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DEVELOPMENT OF NEW FERTILIZER PRODUCTS AND PROCESSES

By

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The purpose of this paper is to review some major projects mainly from the experience of the Tennessee Valley Authority (TVA), to discuss the reasons for their success or failure, and to draw some conclusions as to the necessary ingredients of a successful research and development program, with particular reference to fertilizer technology. By way of introduction, it seems appropriate to explain briefly the origin and character of TVA's fertilizer program.

TVA is a Government-owned corporation that was created in 1933 by an Act of the Congress of the United States. Most of its objectives relate to the region of the valley of the Tennessee River. However, the fertilizer program is national in scope, and TVA is the only agency of the United States Government that has responsibility in the field of fertilizer manufacturing technology.

The inclusion of fertilizer technology in the TVA program resulted from the circumstance that a nitrate plant had been built at Muscle Shoals, Alabama, during World War I to supply munitions. The war ended before the plant was completed, and after trial runs, the plant remained idle until 1933 when it was turned over to TVA.

The Defense Act of 1916, which authorized construction of the plant, also provided that it be made available in peacetime for fertilizer production. Thus, Congress hoped that the sword could be beaten into a plowshare, and that the process would be reversible. Unfortunately the implements of both war and agriculture are subject to rapid obsolescence, and the Muscle Shoals plant was no exception. Recognizing this fact, TVA was authorized:

> To establish, maintain, and operate laboratories and experimental plants, and to undertake experiments for the purpose of enabling the Corporation (TVA) to furnish nitrogen products for military purposes, and nitrogen and other fertilizer products for agricultural purposes in the most economical manner and at the highest standard of efficiency.

TVA also was authorized to cooperate with farmers, farm organizations, and state experiment stations in introducing new fertilizers and in evaluating the economic return of new forms of fertilizers and new fertilizer practices.

In carrying out the wishes of Congress, TVA has concentrated on developing new fertilizer technology and new products, demonstrating the worth of the developments, and creating a market for new products. The resulting information is made freely available to the fertilizer industry so that farmers of the entire nation can enjoy the benefits of better or cheaper fertilizer. Production of fertilizers by TVA is limited to the minimum scale necessary for adequate demonstration of processes and for production of new products in quantities sufficient to establish their place in the industrial and agricultural economy.

In planning TVA's initial fertilizer program, primary emphasis was given to straight phosphate fertilizers. The principal reason for this decision was that the most urgent need for improving agriculture in the southeastern United States (and many other parts of the country), in the opinion of most agriculturists, was the adoption of improved agricultural practices, of which phosphate fertilization was an important part.

Much of the soil in the South had become impoverished. Its native fertility was soon exhausted, and the hilly areas were subject to severe erosion. The remedy proposed for this situation was to convert the steeper slopes to pasture or hay crops, and use only the level or gently sloping land for row crops such as cotton and corn. The improved pasture would contain clover or other legumes which would fix nitrogen from the air. Phosphate fertilizer and (in most cases) limestone were necessary for establishment and vigorous growth of legumes.

Even for growing cotton, corn, and small grains, nitrogen fertilization was considered to have only a minor role. The recommended practice was to supply most of the nitrogen by growing legumes in rotation. It was claimed that 1 pound of phosphorus applied to the soil as phosphate fertilizer would provide 6 pounds of nitrogen through fixation by legumes (1). This system was logical at the time when nitrogen fertilizer was expensive, labor was cheap, and the ratio of population to arable land was not high enough to require more intensive food production.

Naturally the farmers who were as impoverished as their soil required assistance to participate in such soil conservation programs. Government assistance programs were available which would pay for much of the lime and phosphate and terracing (if needed) for those farmers who would agree to enter the program.

The soil conservation program fitted in with other TVA objectives. Control of erosion would prevent rapid silting of the reservoirs that would be created by a system of dams. Protecting the hillsides with cover crops would even out the flow of water to the river and thus aid flood control and hydroelectric power production. Finally a change from the poverty-ridden sharecropper agriculture to a more stable and profitable grassland-livestock agriculture should improve the economic status of the region and provide a better quality diet for its people.

Concentrated Superphosphate

The first fertilizer product chosen for production at the Muscle Shoals plant was concentrated (triple) superphosphate (CSP). To produce the necessary phosphoric acid, the electric furnace method was chosen for the following reasons. Surplus low-cost hydroelectric power was available. Low-cost phosphate rock from nearby areas of Tennessee was suitable for use in the electric furnace but not well suited for the wet process. Certain equipment in the old nitrate plant was available that could be modified for use in the electric phosphorus furnace process. And finally, phosphorus has military usefulness that would contribute to the dual purpose (fertilizer-munitions) of the facility.

CSP was not a new product, but it was new to most farmers at the time. TVA's introduction of the product to the farmers contributed significantly to its subsequent popularity. TVA realized from the start that a major advance in lowering the cost of fertilizers to the farmer could most easily be made through increased concentration to lower the cost of transportation, handling, storage, and bagging per unit of plant nutrient. Introduction of CSP was a start in educating farmers to evaluate fertilizers on the basis of their nutrient content. It was also a start toward introducing straight fertilizers to farmers; previously, only mixed fertilizers were available in many areas.

On the technical side, TVA completed a comprehensive study of the several variables affecting the efficient production of CSP (<u>2</u>). A method for continuous production of CSP was evolved which significantly decreased production cost (<u>3</u>). This process involved the use of a cone mixer and a continuous den which were later used by most commercial producers.

