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NEW DEVELOPMENTS IN FERTILIZER TECHNOLOGY

By
Robert G. Mueller*

The Tennessee Valley Authority was created in 1933 during Franklin D. Roosevelt's administration primarily to work with a very depressed region of the United States--The Tennessee Valley Region. The area makes up parts of seven states and is about one-half the size of Kenya.

The agency also was given one nationwide responsibility--to develop and introduce new and improved fertilizers. Some old, government-owned nitrate plants constructed in Alabama during World War I to make nitrate for explosives were turned over to TVA for use in the fertilizer program. The facilities also were to be used as needed to make munitions in time of war.

In meeting its fertilizer obligations, TVA has developed at Muscle Shoals, Alabama, a National Fertilizer Development Center. In many ways, it also has become an international center for fertilizer information.

It was early decided that TVA's role in fertilizers would be one of research and development. We would research out new fertilizers and ideas, which would be patented, help develop these new processes and products and then license them to industry for further development and production. The licensing of TVA's processes is nonexclusive to U.S. industry. No patents are taken in other countries; thus, developments also are freely available to industry worldwide.

Although we hold the patents for many of the fertilizer processes used in the United States today, we do not sell the products normally found on the U.S. markets. We do not sell urea, ammonium nitrate, triple superphosphate,

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diammonium phosphate or normal NPK grades that are readily available to the American farmer. He must buy these from industry. We manufacture, but only in small quantities, such products as ammonium polyphosphates, urea ammonium phosphates, various base solutions for liquids and suspension fertilizers and numerous high-analysis fertilizers that contain significant levels of secondary and micronutrients. We are also beginning to manufacture controlled-release N fertilizers. Our objective is to make fertilizers that fit crop needs and reduce nutrient losses through volatilization, runoff, or leaching so that a higher percentage of the applied N fertilizer can be used by the crop. At present, in the United States and Europe, much attention is being focused on fertilizer's potential contribution to eutrophication.

Our goal has been primarily one of working through research and development to make fertilizers that are of better quality and cheaper to the American farmer. In the past we have done this principally by increasing the plant nutrient content of the fertilizers--making them of higher analysis--and improving on fertilizer processes to make them more efficient.

Fertilizer analyses in the United States have actually been increased in plant nutrient content from an average of 20% plant nutrients in 1940 to over 40% plant nutrient today. Fertilizers have also decreased in price to the American farmer--the only major input that has decreased.

At the National Fertilizer Development Center we are organized with a Division of Agricultural Development, a Division of Chemical Development, and a Division of Chemical Operations. We have a total employment of about 1100 people and a professional staff of scientists and engineers that number over 200. Disciplines include chemists, chemical engineers, agronomists, economists, marketing specialists, transportation specialists, communication specialists, etc.

We also have a small International Fertilizer Development Staff that coordinates technical assistance programs with developing nations. This staff calls on people from all of these disciplines to help solve problems and to advise those in the developing countries on problems related to fertilizers. This we do at the request of our Agency for International Development; various UN organizations, including FAO; the World Bank. Regional Development Banks, and the governments and industries of the developing countries.

Since 1964 we have responded to requests from some 25 countries and have sent some 60 teams utilizing over 60 different people as team members.

In addition, we offer training courses at TVA and will assist in organizing or conducting training courses in the developing countries. Since 1965 TVA has had over 300 participants in training courses on fertilizer production, distribution and sales. We have also, during the past five years, improved our library to make it a more complete working library on matters pertaining to fertilizers. We also encourage the use of this facility either by direct visits or through correspondence.

We make numerous studies that are of worldwide importance and interest. As one example we try to keep an up-to-date record of fertilizer production capacities--in operation, under construction and being planned. Then by working with FAO statistics on fertilizer production and use we can have available a better picture of fertilizer production in relation to demand. We keep all of this information available by computer methods and can easily make this information available to anyone who wants it.

From this information our projections show that world consumption of plant nutrients is forecast to climb from the 1971 level of 68 million metric tons to more than 105 million metric tons by 1980. Growth rates between now and 1975 should be about 6%/year. Over the longer term, the rate is expected

to average 5%/year from 1972 to 1980. By 1980, nitrogen use should exceed 51 million tons, P_2O_5 over 29 million tons, and K_2O almost 25 million tons (table 1).

Rates generally will increase faster in developing than in developed regions, but may not equal the rapid gains of recent years. The world fertilizer market is maturing to a point where in many areas the greatest impact of increased use may have already been achieved; in such areas the future increases in agricultural productivity will depend to a greater extent on the optimum combination of all farm inputs.

World nitrogen supplies should easily stay ahead of forecast demand, with little overall improvement indicated by 1975 in the supply-demand balance. Capacity is being added more slowly than recently in developed regions, but developing regions are expected to continue to expand capacity rapidly. This will bring nitrogen supplies in developing regions much closer to demand levels in the next 4 years; achievement of significantly higher operating rates could bring these areas as a whole close to self-sufficiency in nitrogen.

Phosphate capacity is not expanding as fast as demand is expected to increase; however, a new wave of construction of new capacity may be on the horizon which could result in a return to an oversupply situation. While the developing regions have scheduled significant increases in capacity, they will not be able to meet expected demand levels; continued trade in phosphate materials or intermediates such as phosphoric acid can be expected.

The world potash production potential remains more than adequate to supply anticipated demand. Potash use and trade will remain primarily in the developed regions. Some improvement of the potash market is foreseen as capacity additions are at a minimum and a steady increase in demand is expected.

