybean farmers were faced with a serious labor shortage, were in the early stages of what was to become a very severe cost-price squeeze, and as a result began to rapidly mechanize their operations in an effort to make more efficient use of labor

(condition 1). Prior to this period, they had applied most of their fertilizer to the crop through the planter at time of planting. As rates of application increased (condition 4), it slowed their planting operation sufficiently to warrant investigation of alternate means of applying fertilizer. Then, too, the high rates placed in a band near the seed afforded an undue hazard to the germination of the crop.

Also during this period, much of the fertilizer industry was very product oriented. Promotion programs for a particular company were geared around proving that somehow their product was superior to any other on the market. Little or no attempt was made at that time to gear fertilizer use of a product to an entire crop production system. As a result, a multitude of grades and ratios began to develop, each designed to provide some degree of product distinction, and all too often failing to satisfy the needs of a growing number of farmers. Grades became very numerous. This coupled with a wholesale, dealer marketing system insensitive to the needs of the farmer led to rather excessive costs of selling fertilizers (condition 2). Thus, the farmer was actively looking for more efficient ways of applying fertilizers.

New developments in soil testing and prescription fertilizer recommendations by the college, which included recommendations of preplant (broadcast and plowdown) applications of fertilizer, set the stage for the farmer to want bulk spread and eventually a bulk blend service. During the early stages of development of bulk blends, the major portion of the fertilizer was sold in bags. Little or no fertilizer was sold to the farmer in bulk. The only fertilizers or soil amendments sold in bulk were rock phosphate and limestone. Because of the scarcity of labor during and right after World War II, much of the spreading of limestone and rock phosphate

Table 1.

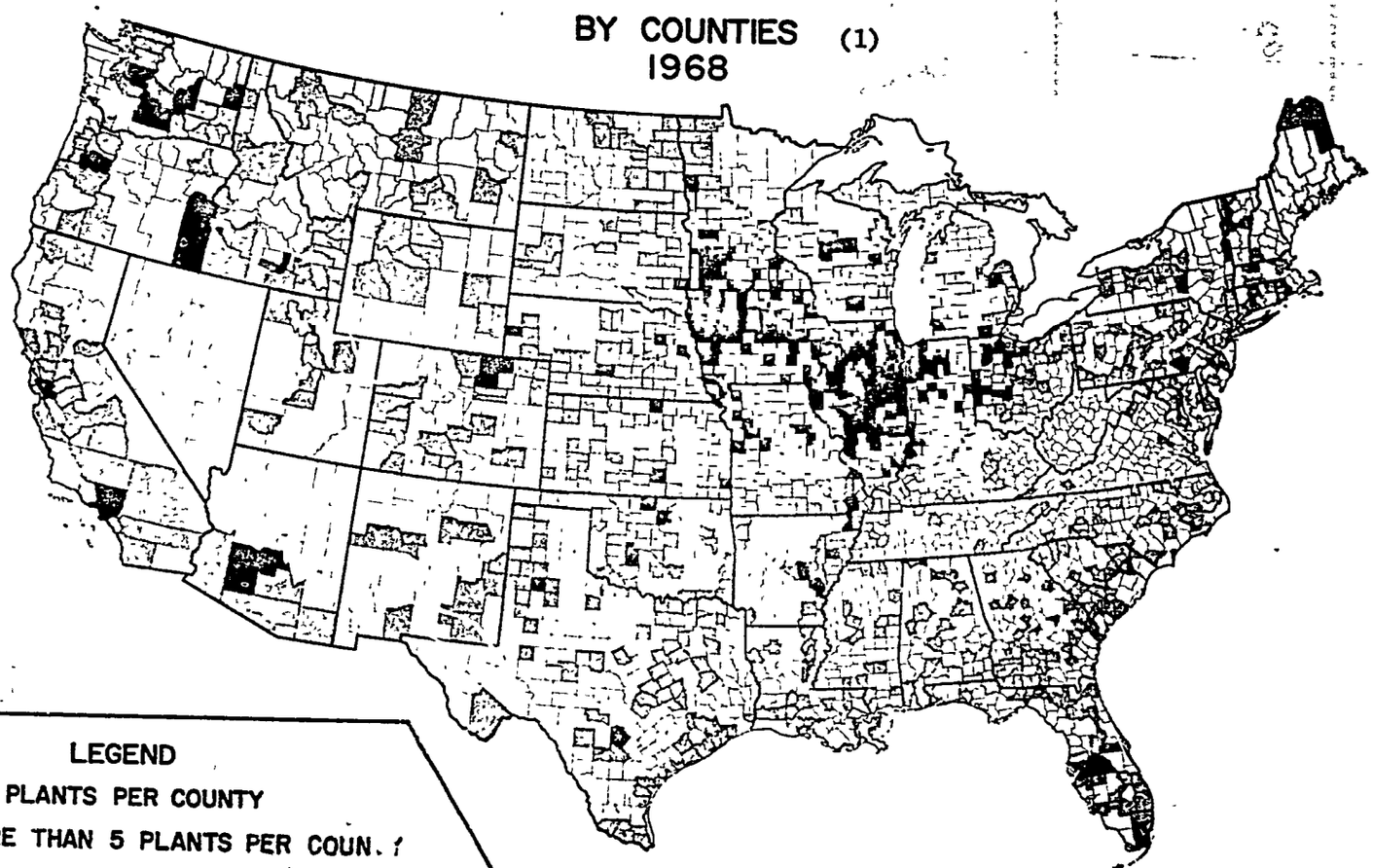
Estimated Number of Bulk Blend and Liquid Mixed Fertilizer Plants in the United States 1959-68 (1)