Table 1 Consumption of plant nutrients (N, P₂O₅, K₂O) (1)

Region	1965		1971			1975			1980		
	Total demand (mil tons)	Market share	Total demand (mil tons)	Annual growth '65-71	Market share	Total demand (mil tons)	Annual growth '71-'75	Market share	Total demand (mil tons)	Annual growth '71-'80	Market share
Developed Regions											
North America	10.5	25.7%	16.1	7.3%	23.6%	19.9	5.4%	23.2%	24.5	5.0%	23.2%
Western Europe	12.5	30.5	16.7	4.9	24.6	18.9	3.0	22.0	21.8	3.0	20.1
Eastern Europe	8.9	21.7	17.8	12.3	26.2	23.5	9.5	27.4	30.0	5.9	28.4
<i>Total^a</i>	<i>35.5</i>	<i>86.7</i>	<i>54.8</i>	<i>7.5</i>	<i>80.4</i>	<i>67.1</i>	<i>5.2</i>	<i>78.2</i>	<i>81.8</i>	<i>4.5</i>	<i>77.4</i>
Developing Regions											
Asia ^b	2.1	5.0	5.2	16.6	7.6	7.1	8.3	8.3	9.0	6.4	8.6
Africa	7	1.6	1.1	8.9	1.6	1.3	4.6	1.6	1.6	3.8	1.5
Latin America	1.4	3.5	3.1	13.8	4.5	4.6	10.7	5.3	5.8	7.4	5.5
<i>Total</i>	<i>4.2</i>	<i>10.1</i>	<i>9.4</i>	<i>14.6</i>	<i>13.7</i>	<i>13.1</i>	<i>8.7</i>	<i>15.2</i>	<i>16.5</i>	<i>6.5</i>	<i>15.6</i>
Communist Asia	1.3	3.2	4.0	19.8	5.8	5.6	9.0	6.5	7.4	7.1	7.0
World	41.0	100.0	68.2	8.8	100.0	85.8	5.9	100.0	105.7	5.0	100.0

^aIncludes Oceania, Japan, Israel, and South Africa^bExcludes Communist Asia (Peoples Republic of China, North Vietnam, and North Korea)

Now briefly let us take a look at developing Africa (excludes South Africa).

Table 2 illustrates the past trends and projections in NPK production and consumption.

Table 2. Past Trends and Projections in NPK Production and Consumption for Africa

Year	Consumption			Production			% of World Consumption
	N	P	K	N	P	K	
1967	452	176	116	163	331	0	1.6
1968	476	207	119	150	391	0	
1969	540	218	118	144	446	0	
1970	587	239	131	163	426	67	
1971	665	309	150	197	426	160	1.6
1972	684	311	167				
1973	712	337	178				
1974	739	362	183				
1975	764	383	193				

While Africa's annual growth rate of fertilizer consumption 1965-71 has averaged a healthy 9% its world market share has remained the same, 1.6%. These figures are based on a relatively small tonnage when considering Africa's size and population.

Any time one makes comparisons he risks abstraction. However, Africa and Brazil are about equal in consumption and production of fertilizer now. Brazil's consumption is growing at 15% to 20%/year. The reasons are many, but at some time during this seminar Brazil's recent experiences would be of some value to African planners, particularly in the areas of rural credit, foreign investment policy, fertilizer education, etc.

Until 1968, this continent's only nitrogen production outside of South Africa was in Egypt. However, several new ammonia plants have been constructed in other countries, primarily in North Africa, and Egypt no longer dominates the region's supply pattern. Developing Africa has only 10% of total nitrogen capacity in the developing regions. By 1975, it could have 13% of the total. However, because of its current limited demand, Africa is the only one of the three major developing regions that could become self-sufficient by 1975, even with operating levels at only 60% of capacity. Location of capacity away from potential heavy use areas will mean that producer nations will face stiff competition for these African markets.

Improving operating rates to 80% would create an apparent surplus of over 250,000 tons N by 1975. Consumption forecasts for Africa have been heavily weighted by the lack of a significant long-term growth in use in Egypt. Other African nations have experienced much higher rates of increase and the potential exists for further rapid gains. A significant gain in the demand for nitrogen could quickly take up any surplus production within the region.

With regard to phosphate, the developing countries of Africa have a total estimated production level of more than double their current consumption. Long a major exporter of phosphate rock, this region has also established phosphate fertilizer production facilities at mine or port sites to upgrade phosphate rock to finished materials, also for the export market. A steady increase in trade between 1965 and 1968 was recorded; however, in the last 2 years increased domestic consumption and lower production rates reduced the trade balance to 130,000 tons of P_2O_5 in finished goods form.

Capacity additions in the next few years will be more in line with projected demand levels, allowing this region to maintain its current balance of trade.

Increased trade can only be achieved with improvement in operating levels well above the poor performance of the past two seasons.

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

Urea, high-analysis compound fertilizers, and diammonium phosphate are experiencing and will continue to experience the greatest acceptance and offer the greatest growth potential in Africa of all the fertilizers on the market today. These projections are based in part upon the analysis presented in Part I, in part on trends of use by product that have occurred in the past 10-15 years, and on new fertilizer capacity scheduled to be built in Africa in the next 3-5 years.

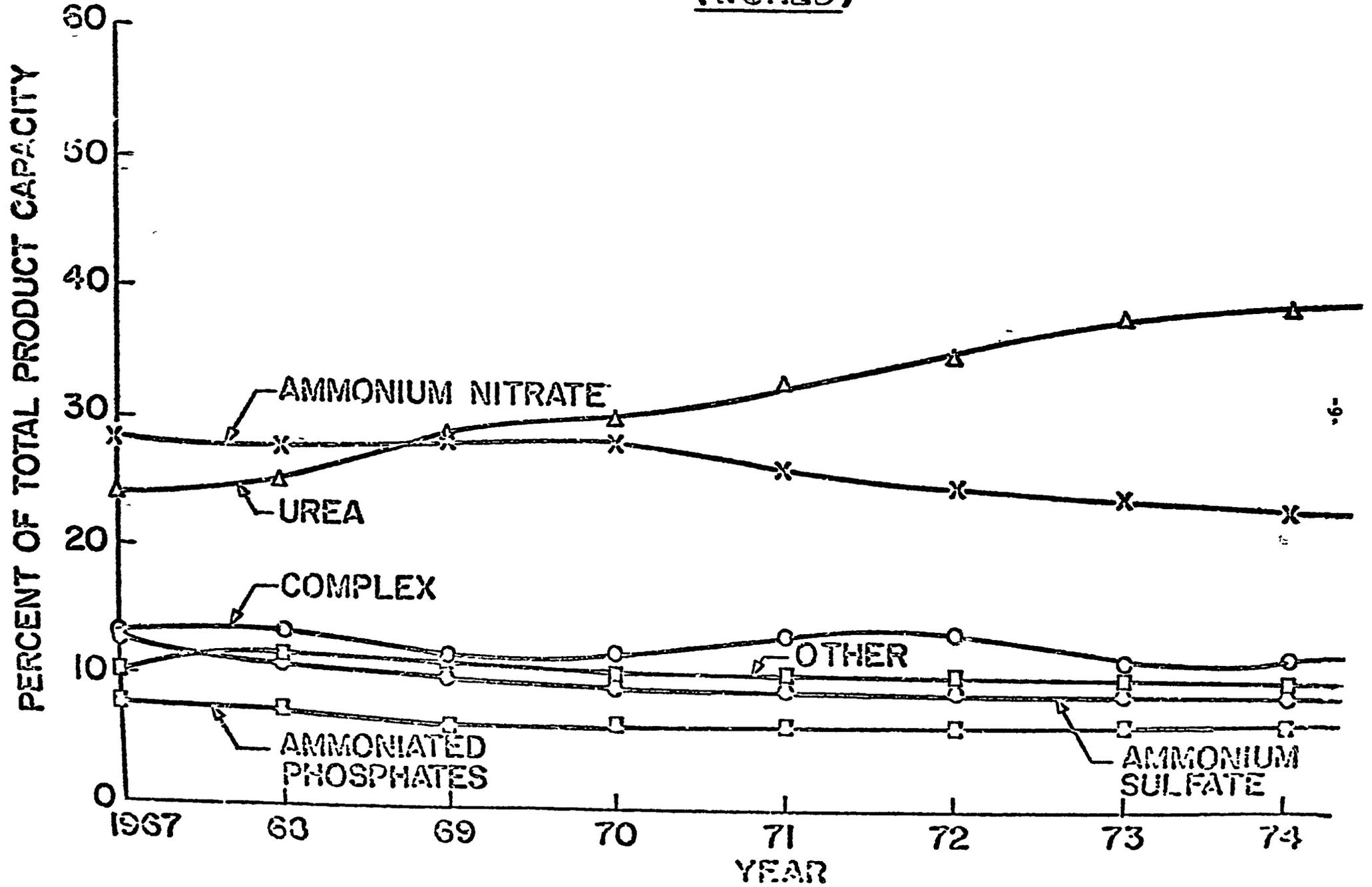
Although special local situations may dictate otherwise, the materials in decreasing order of immediate potential in Africa are as follows:

Urea

Potential--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 growth potential in Africa than liquids due mainly to the simplicity of shipping and handling dry materials in areas of small land holdings and the lack of widespread availability of sophisticated equipment, urea has proved very attractive to a very large number of farmers and fertilizer manufacturers.

For these and other reasons, urea has played an increasingly dominant role as the main nitrogen fertilizer in the world in general (figure 1). Although these generalizations hold for a given region, the actual dominance of urea on a per-country basis is somewhat dependent upon the amount and type of other nitrogen capacity that now exists within the country.

FIGURE 1
MARKET SHARE OF MAJOR FERTILIZER PRODUCTS-NITROGEN(2)
(WORLD)



When properly applied, urea has been shown to be equal or nearly equal to ammonium sulfate as a source of N to a wide range of crops, including maize, wheat, and rice (2). 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. No other single-nutrient fertilizer has captured the attention of agricultural and fertilizer production specialists as has urea. 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 its current rate 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 (figure 2). This causes problems in bulk blending, bulk transport, and mechanical bulk spreading. Unless corrected, this disadvantage could restrict its use; 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 immediately after application (3, 4, 5). As much as 60% of the N applied as urea may be lost through this mechanism. Even on flooded rice, urea has occasionally been shown to be vastly inferior to ammonium sulfate as a source of N to the crop (6). The reasons for this have not all been identified. These problems are real and will be more apparent as fertilizers become more available and farmers have an opportunity to compare various nitrogen sources in supplying the needs of the crop.

Figure 2

**CRITICAL HUMIDITIES OF FERTILIZER SALTS
AND MIXTURES AT 30°C.(86°F.)**
(VALUES ARE PERCENT RELATIVE HUMIDITY) (10)

CALCIUM NITRATE													
45.7	AMMONIUM NITRATE												
23.5	59.4	SODIUM NITRATE											
57.7	43.3	72.4	UREA										
-	16.1	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	60.5	75.5	71.3	70*	84.0	POTASSIUM NITRATE					
31.4	59.9	64.5	65.2	57.9	69.2	-	78.6	90.5	MONOAMMONIUM PHOSPHATE				
52.8	53.0	53.8	65.2	-	75.8	78*	72.3	59.8	91.6	MONOCALCIUM PHOSPHATE			
46.2	52.8	68.1	65.1	73.9	87.7	78*	-	87.8	68.2	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	
-	-	-	-	-	-	-	45*	-	-	-	-	57*	UREA-AMMONIUM PHOSPHATE†
-	-	-	-	-	-	-	50*	-	-	-	-	57*	20-20-0
-	-	-	-	-	-	-	-	-	-	-	-	-	NITRIC PHOSPHATE‡
-	-	-	-	-	-	-	-	-	-	-	-	-	15-50-0
-	-	-	-	-	-	-	-	-	-	-	-	-	AMMONIUM POLYPHOSPHATE‡

NOTE: VALUES FROM LITERATURE FOR PURE SALTS EXCEPT AS NOTED BELOW:
 † TVA EXPERIMENTAL PRODUCTS (CONTAIN IMPURITIES)
 * APPROXIMATE VALUES OBTAINED BY TVA

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 0.7% and not be harmful, and 2% biuret is acceptable if the urea is applied to the soil (7, 8, 9).