Region	Bulk blend				Liquid mix			
	1959	1964	1966	1968	1959	1964	1966	1968
New England	0	0	21	28	2	2	8	18
Middle Atlantic	1	25	137	125	15	21	26	24
South Atlantic	1	34	255	204	12	37	68	126
East, North Central	103	515	900	1,360	104	190	339	394
East, South Central	3	39	107	139	8	35	35	50
West, North Central	83	708	1,110	1,554	59	201	375	626
West, South Central	0	65	254	325	26	56	125	173
Mountain	3	88	191	220	16	38	72	100
Pacific	4	59	174	181	90	134	181	214
Hawaii	3	3	4	4	3	3	2	2
TOTAL United States	201	1,536	3,153	4,140	335	717	1,231	1,727

Figure 1. BULK BLEND FERTILIZER PLANTS IN THE UNITED STATES

BY COUNTIES (1)

1968

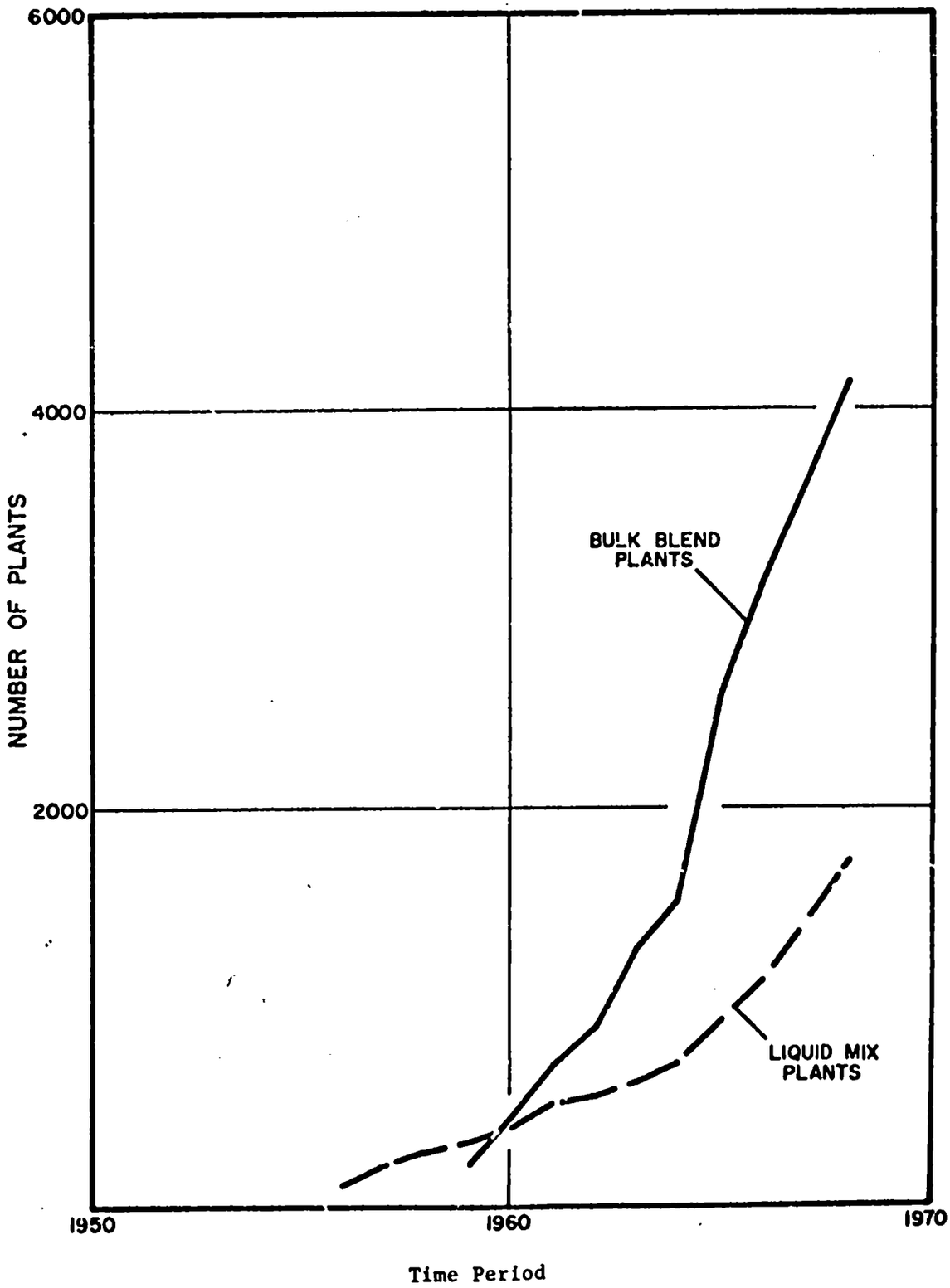


LEGEND

1-5 PLANTS PER COUNTY

MORE THAN 5 PLANTS PER COUN. 1

Figure 2. GROWTH OF BULK BLEND AND LIQUID MIXED FERTILIZER PLANTS IN THE UNITED STATES (1)



was mechanized, using road vehicles equipped with limestone or phosphate rock spreaders. Because of a demand for bulk spreading of fertilizer (to save labor) and because the regular marketing system (bagged) was slow in satisfying this need (condition 2), some of the rock phosphate and limestone vendors started mixing potassium chloride with phosphate rock and spreading the combination in one operation. Later, ammonium sulfate was added to the mixture. This was the beginning of bulk blending.

Probably the major reason bulk blends were initially accepted was that the blender and not the conventional fertilizer dealer offered bulk spreading of fertilizers. Had the dealers offered this service, it is doubtful whether there would have been such a rapid growth of blenders and a reduction in ammoniators as did occur in the late 1950s and early 1960s.

From this crude beginning, the practice of bulk blending and associated bulk spreading gained such momentum that by 1964, 1,536 plants existed in the United States and by 1968 this had grown to 4,140 (table 1, figures 1, 2) (1).

Where in the United States did this growth first occur and what lessons can be applied toward determining the potential of bulk blends in the LDCs? Major growth first occurred in the Midwest where, relative to other areas, the agriculture was already highly mechanized. Farms were large, fields uniform, fertilizer demand was high, and probably most important, labor was scarce. This was compounded by the importance placed on timeliness of planting. Great stress was placed on completing many jobs during the short time between the spring thaws and planting operations. Thus, speed of planting was important. A major factor, but one that was not always recognized, was that college specialists in the Midwest sanctioned broadcast applications of fertilizer, whereas, some specialists in other parts of the United States were at first skeptical as to the effectiveness of bulk spreading compared to band applications of fertilizers.