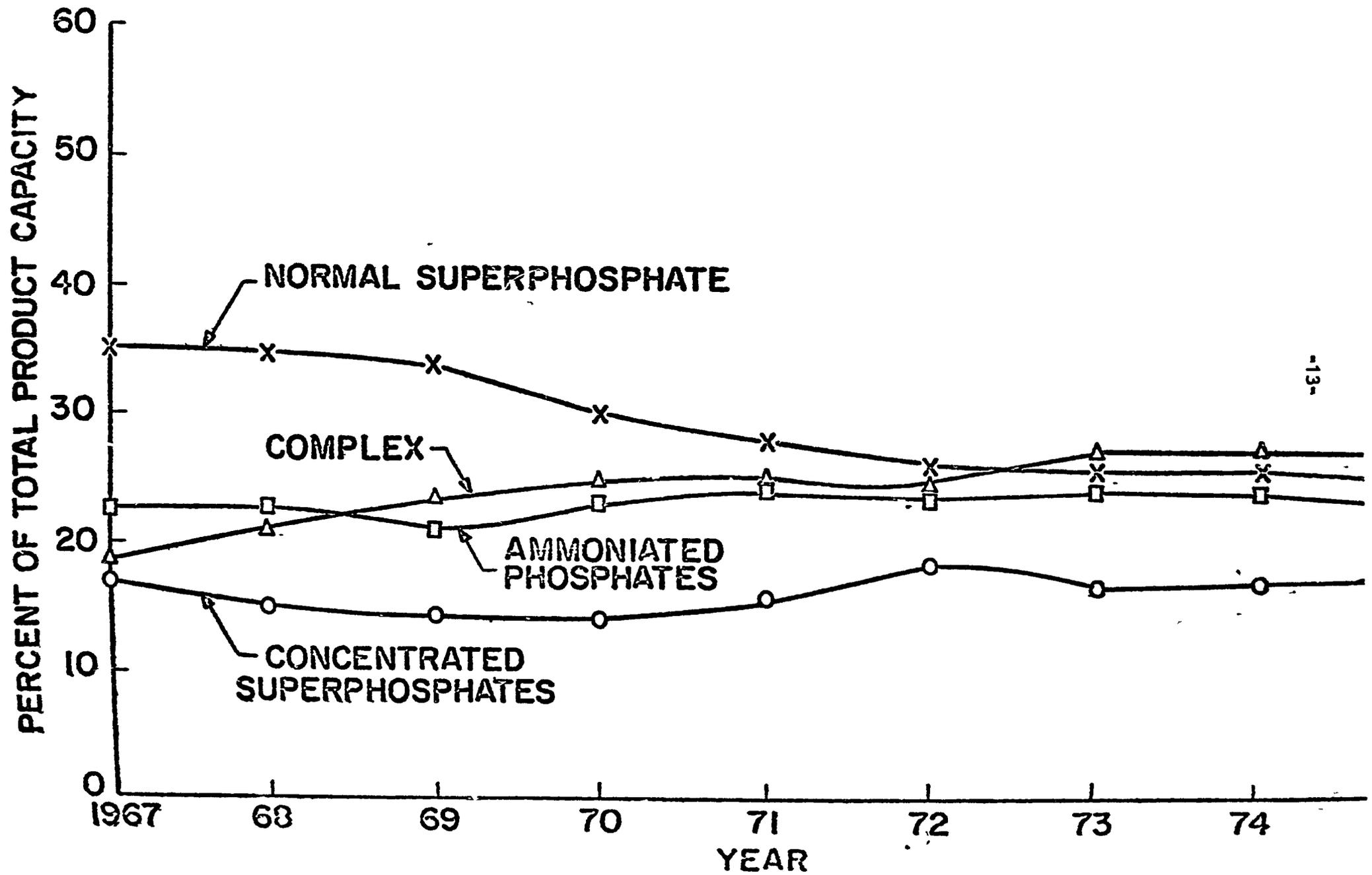
Ammonium Phosphates

(11-48-0, 18-46-0, 16-20-0, 16-48-0, 13-39-0) For reasons that will be apparent later, it is difficult to determine whether ammonium phosphates or complex (N-P-K) fertilizers will experience a growth rate second only to urea. In the author's opinion that, because many of the developing countries of Africa are still at a relatively low overall use rate, ammonium phosphates (N-P) will receive major attention.

Potential--It is difficult to forecast the role ammonium phosphates will play in the total phosphate market in Africa. Although their popularity has increased greatly in recent years and, on a world basis, they promise to replace normal superphosphate in 1973 as the number one phosphate fertilizer. This growth has occurred primarily in the developed countries where bulk blending has become very popular (figure 3) (11).

The direction in growth of ammonium phosphates depends on whether bulk blends or complex (N-P-K) fertilizers become popular. This in turn is dependent upon the type of phosphate capacity that already exists within a country. Where little or no phosphate capacity exists, ammonium phosphates may well prove very popular--first because their high analysis and good handling qualities make them easy to import, and second, as consumption increases, this may lead to the building of large, efficient monoammonium and diammonium phosphate (MAP, DAP) facilities within the country. Thus,

FIGURE 3
MARKET SHARE OF MAJOR FERTILIZER PHOSPHATE PRODUCTS
WORLD (2)



this provides a basic ingredient essential to the start or continuation of a blending industry.

Where blending has been accepted, such as in the United States, a phenomenal increase in 18-46-0 and 0-46-0 has been observed. 18 46-0 now supplies 50% to 55% of the P_2O_5 used in the United States. Where substantial superphosphate capacity already exists within a country, it may well be used directly in small N-P-K granulation plants. Under these circumstances, the potential for ammonium phosphates will be quite limited.

Agronomic and Chemical Properties--The term "ammonium phosphates" encompasses a wide variety of fertilizers produced by the ammoniation of phosphoric acid, often in mixture with other materials. Because of their binutrient content, low hygroscopicity, high analysis, excellent handling qualities, 100% water solubility of nitrogen, and near 100% solubility of phosphate--offer considerable advantages not only in savings accrued in transport and application but also agronomically because of their quick-acting effect on crops.

Ammonium 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 ammonium phosphates is in the ammonium form, they are particularly well suited for rice (1).

In contrast to urea, there are few physical or chemical problems associated with the use of ammonium phosphates in the humid tropics. They 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 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 injure young seedlings (12). This can be easily avoided by placing the fertilizer, by hand or with special banding equipment, at least 1 to 2 inches to the side and below the seed.

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

Potential--Complete high-analysis N-P-K grades (30+ units plant food) of fertilizer have received consumer acceptance in Africa. In fact, these complex fertilizers are the fastest growing materials in many tropical and subtropical countries--Japan, Taiwan, Philippines, Korea. In Brazil, N-P-K complexes supply 70% of the plant nutrients sold.

The frequency of potash deficiency is less than one-tenth that for nitrogen and one-third that observed for phosphates. 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, physically-mixed N-P-K grades which include ammonium phosphates will probably increase in demand. In regions where bulk blends do not have great potential, such as in parts of 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.

Chemical and Agronomic Properties--The products are usually granular. Color is variable in blends but generally grayish if chemically combined. They usually contain in excess of 30 units of plant food, and are available in a number of ratios. They are chemical or physical combinations of two or three major nutrients, 100% water-soluble N, and 50% to 100% water-soluble P depending upon the choice of phosphate materials and production processes. The agronomic properties of these products are based upon the form of the individual plant nutrient present.

Triple Superphosphate (0-46-0)

Potential--Triple superphosphate is a high-analysis phosphatic fertilizer that has become more important in the last 20 years. Its use in Africa is expected to increase substantially from its current 5% share of the total phosphate market; by 1972, it may hold 20% of the market for the developing portion of Africa.