There were other reasons for the success of bulk blending. Among these were: the belief by much of the established industry that compound fertilizers were superior to blends as a source of nutrients to plants, the natural aggressive nature of the group which advocated bulk blending and their quickness in offering the farmer services that he wanted including bulk spreading and soil and tissue testing. Basically, it was prescription farming involving a total crop production system. Bulk blends were a natural to fit this concept. Finally and by no means minor in importance was the chance for the blender to own his own business with a very modest cash outlay. Bulk blending, more than any other single item, gave rise to a substantial number of independent fertilizer dealers free to buy basic raw materials from whomever they chose. The importance of this cannot be overlooked for it was not accomplished without considerable difficulties. In its early stage of development, sales personnel of basic producers of N, P, and K either were not aware of or deliberately ignored the blender both as a purchaser and as a merchanciser of fertilizers.

Along with the rapid growth of retail outlet blenders came the development of large urea, ammonia, MAP, and DAP facilities which, although located some distance from the market, produced products of sufficient quality which could be readily blended and/or applied directly to the soil with no chemical alteration. Furthermore, research had shown that in the areas where blends first became prominent only N, P, or K nutrients were needed. Secondary nutrients such as S which were present in significant quantities of many of the compound fertilizers was a factor only in certain isolated areas. Thus, through a combination of circumstances, catalyzed first by the void which developed when the ammoniator failed to service the needs of the farmer (bulk spreading), an industry was born which altered the face of the U.S. industry in 10 short years.

Potential of Bulk Blends in Developing Countries

Based upon the conditions that prevailed during the early acceptance of bulk blending in the United States, one might conclude that this practice has very limited potential in many of the developing countries. In some instances, this may be a correct conclusion. This may be particularly true if the practice is to be applied directly to the farmer level. In the opinion of the author, bulk blending in a number of countries will be practiced first at the import and intermediate levels and eventually also will become common at or near final points of distribution.

There are several reasons for this. First, import of a wide range of fertilizer in bag or bulk is just now becoming common between the basic producing areas of the World (Japan, North America, and Europe) and the developing countries such as India, Pakistan, Southeast Asia (Singapore), and certain countries of Latin America. Diammonium phosphate, muriate of potash, triple superphosphate, ammonium sulfate, and now urea have been successfully shipped in bulk to the major fertilizer using areas of the developing world. Furthermore, these products are or can be made available to fit a very specific set of conditions, i.e., particle size and bulk density. Although it is true that the major portion of these imports is still in bagged form, cost-conscious governments and private companies will force this practice to become very widely accepted because of substantial savings in foreign exchange that can be accrued by shipping in bulk. Thus, the greatest deterrent(import of material already in bags) to bulk blending will have been eliminated.

The second major reason bulk blends will probably become widely accepted (in those countries having high imports) is due to the peculiar nature of the local marketing and distribution systems in many of the countries.

As was the case in the United States in the early 1950s, much of the domestic as well as imported fertilizer is handled in bags. Furthermore, much of the domestic production is also sold in bags. These producers already have or soon will experience difficulty in moving production. In addition, many of the current distributors of fertilizers have not recognized that there has been a shift from a sellers to a buyers market. This is a critical new experience for those not completely sensitive to customers' needs. This is further complicated by the way the distribution system is established--where many produce or handle only one product, either nitrogen, phosphate, or potash. Again, it may be only one form of either of these three ingredients. The markets that are now developing are far more complex than this. In all too many instances, no attempt has been made to offer the consumer a complete line of products. To further complicate matters, many of these local products are fine crystalline or pulverized materials unacceptable to all but the crudest forms of blending.

A third reason bulk blending will grow in certain developing countries and the one that actually may provide the greatest impetus is that the local fertilizer market in many of these developing countries is expanding at a very rapid pace, in many cases more rapid than the local industry can efficiently service. This, coupled with a serious oversupply of a wide range of high quality N, P, and K fertilizers in a number of the developed countries as well as at production points in the developing countries, will bring active pressure from the surplus areas to find new uses for their products. This might be brought about in two ways: through low prices for their products (very competitive with locally-produced fertilizers) and through the availability of technical expertise to use these products (bulk shipment is one example).

Fourth, this entire system will probably be made possible through the development of a rather large number of independent importers who control an extensive wholesale-retail distribution network. Many of the essential ingredients needed to start a bulk blend industry are already available. This coupled with a desire, often encouraged by the national government, to develop a private sector leads one to conclude that in many of the developing countries all of the ingredients essential to the development of a bulk blending industry are already available.

Areas of Potential

Thus, bulk blending shows potential of becoming acceptable in certain developing countries in a number of ways. This may be at an intermediate point of distribution where land holdings are small and at the retail level where land holdings are large and/or concentrated. Where fertilizers are imported in bulk, they can be either blended at the port area according to the needs of a particular region or shipped from the port in bulk if satisfactory equipment is available and then blended according to the needs of a region or subregion. Under these circumstances, the fertilizers could be bagged at the point of blending and sold at a further retail point. This approach should become very common in Pakistan, India, Indonesia, and certain countries of Africa and Latin America. In most instances, the farmer will not be aware that he is buying a blend for the "prescription" would have been written by government or private fertilizer officials on a regional basis with little attempt to fill the individual needs on a farm or field.

Estates, plantations, and large private or government holdings represent the second major area where blends may develop and the first where they are sold at the retail level. Although the volume of this group is small, it is usually located in a concentrated area where rail and road systems are usually quite good, land holdings are usually large, fields

quite uniform in size, labor is in short supply, and as a result the entire operation lends itself to a fairly high degree of mechanization. There are two other factors favoring the acceptance of bulk blends under these circumstances. These are: the desire of management to fertilize according to the prescription concept and the availability of management personnel with sufficient skills to manage the bulk blend system. This will not be an easy market for advocates of blending to capture since those producing compound fertilizers (chemically-combined N-P-K) are already doing an excellent job of servicing this market. Nevertheless, this does represent a good potential and in certain areas they will adopt the blending concept.

Areas where bulk blending is likely to develop under the conditions described above are: the estate areas of Malaysia and Sumatra, Indonesia, large farm holdings in the Punjab of India, West Pakistan, Chile, Brazil, the high plains in Colombia, and certain areas of North Africa.

A third area where bulk blends are likely to develop is where farms presently are too small for individual mechanization, but could become large enough if farmed cooperatively. In large areas of Japan, Korea, Taiwan, and certain regions of Latin America, industrialization is moving at a rapid rate, absorbing considerable labor from agriculture, so much so that certain phases of agriculture must be mechanized to maintain, much less increase, the current level of productivity. To accomplish this will require possible consolidation of land, at least pooling of equipment. When these conditions develop, it may be that mechanized bulk applications of fertilizers as well as bulk blending will be economical. Until this occurs, most of the areas will continue to use fertilizer in bags with the blending, if it should occur, performed at an intermediate level in the marketing chain.

Fertilizers Commonly Used For Bulk Blending

Bulk blending works best with materials that are well granulated, closely sized, and sufficiently dry and strong to avoid caking or deterioration during storage or processing. Many materials are used in bulk blending. These are ammonium nitrate, urea, ammonium sulfate, triple superphosphate, monoammonium phosphate, diammonium phosphate (18-46-0 and 16-48-0), potassium chloride, potassium nitrate, potassium sulfate, ammonium phosphate sulfate, and ordinary superphosphate. The popularity and frequency of use for these products varies according to their availability, price and capabilities in meeting the needs of the crop. Some of the more commonly used materials and their properties appear in table 2.

Although there is a wide range in apparent specific gravity and shape of particle of these materials, those that have been successfully used by blenders fall within a fairly narrow screen size range. Therefore, the popularity of blending and the selection of materials to be used will to a large extent depend upon the degree of availability of fertilizers which fall within a specific screen size.

Prilled ammonium nitrate is usually the most common form available; however, some firms do produce flakes of a block configuration. Granular ammonium phosphates and triple superphosphate are the usual phosphate sources used for bulk blends with coarse or granular potassium chloride comprising the major potassium material used in this practice.

Byproduct ammonium sulfate is available in a number of sizes. The most common ones used successfully in blends have one of two crystal shapes, either rice grain or tabular.

By far the most popular phosphate source for blends in the United States is the ammonium phosphates, especially diammonium phosphate. According to Hignett (2), the rise of bulk blending has been accompanied by an equally

Table 2. Apparent Specific Gravity, Particle Size Distribution, and Particle Shape of Some Granular Fertilizer Materials (2)

	Apparent specific gravity	Grade	Tyler screen range, wt. % +6	-6 +8	-8 +10	-10 +16	-16	Particle shape*	Critical relative humidity 86° F %
Ammonium nitrate									
Prills	1.29	33.5-0-0	0	6	65	25	4	WR	59.4
Prills (high density)	1.65	33.5-0-0	0	0	8	89	3	EWR	
Granules	1.50	33.5-0-0	1	35	54	8	2	FWR	
Flakes	1.63	33.5-0-0	0	25	43	28	4	B	
Ammonium nitrate sulfate									
Granules	1.51	30-0-0	2	29	56	10	3	FWR-PR	62.3
Urea									
Prills, unconditioned	1.32	46-0-0	0	1	17	78	4	EWR	72.5
Prills, conditioned	1.31	45-0-0	0	0	1	94	5	EWR	
Ammonium sulfate									
Compacted flakes	1.64	21-0-0	0	6	46	41	7	I	79.2
Crystals	1.75	21-0-0	0	2	38	51	9	R	
Ammonium phosphate nitrate									
Prill-like granules	1.27	30-10-0	0	5	63	31	1	WR	-
Granules	1.56	30-10-0	0	33	55	9	3	FWR	
Diammonium phosphate									
Granules (from wet-process acid)	1.63	18-46-0	0	5	83	12	0	WR	86.1
	-	18-46-0	0	42	57	1	0	WR	
Crystals (from furnace acid)	1.62	21-53-0	0	8	45	39	8	B	
Triple superphosphate									
Granules	2.12	0-46-0	1	29	56	14	1	WR	
	-	0-46-0	1	21	37	31	10	FWR	
High-analysis superphosphate									
Granules	1.90	0-54-0	1	29	41	27	2	FWR-PR	-
	2.15	0-56-0	1	14	37	46	2	FWR-PR	
Potassium chloride									
Flotation product, granular**	1.97	0-0-60	2	36	52	10	0	B	83.0
Flotation product, coarse**	-	0-0-60	0	0	19	51	30	B	
Solution-rounded crystals	1.93	0-0-62	0	5	29	58	8	WR	
Compacted flakes	1.96	0-0-60	0	14	65	20	1	I	
Filler									
Crushed limestone	2.53	0-0-0	0	9	60	26	5	I	
	2.56	0-0-0	0	22	42	24	12	I	

*B = block, I = irregular, R = rounded (PR = poorly rounded, FWR = fair well rounded, WR = well rounded, EWR = exceptionally well rounded).

**"Granular" and "coarse" are terms used by the industry; "granular" usually is 6 to 20 mesh, and "coarse" is mainly 10 to 28 mesh.

spectacular rise in production and consumption of diammonium phosphate (figure 3). Diammonium phosphate is particularly suited for bulk blending. Its high analysis means savings in costs of transportation, storage, handling, and application per unit of plant food; its good storage properties and its compatibility with all common potash and nitrogen sources give the blender flexibility in his operation; and its delivered cost usually falls below the cost of equivalent amounts of granular triple superphosphate and ammonium nitrate, urea or ammonium sulfate.