The most economical production of triple superphosphate occurs when a supply of phosphate rock is nearby and the phosphoric acid is produced in large and continuously-operating plants.

Agronomic Properties--The phosphorus 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 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 ammonium 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.

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 and certain other essential nutrients. 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 (21-0-0)

Potential--Because of its low nitrogen content (21%, all ammonium nitrogen), the downward trend in use of ammonium sulfate was predictable (figure 1). In most fertilizer research tests, and in many government fertilizer education programs, it has been replaced by other nitrogen sources, usually urea. Under the present circumstances, and in most instances in the future, this decision is 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 (13). This, coupled with increased emphasis on pollution control, has led to a variable supply of ammonium sulfate in recent years.

Pan Granulated Urea Ammonium Sulfate--Considering the good agronomic characteristics of ammonium sulfate and the more fragile physical characteristics of urea, TVA about 2 years ago felt that a compromise material might be developed which would incorporate the favorable characteristics of each.

The mixed product would have a higher nitrogen content than ammonium sulfate, contain available sulfur, and possibly have better physical properties than straight urea. TVA initiated studies to determine if a suitable and relatively simple process could be developed to produce such a material. The studies were carried out in a pan granulator as described below.

This process was studied in a large pilot plant in which the production rate was about 0.45 mt/hr (figure 4). Most of the test work was carried out for production of a 40-0-0-4S material, although some tests were made of a 35-0-0-10S grade. In these tests, a concentrated urea solution was prepared by melting urea prills in steam-heated tanks. This solution was fed to two spray nozzles arranged to deliver solution to the moving bed of recycle. The solid ammonium sulfate is added to the urea prills prior to melting. This method appeared to be superior to feeding the ammonium sulfate directly to the granulator. By use of a concentrated urea solution no dryer is needed. Granules flow from the pan granulator to the cooler and screens. The oversize is crushed and mixed with recycle fines.

Results--The granules were rough in appearance compared with pan-granulated urea, but this should not detract from its use in bulk blending or direct application.

Pan-granulated urea-ammonium sulfate of 40-0-0-4S grade would, on the basis of small-scale storage tests, have to be conditioned (preferably with a high-efficiency conditioner such as diatomaceous earth) to remain in satisfactory condition in bulk or bag storage for longer than a month.

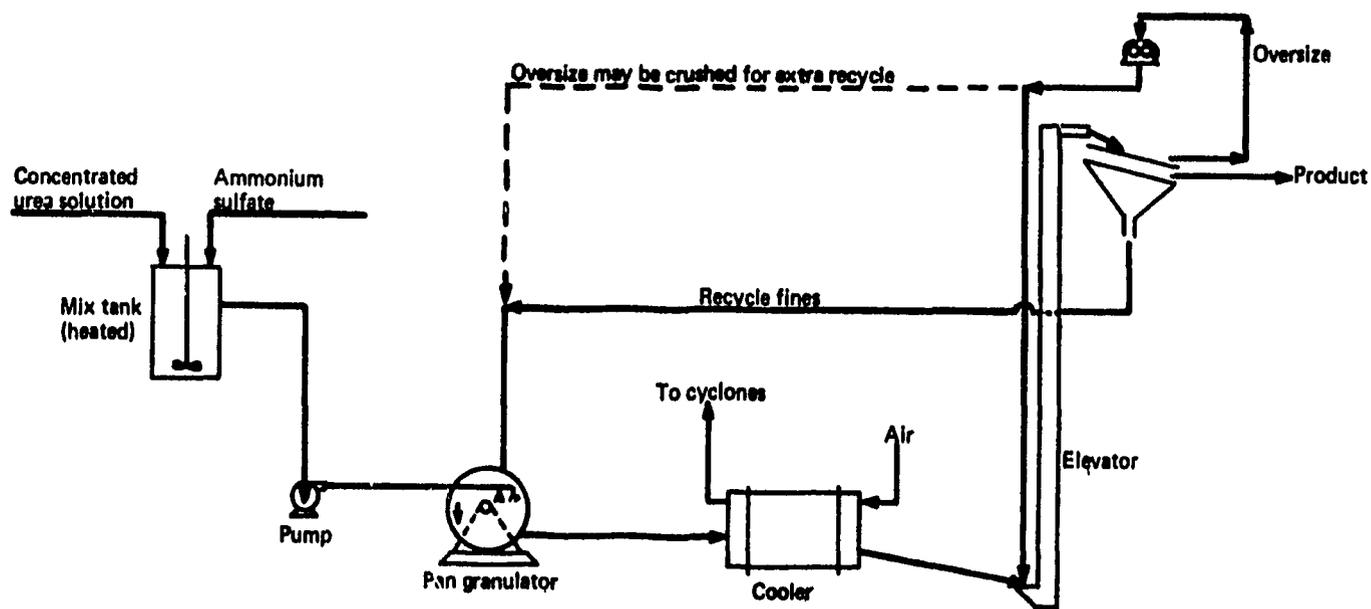


Figure 4. Flow diagram for pan-granulated urea-ammonium sulfate

Precautions should be taken when the material is stored in bulk as moisture would be absorbed somewhat like ammonium nitrate. Protection could be provided in the form of a tightly closed building, plastic pile covers, or dehumidified storage. The critical relative humidity was in the range of 55% to 60%.

Urea-Single Superphosphate--Single superphosphate (SSP, 0-20-0) is often a very economical source of phosphate in many developing countries, and also it is a source of sulfur. In many cases, it is a good outlet for utilization of byproduct sulfuric acid. However, due to the relatively low analysis (20% P_2O_5) it is difficult to bag and ship the material over long distances and remain competitive with higher analysis materials such as diammonium phosphate (DAP, 18-46-0), monoammonium phosphate (MAP, 11-55-0), or triple superphosphate (TSP, 0-46-0). TVA in cooperation with AID has been testing the production of urea-single superphosphate based compound NPK granular products for these situations. Many countries market phosphates on the basis of water solubility. When single superphosphate is ammoniated, the water solubility is significantly reduced. Therefore, the process studied involved little or no ammoniation.

Generally mixtures of urea-single superphosphates or triple superphosphates have been avoided because of the possibility of formation of an adduct which releases water and renders these fertilizers tacky and wet during processing. Some work has been done in India on this process. Also, some products are made in Great Britain and Japan containing urea and unammoniated or lightly ammoniated single superphosphate.