Problems with Bulk Blends in Developing Countries

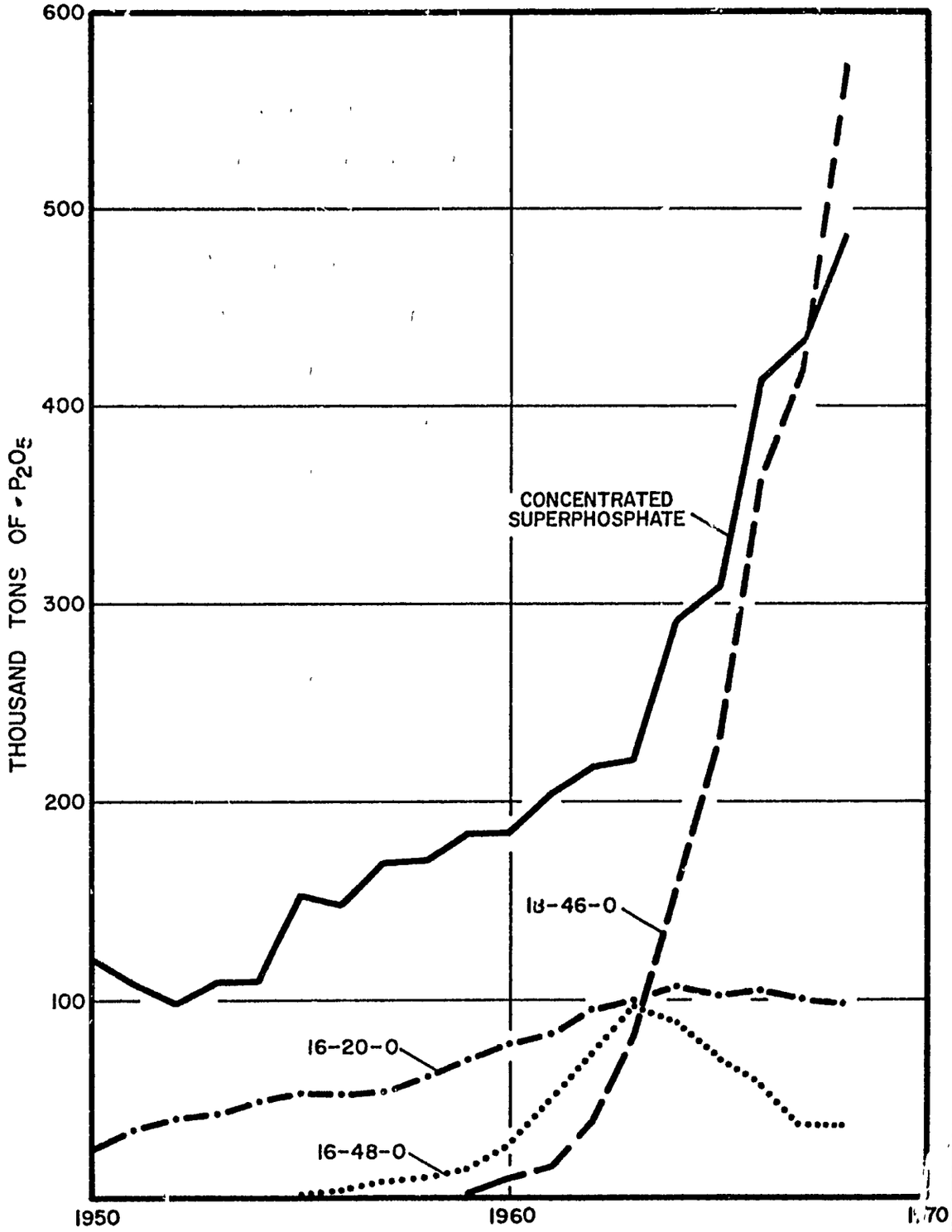
The face of the fertilizer industry is rapidly changing in many of the developing countries. New technology is rapidly being introduced at the production level and now appears to be carrying through to the distribution and use portion of the system as well.

The farmer is now changing from low-analysis to more sophisticated high-analysis products. Previously, he expected and accepted fertilizers in lumps for he merely hit them with a stick with no complaints. He did not question the composition of the product because it was the only one available.

The question now is: Will the farmer continue to accept poorly conditioned product, which may also be off grade, or will he, as is the case in most of the developed world, demand high-analysis products that are free flowing, accurately formulated, and designed to be shipped, mixed, and stored in bulk or bags in hot, humid climates for relatively long periods of time?

Figure 3. CONSUMPTION OF PHOSPHATE FERTILIZERS AS STRAIGHT MATERIALS

UNITED STATES (1)



These problems fall into three broad categories--hygroscopicity, caking, and nonuniformity of composition.

Hygroscopicity

Probably the number one problem facing all people working with fertilizers in the hot, humid, tropical LDCs, one that will severely hamper the acceptance of bulk blends if not solved, is the tendency of certain fertilizers to readily take on moisture when exposed to the atmosphere; this is termed critical relative humidity (CRH). An excellent discussion of this has been given by Silverberg (3) and is summarized as follows.

Figure 4 shows these values for several pure salts and combinations of salts. The CRH of ammonium nitrate at 30° C (86° F) is 59.4. This means that when the temperature is 86° F and the relative humidity of the atmosphere in contact with the fertilizer is above 59.4% the ammonium nitrate will absorb water. When the relative humidity is below 59.4, it will lose water (crystallize). The CRH of urea is 75.2; diammonium phosphate, 82.5; and potassium chloride, 84.0. The TVA nitric phosphates have a CRH of about 57; urea-ammonium phosphate, about 57; and ammonium polyphosphate, 63.

This is a significant problem with nitrogen products. For example, the relatively low CRH of ammonium nitrate can present a serious problem in many LDCs. It is followed in order of severity by urea and ammonium sulfate.

Whenever two or more sources of solid nitrogen are combined, the critical relative humidity for the combination is usually lower than that of the individual salts. The relative humidity for some of the nitrogen salt combinations also appears in figure 4. Clearly, a mixture of urea and

Figure 4

CRITICAL HUMIDITIES OF FERTILIZER SALTS AND MIXTURES AT 30°C.(86°F.)

(VALUES ARE PERCENT RELATIVE HUMIDITY) (3)

	CALCIUM NITRATE	AMMONIUM NITRATE	SODIUM NITRATE	UREA	AMMONIUM CHLORIDE	AMMONIUM SULFATE	DIAMMONIUM PHOSPHATE	POTASSIUM CHLORIDE	POTASSIUM NITRATE	MONOAMMONIUM PHOSPHATE	MONOCALCIUM PHOSPHATE	POTASSIUM SULFATE	29-29-0 UREA-AMMONIUM PHOSPHATE†	20-20-0 NITRIC PHOSPHATE†	15-50-0 AMMONIUM POLYPHOSPHATE†
CALCIUM NITRATE	46.7														
AMMONIUM NITRATE	23.5	59.4													
SODIUM NITRATE	37.7	46.3	72.4												
UREA	-	18.1	45.6	75.2											
AMMONIUM CHLORIDE	-	51.4	51.9	57.9	77.2										
AMMONIUM SULFATE	-	62.3	-	56.4	71.3	79.2									
DIAMMONIUM PHOSPHATE	-	59*	-	62*	-	72*	82.8								
POTASSIUM CHLORIDE	<22.0	67.9	66.9	60.3	73.5	71.3	70*	84.0							
POTASSIUM NITRATE	31.4	39.9	64.5	65.2	67.9	69.2	-	78.6	90.5						
MONOAMMONIUM PHOSPHATE	52.8	58.0	63.8	65.2	-	75.8	78*	72.8	59.8	91.6					
MONOCALCIUM PHOSPHATE	46.2	52.8	68.1	65.1	73.9	87.7	78*	-	87.8	88.8	93.7				
POTASSIUM SULFATE	76.1	69.2	73.3	71.5	71.3	81.4	77*	-	87.8	79.0	-	96.5			
29-29-0 UREA-AMMONIUM PHOSPHATE†	-	-	-	-	-	-	-	45*	-	-	-	-	57*		
20-20-0 NITRIC PHOSPHATE†	-	-	-	-	-	-	-	50*	-	-	-	-	-	57*	
15-50-0 AMMONIUM POLYPHOSPHATE†	-	-	-	-	-	-	-	-	-	-	-	-	-	-	83*

NOTE: VALUES FROM LITERATURE FOR PURE SALTS EXCEPT AS NOTED BELOW:

† TVA EXPERIMENTAL PRODUCTS (CONTAIN IMPURITIES)

* APPROXIMATE VALUES OBTAINED BY TVA

ammonium nitrate can result in a highly unacceptable conditioned product, particularly in humid or even semihumid areas, for it begins to take on moisture when the CRH at 86° F is 18%. The mixture quickly becomes wet and actually turns to liquid. For these and other reasons, we see major problems for solid ammonium nitrate in many countries of the developing world.

Exposure to the atmosphere can and does cause the prill or granule to lose its hardness, become mushy and in many cases lose its free-flowing ability. To offset this problem all hygroscopic bulk materials should be stored in bins that expose the smallest possible surface area to the atmosphere. The exposed surface will absorb moisture and form a "crust" over the remaining material. In most cases, when the crust reaches a thickness of approximately one-half inch the salt crystals in the crust will knit together to form a moisture impervious surface. For hygroscopic materials to be stored in bulk over long periods, this may also be minimized by spreading fine rock phosphate or ground limestone over the surface of the pile (3). When it is necessary to combine nitrogen sources that produce low critical relative humidity conditions, the mixing should take place at the time of sale and the product should be applied very soon after being mixed.

Where materials of high hygroscopicity are placed in bags, they should be coated with conditioners of kaolin or calcined limestone or some other suitable coating agent. Bags should have multiwalled liners and be stacked in rows no more than 12 feet high.

Chemical Reactions

Some nitrogen materials will react with other plant food sources to create severe caking problems in bulk or bagged storage. An example of

a reaction of this type is one that may occur when triple superphosphate and ammonium sulfate are combined (4).

$$Ca(H_2PO_4)_2 + (NH_4)_2SO_4 \longrightarrow 2(NH_4)H_2PO_4 + CaSO_4$$

mono-calcium phosphate — ammonium sulfate — monoammonium phosphate — gypsum

When this reaction occurs in a pile or bag, severe caking may result.

Failure to observe these basic rules will virtually eliminate bulk blending as a practice offering appeal to the retail customer.

Nonuniformity of Composition

Another problem, one which caused considerable trouble during the developmental stages of bulk blending in the United States and which could prove to be a very severe obstacle in the developing countries, is nonuniformity of composition of blended grades. This occurs mainly when fertilizer materials varying widely in particle size are mixed together and collectively handled in bulk. Differences in specific gravity and particle shape cause little or no problem in blend composition.

Nonuniformity problems can develop as a result of poor mixing or of segregation after mixing (5). This problem may be serious in the developing countries for at least two reasons. First, customer-dealer confidence is very important in selling fertilizers to the farmer. Many farmers in the LDCs lack faith in the honesty of the local merchant. Past experience has taught him to be wary of such practices as short measure and false representation of product. It is a fact that in some developing countries materials bagged and sold under a reputable name will often outsell local products both in price and quantity even though the products may be exactly the same. Clearly, the blender working at the local level could

have a problem to overcome. This can be overcome through proper quality control laws and their enforcement through a joint industry-government effort.

A second reason nonuniformity of composition presents a problem is that segregation in the bag or distribution in the field of machine bulk spread materials may be so irregular as to cause spotty crop growth and resultant dissatisfaction to the farmer. To the small farmer consuming one or two bags of fertilizer, this can be a very real problem; for although the analysis may be approximately correct in a two-ton batch of mix, there may be wide variation between bags. Thus, accuracy of analysis on a per bag basis is highly important, and particularly so for the small farm operation (6).