Process--The flow diagram for production of urea-single superphosphate based granules is shown in figure 5. In order to make relatively high analysis grades, it is necessary to supplement the single superphosphate with other phosphate materials such as diammonium phosphate or monoammonium phosphate.

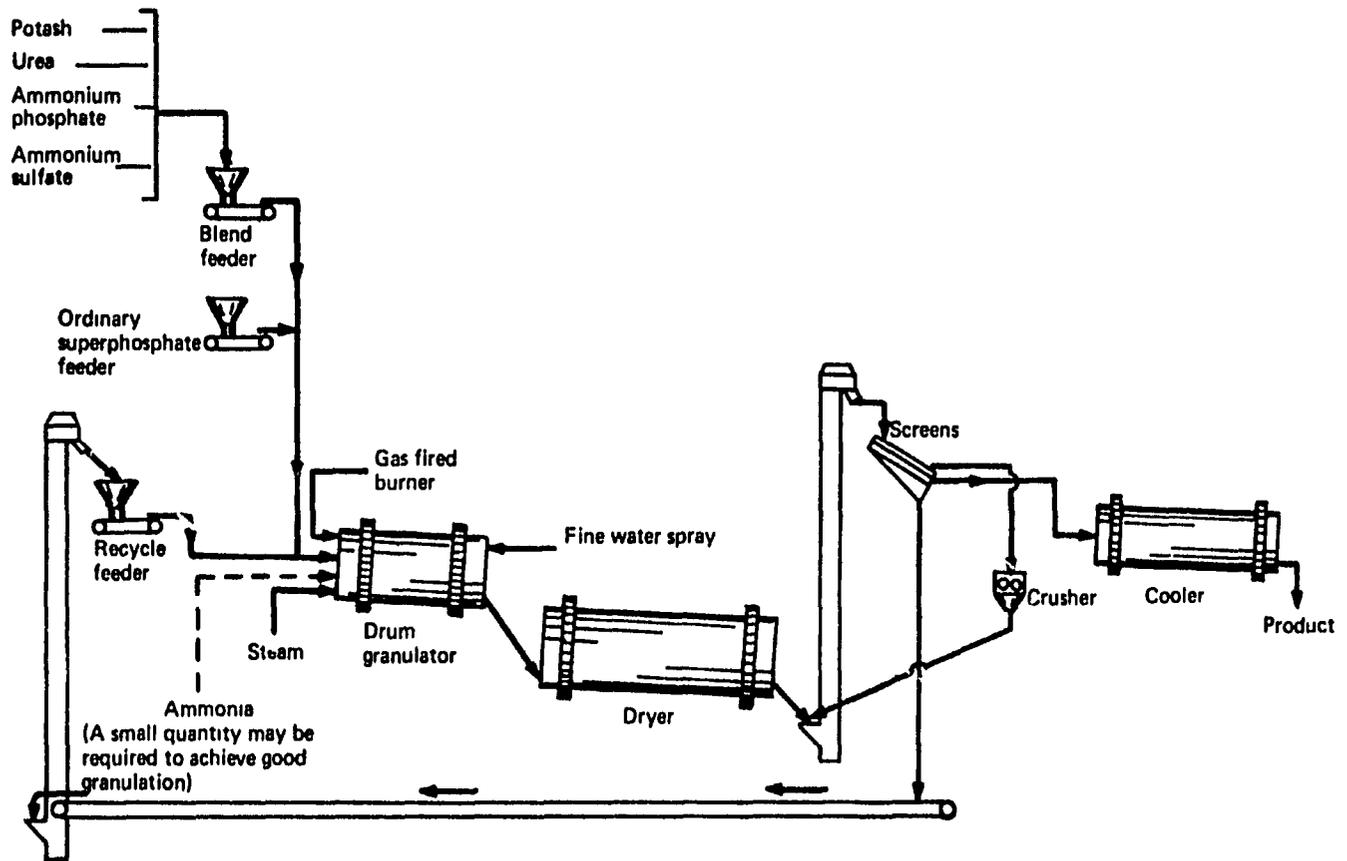


Figure 5. Flow diagram for urea single superphosphate based granulated products

Results--Granulation was quite poor with test conditions for a 14-14-14 and a 10-20-10. In both formulations, there was a tendency toward either undergranulation or overgranulation.

From data obtained thus far at TVA, the granulation of compounds based on urea and single superphosphate without ammoniation appears to be difficult. It appears that some specific equipment changes would be required for formulations of this type. The drying and feeding of hot single superphosphate to the granulator may be helpful. The use of a small quantity of ammonia in the granulator eliminates many of the operational problems, but lowers the phosphate water solubility to about 80%. TVA plans to conduct further studies of the process.

Granulated Urea-Phosphate Rock--Granulated urea-phosphate rock is a homogeneous mixture of urea and fine-ground phosphate rock. Urea provides the granulating medium for binding together the small rock particles. In order for the rock to be available to crops, it must be either applied as a fine grind or rapidly converted to its original fine-ground form. This is accomplished by the rapid dissolution of the urea in water which allows fast disintegration of the granules to provide fine-ground material. Obviously, the handling, storage, transport, and application characteristics of granulated materials are preferred over a dusty material such as ground rock. Two grades of materials were produced, 26-13-0 and 18-18-0.

Figure 6 shows one process used for production of the urea-phosphate rock granules in the TVA pilot plant. Tests have been conducted in two types of granulation equipment, a pan-type and rotary drum granulator. Results were superior when the pan method was used.

Applications--Some developing countries use phosphate rock for direct application, and farmer complaints have been received for handling and application of the fine-ground rock. Various methods are being sought to granulate the rock. The use of urea would be a very convenient way to achieve granulation.