The difficulty of blenders keeping on specifications is well known in the United States. Numerous tests conducted by Scholl (7) and also discus d by Hignett (2) revealed that registered mixtures, mostly compounds, were almost always above the guaranteed analysis; whereas a wide variation was noted in customer-ordered mixtures. Figure 5 shows the deviation of available P_2O_5 content as determined by official analysis from guaranteed values for two groups of mixed fertilizers, registered grades and customer-ordered mixtures. The customer-ordered mixtures are mainly compound fertilizers. According to Hignett (2), of the 81 customer-ordered mixtures, 12 fell below the guarantee by more than 1 percentage point, and 16 exceeded the guarantee by more than 2 percentage points. Of the 111 registered mixtures, none fell below the guarantee by more than 1 percentage point and 8 exceeded the guarantee by more than 2 percentage points.

It is not the intent of this paper to discuss all the ramifications of bulk blending, particularly those associated with equipment requirements and nonuniformity problems associated with mixing. For an excellent

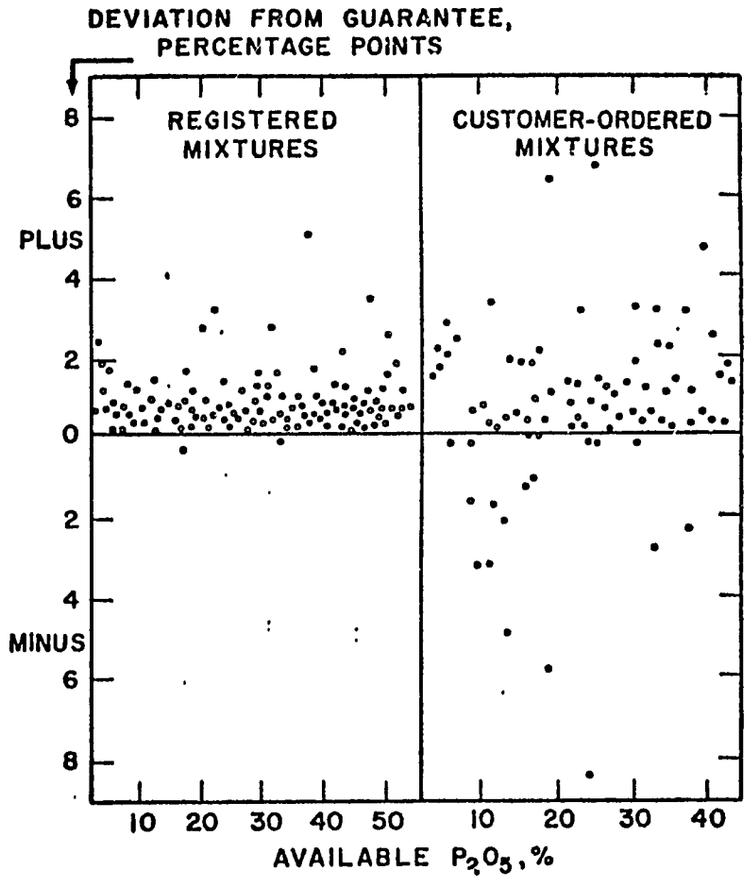


Figure 5. Comparison of Deviation From Guaranteed Analysis of Registered and Customer-Ordered Mixtures (2, 7)

discussion on this, the reader is referred to an intensive discussion of the subject by Hignett (3).

Segregation After Mixing. One area of nonuniformity that is important to the current discussion is segregation that occurs after mixing. This could prove to be the most serious in the LDCs, for blends probably will be transported over long distances. Because of limited availability, the probability of using closely-sized materials is low. And finally, lack of suitable mixing and handling equipment only adds to the danger of nonuniformity achieving serious proportions in certain developing countries.

Segregation that occurs in handling and distributing blends can be traced to three general causes (8, 2): (a) Rolling action of particles allowed to drop onto sloping piles in storage areas, hoppers, bins, or spreader vehicles; (b) vibration or agitation as in a moving spreader vehicle: and (c) ballistic action or similar sorting effects induced by spreader mechanisms.

A very simple, yet highly illustrative, device developed by TVA (2, 9) allows for the study of segregation by rolling action. The device can be used in quantitative study of the effects of particle size, shape, and density on segregation. A diagram of the device used by TVA appears in figure 6 and the results of the studies are summarized in Table 3, where the degree of segregation is expressed as spread in composition of pile segments (9, 2).

The conclusions of these tests were as follows:

1. Segregation was greatest when particle size of various materials differed. Small differences in size such as -6+8 versus -8+10 mesh caused serious segregation.

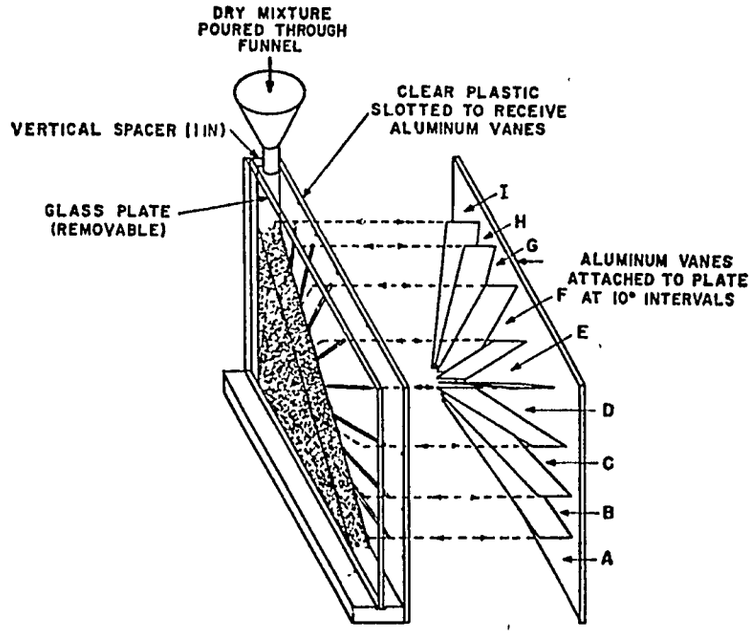


Figure 6. Segmentation of Pile (2, 9)

2. Differences in particle shape had no detectable effect on composition.
3. Differences in apparent specific gravity between various materials caused very little segregation.
4. Segregation was greater when large particles were in the minority than when in the majority.