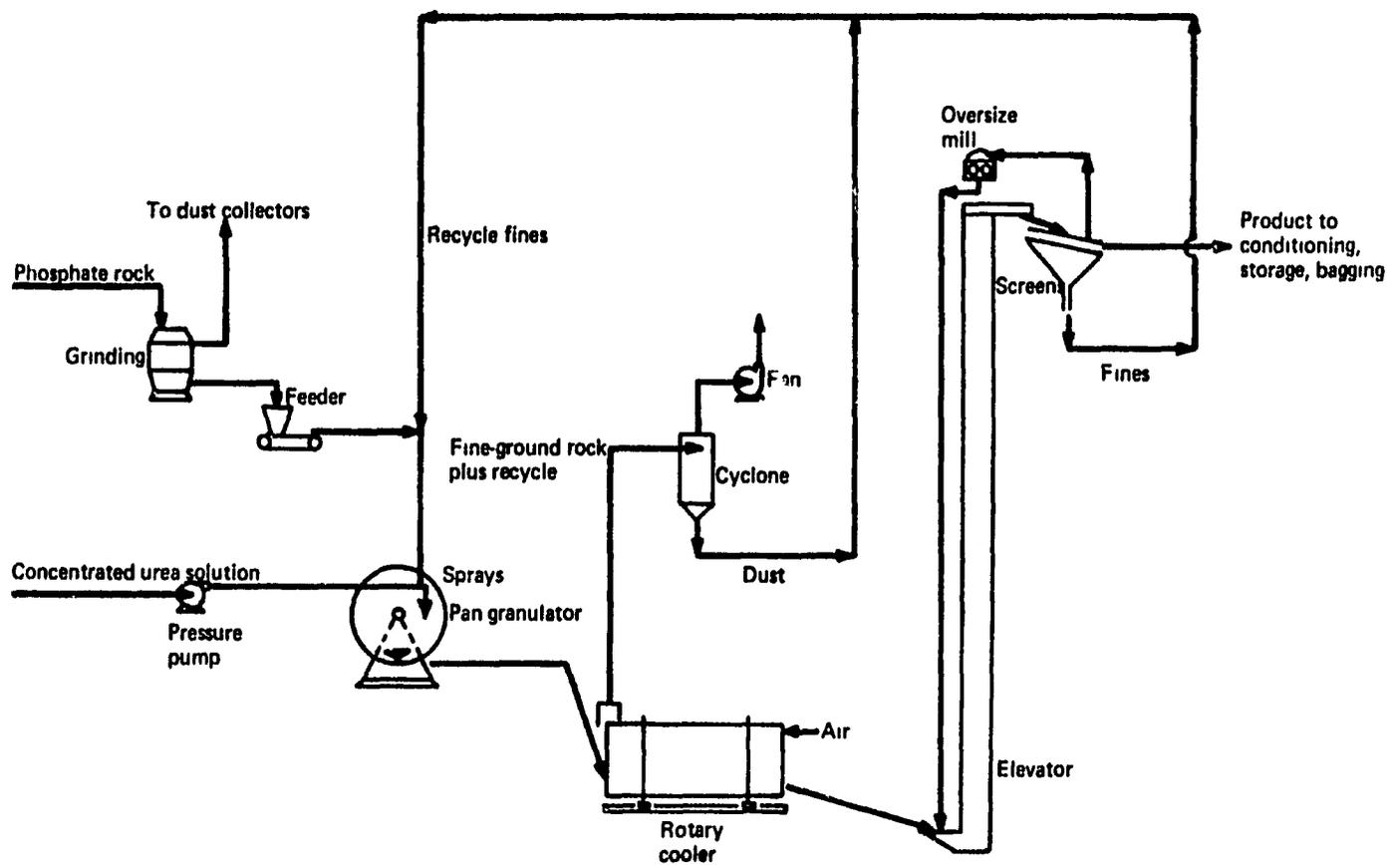


Figure 6. Flow diagram for urea-phosphate rock granules

Further tests are needed on ways to granulate urea-phosphate rock. For example, the use of crushed urea prills and fine-ground rock with steam granulation in a rotary drum should be tested. Also, a pugmill might be used for this process. Inclusion of other materials such as a small quantity of water-soluble phosphate for early crop response might be helpful.

The products are being tested agronomically for rice and much interest in such products is being shown in Indonesia. However, the agronomic effectiveness of ground rock is dependent on its reactivity and TVA is evaluating various rocks in this respect. A report is available which discusses the relative reactivity of selected rock phosphates.

Urea with Improved Physical Properties--The attractiveness of urea as a nitrogen fertilizer could be increased even further if simple and inexpensive methods could be found to significantly improve its physical properties, especially for handling, storage, and transport in humid areas. A urea that is readily compatible with granular triple superphosphate for bulk blending would be helpful. This, of course, would be attractive for industry in the United States as well as in developing countries. With these objectives, TVA has been conducting tests to evaluate various materials that could be applied to urea after the product has been air-prilled, spheroidized, or pan-granulated. This mainly involves application of a coating to the particle surface in small quantities with evaluation of this coating as a moisture barrier. This is not part of the sulfur-coated urea project in which the objective is to control the dissolution rate of urea in the soil, although thin sulfur coatings may be effective under some conditions.

Numerous materials including oils, waxes, and resins have been evaluated. The materials are applied, usually in the form of liquids, to the urea particles while tumbling in a rotary drum.

Several types of coatings were promising as materials to retard moisture absorption at 32°C (90°F) and 90% relative humidity. Normal sulfur-coated urea (20% coating) was outstanding and only absorbed 3 and 17 mg/cm² in 4 and 24 hours, respectively. Other materials such as Bunker C fuel oil, mixtures of paraffin and oil, and mixtures of petrolatum, resin, and paraffin were effective in the laboratory tests.

Work is continuing on improvement of physical properties of urea with the objective of finding a coating that will be effective in dosages small enough to give 45% nitrogen product, that will limit absorption to a degree equal to the above coatings, but will cost only in the order of \$1.50-\$2.00/ton for the coating material, not including the cost of application. One material that appears especially promising is a 1% coating of a mixture of wax (62°C; 143°F melting point) and Bunker C fuel oil which would cost no more than \$0.50/ton. One possible disadvantage of this material is that a discoloration of the urea is noted when this material is used.

Applications--As pointed out previously, an improved urea would have good potential for developed as well as developing countries. Perhaps the largest need is for a urea product that could be blended with unammoniated granular triple superphosphate. However, almost any treatment, coating, conditioner, or whatever, will increase product cost. No one seems prepared to say what increased cost can be tolerated, although some have suggested that a product containing as little as 40% nitrogen and costing 10% more per unit of nitrogen might be acceptable. Sulfur-coated urea prepared to control the dissolution rate of nitrogen has been shown to be compatible with granular triple superphosphate as well as resistant to extreme conditions of humidity and temperature, but the cost of this type coating could not be tolerated solely for improvement of physical properties.

Anhydrous Ammonia

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.

When properly used, anhydrous ammonia is equal to any other form of ammonium nitrogen but does require special management or its agronomic performance can be affected (2). 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 urea or 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, which is very expensive in developing countries.