Other researchers have confirmed these findings (10).

The seriousness of the problem was well illustrated by another test at TVA (2) where a 14-14-14 blend was prepared with materials having a poor particle size match of all ingredients. Composition of pile segments ranged from 19-10-12 to 7-21-17. Less but still serious deviation from the intended grade was observed when two of the three ingredients were fairly closely matched.

Size segregation can and does occur in large bulk storage piles maintained by producers of granular materials. Similar problems can occur in storage piles of local blenders. In another study conducted by TVA (2), two samples of granular potash were taken, one near the top and the other near the bottom. The variations in screen analysis are as follows:

	Tyler screen range wt. %				
	+6	-6+8	-8+10	-10+16	-16
Near bottom of pile	1	46	37	15	1
Near top of pile	0	12	24	40	24

Obviously, serious segregation of blends can occur particularly if materials are not carefully sized.

Table 3. Effect of Particle Size, Particle Shape, and Specific Gravity on Pile Segregation (2, 9)

Material A			Material B			Material A in pile section, %			
Particle size, Tyler mesh	Particle shape	Specific gravity	Particle size, Tyler mesh	Particle shape	Specific gravity	Av.	Max.	Min.	Spread
Effect of Size (Round Particles)									
−6 + 8	Round	2.12	−10 +14	Round	2.12	50	85	30	55
−6 + 8	Round	2.12	− 8 +10	Round	2.12	50	70	35	35
−8 +10	Round	2.12	−10 +14	Round	2 12	50	75	30	45
−6 + 8	Round	2.15	−10 +14	Round	2.15	30	86	4	82
−6 + 8	Round	2.15	−10 +14	Round	2.15	70	93	49	44
Effect of Size (Irregular Particles)									
−6 + 8	Flake	1 96	−10 +14	Flake	1.96	50	85	30	55
−8 +10	Flake	1 96	−10 +14	Flake	1.96	50	75	35	40
Effect of Shape									
−6 + 8	Flake	1.96	− 6 + 8	Round	2.12	50	53	49	4
−8 +10	Flake	1.63	− 8 +10	Round	1.63	50	55	48	7
Effect of Specific Gravity									
−8 +10	Round	2.12	− 8 +10	Round	1.27	63	57	69	12

The blender must establish practices to minimize this. Ways this may be accomplished are as follows:

1. Select materials that are closely or similarly sized.
2. Avoid coning of piles (bins or hoppers).
3. Minimize handling.
4. Use multicomponent materials.

Other Problems With Bulk Blends

More and more, micronutrient problems are becoming apparent in the LDCs . This will increase at an even faster rate as more fertilizer and higher yielding varieties are used. Bulk blends can, if properly used, serve as a major vehicle in solving these problems. One of the major arguments for bulk blends is the flexibility of mixing fertilizers on a prescription basis. This flexibility is a very decided advantage when it comes to satisfying the micronutrient needs of an area.

Nevertheless, the addition of micronutrient materials presents difficult problems. Micronutrient materials come in a wide range of sizes, some in granular form, but most as fine powders, often finer than 100 mesh.

It should be obvious from the previous discussion that serious segregation can occur when substantial amounts of a fine powder are blended with the main granular fertilizers.

Segregation of micronutrients in blends can cause two distinct and very real problems. First, yield increases can be lost if the essential nutrient is not applied. And second, yields can actually be reduced because excessive amounts can cause toxic conditions to the crop. High amounts of boron and manganese in particular can be toxic to crops.

There are several ways to minimize this problem. One way is to use granular micronutrients in the blends and match them with the particle sizes of the major components. This is not always satisfactory since the availability of micronutrients in a wide range of sizes and products is somewhat limited.

Another approach is to coat the finely divided material in the granule. Powdered materials have been successfully mixed by the addition of a binder that causes the fine material to adhere to the surface of the granules. Although water in quantities of 1%-2% by weight has been used as a binder, No. 2 diesel fuel oil in quantities of 1.5%-3% by weight resulted in 90% adherence of the materials (2). Examples of the effectiveness of the oil method appear in table 4.

Conclusion

Based upon the information presented in this portion of the paper, bulk blends do have sizable potential in the LDCs. Although many signs point toward this practice receiving customer resistance, principally because of potential problems in quality control, the technology has been worked out to circumvent these and other problems.

All signs point toward technical personnel recognizing these problems and applying successful solutions early in the developmental stage of this practice.

Table 4. Micronutrient Adherence to Oil-Treated Products (2)

Micronutrient carrier			Micronutrient adherence, % of that added				
Kind	Addition, %	Materials[a] in blend	No oil	1.5 = 1.7% oil	2.0% oil	2.5% oil	3.0% oil
Frit	2.2	APN, DAP	45	82	91	–	–
Frit	4.4	APN, DAP	23	–	–	91	–
Oxide	6.3	DAP	31	68	100	–	–
Oxide	12.5	DAP	40	–	74	–	97
Oxide	8.6	MAP, KCl	11	–	–	94	–
Oxide	12.2	MAP, KCl	41	–	–	95	–
Salt	5.0	APN, GHAP, KCl	0	–	38	–	92
$ZnSO_4 \cdot H_2O$	4.4	APN, GHAP, KCl	0	95	99	–	–

[a] APN, ammonium phosphate nitrate (30-10-0); DAP, diammonium phosphate (18-46-0); KCl, potassium chloride (0-0-60); MAP, monoammonium phosphate (14-48-0); GHAP, granular high-analysis phosphate (0-60-0).

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