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 potentials 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 solutions, could very well make substantial advances in the next few years. This will occur for at least three 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.

Under these 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 nonpressure nitrogen solutions. There are vast areas of Africa where crops are 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 might be profitable to apply, by airplane, 12-30 kg of nitrogen per hectare, 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 Africa.

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.

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 a "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.

Ammonium polyphosphate can also be produced as a solid by ammoniation under pressure (19).

Work in the United States (20) has led to the conclusion that no clear-cut difference exists between monoammonium phosphate and ammonium polyphosphate (APP), although both are superior to concentrated superphosphate.

Of the materials in this family solid ammonium polyphosphate (15-62-0 or 12-57-0) offers the greatest potential for use in developing countries. This is because (a) it is a high-analysis, binutrient fertilizer, and

Table 3. Comparison in Properties Between Ordinary and Superphosphoric Acid Made With Electric-Furnace Acid (26)

<u>Parameter</u>	<u>Type of Acid</u>	
	<u>Ordinary</u>	<u>Super</u>
Acid concentration (% P ₂ O ₅)	54	76
Lb P ₂ O ₅ /gal	7.1	12.2
Percentage of P ₂ O 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

(b) it can be shipped in the solid form to intermediate points where it in turn can be readily converted to a liquid (10-34-0) 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 make it a product with good potential in Latin America, Asia, and Africa.

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 solid fertilizer currently available. Research amounts of very long-chain APP and ammonium tetrametaphosphate of approximately 14-73-0 grade have been prepared and tested. It now appears that 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.

Ultra-high-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 (21, 22, 23).

Vapor Phase Reaction Products--(NH₃-P-O). One of the more promising routes to ultrahigh-analysis P sources is the direct reaction of NH₃ and P in the presence 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 a soluble P at rates sufficient for optimum growth. The nitrogen component appears to be completely available to the crop.

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.

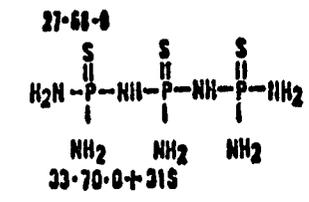
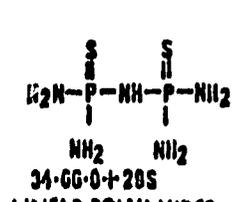
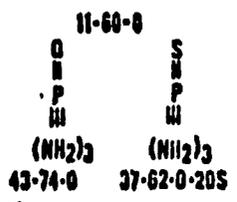
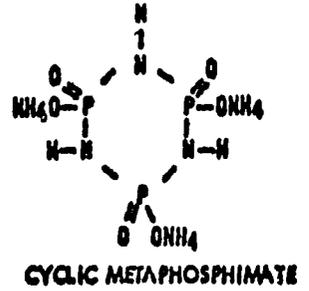
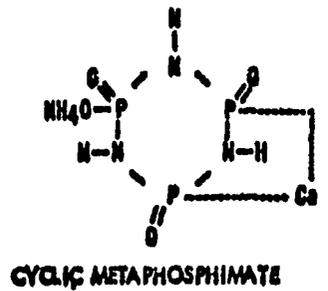
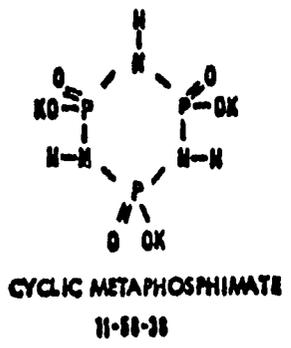
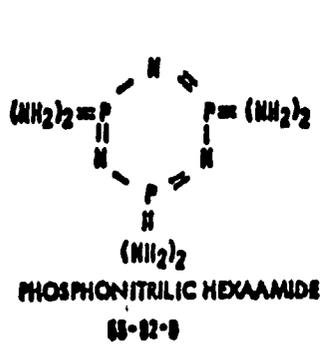
Three of the four compounds shown in figure 7 include substantial amounts of sulfur. All contain little or no oxygen. This plus the S results in a much higher content of plant nutrients. The phosphate availability of these compounds decreases with increase in molecular size. With the exception of thiopolyamides, the nitrogen sources were 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.

SUMMARY

The problem we face as promoters of fertilizer production and use has been well documented and could be summarized in Table 4.

Figure 7. Structural formulas and analyses ultra high analysis fertilizers. (21; 22, 23)



LINEAR CYANAMIDES

Table 4. Per Capita and Per Hectare Consumption of Fertilizer in Kilograms--1969 (2)

	<u>Per Capita</u>	<u>Per Hectare</u>
Western Europe	61.9	158.9
North America	66.2	67.7
Latin America	9.0	20.7
Asia	4.8	21.2
Africa	4.2	6.4

Just 10 short years ago, noted social and agricultural scientists of the developed nations forecast impending disaster for many of the developing nations. These predictions were based on the assumption that the world, in total, and the developing nations, in particular, were rapidly outstripping their food-producing capabilities. Disaster in the form of famine and on a scale never before known to man was forecast to occur by 1970.

What has occurred during these past 10 years has been well documented. Widespread famine has not taken place. No longer do people look at the food situation in despair. More and more they see hope--hope that has been kindled by the start of a green revolution which, if it continues its momentum, gives promise of continued meeting of food demand in most of the world.

Although credit for much of this success, no doubt, must go to the development and widespread use of the high-yielding varieties of rice and wheat--varieties which incidentally are very responsive to fertilizers, credit must also be given to an equally great revolution that has occurred in fertilizer technology and fertilizer use.

During the 1960s, strides were made in fertilizer technology of a magnitude equal to those made in the breeding of the high-yielding varieties of rice and wheat.

Engineers succeeded in designing and building fertilizer plants capable of producing 1,500 tons/day of ammonia thus making low cost nitrogen a reality. Transport facilities and marketing systems were also developed thus assuring amounts of fertilizer at a price that makes its use profitable even at rather high rates per hectare. These and many more developments have gone a long way to help kindle the flames of the green revolution.

To continue to keep the green revolution alive, we at TVA feel our future opportunities are:

A. Tailoring of fertilizers for your tropical soils

Controlled release fertilizers

Improved phosphatic fertilizers

Addition of needed secondary and micronutrients to macronutrient fertilizers

B. Future teams

Requests will probably require expertise in: Marketing organization

Production capacity planning

C. Guidance and cooperation with other proposed technology centers similar to NFDC in developing countries.

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