Little consideration was given to producing a granular product, since granulation was then practically unknown and was considered to be an unnecessary expense. In the 1950's, production of CSP by industry increased rapidly.

Most of the plants produced a nongranular product, many of them by an adaptation of the TVA process. The most important use was for inclusion in compound fertilizer, replacing part or all of the single superphosphate. In the 1960's the preference shifted to granular material mainly for use in bulk blends. TVA developed a process for producing granular CSP using phosphoric acid, ground phosphate rock, and nongranular cured CSP. The reaction of ground rock and acid supplied heat and plasticity from fresh superphosphate that aided granulation.

Defluorinated Phosphate Rock

Shortly before TVA was established, research by the US Department of Agriculture showed that phosphate rock could be defluorinated by heating at about 1400^0C in an atmosphere containing water vapor, and that the product was an effective fertilizer. The reaction may be represented by the following equation.

$$Ca_{10}(PO_4)_6F_2 + SiO_2 + H_2O = 3Ca_3(PO_4)_2 + CaSiO_3 + 2HF$$

This apparently simple process seemed potentially more economical than the more drastic treatment with strong acids or reduction to phosphorus in an electric furnace followed by oxidation of the phosphorus to phosphoric acid. However, 'merely' removing the fluorine proved to be far from simple. The phosphate rock from Tennessee, and even most of that from Florida, contained so much Fe_2O_3, Al_2O_3, and other impurities that it sintered at 1400^0C, thus preventing adequate contact between the fluorine of the rock and the water vapor. Therefore, TVA concentrated most of its efforts on defluorination by fusion, while the US Department of Agriculture continued study of solid state defluorination.

In all, ten pilot plants of various sizes and two larger scale plants were built and operated. One of the pilot plants was a rotary kiln for defluorination without fusion; the other nine were various fusion processes. Much of the pilot-plant work was wasted for lack of fundamental data on the mechanism of the reaction which was elucidated subsequently by Elmore et al. (4).

Finally, a moderately successful process was developed and carried out in a demonstration-scale plant having two furnaces, each rated at 60 tons per hour. This plant was located in Tennessee near the phosphate rock mines. Operation started in 1945 and continued for 10 years, producing a total of about 190,000 short tons. The product, called 'fused tricalcium phosphate,' contained about 28% P_2O_5, of which about 75% was soluble in neutral ammonium citrate. The fluorine content was about

0.3%. The product was normally ground to such fineness that 80% passed a 40-mesh screen (0.42mm opening). The economics of the process was considered favorable, if carried out on a commercial scale and if evaluated on the basis of total P_2O_5 content. Numerous field tests indicated that the product was as effective, per unit of total P_2O_5, as superphosphate, particularly on forage hay and cover crops which were then TVA's main concern. It was often less effective on row crops in the first year of application.

The main disadvantages of the product are listed below.

- It was dusty if finely ground and less effective if not finely ground.

- It was not well suited to use in compound fertilizers.

- Only about 75% of the P_2O_5 was citrate soluble which is the basis for judging commercial value in the United States. On this basis the product had no economic advantage over soluble phosphates.

- In comparison with CSP, the concentration was low.

Calcium Metaphosphate

Calcium metaphosphate, $Ca(PO_3)_2$, was of particular interest to TVA because of its high concentration which provided opportunity for reduction in transportation and associated costs. The pure compound contains 71.68% P_2O_5. Various products made by TVA ranged from 62 to 67% P_2O_5, depending on the impurity content, mole ratio of $CaO:P_2O_5$, and amount of conditioner added, if any. Calcium metaphosphate may be formed by dehydration of monocalcium phosphate, but the TVA work was concerned with processes that involved reaction of phosphate rock with hot P_2O_5 vapor from combustion of phosphorus. The reaction temperature was about 1100°C, and the product was a melt at that temperature and became vitreous when cooled.

Development of a process for production of calcium metaphosphate involved three pilot plants and three demonstration-scale plants, as well as a considerable amount of laboratory and bench-scale work. The third demonstration-scale plant was technically successful and operated about 16 years, starting in 1949. A total of nearly 1 million tons was produced, including relatively small amounts from the first and second demonstration-scale plants. The process was economically competitive with concentrated superphosphate when both products were based on elemental phosphorus made by the electric furnace process.

The solubility of calcium metaphosphate in neutral ammonium citrate is 97 to 98%. It is essentially water insoluble by the usual analytical methods, but it dissolves slowly in water or moist soil through hydrolysis. Brown et al. (5, 6) have identified some of the products of hydrolysis in water and soil.

The main disadvantages of calcium metaphosphate are:

- The process developed by TVA is dependent on elemental phosphorus as a starting material which is usually a more costly source of P_2O_5 than wet-process phosphoric acid.

- For a reasonably rapid availability to crops, the product should be finely ground. The TVA product was ground to pass a 10-mesh screen; 15 to 30% was minus 100-mesh. Product of this size fell into disfavor when granular fertilizer became popular.

- Calcium metaphosphate was not as readily adaptable to use in granular compound fertilizers as competing materials such as CSP.

To overcome the last two disadvantages, pilot-plant studies were undertaken to devise methods for partially hydrolyzing and granulating calcium metaphosphate either alone or in compound fertilizers. A granular product containing 60% P_2O_5 with at least 20% of the P_2O_5 in a water soluble form was produced by TVA for several years. It was well received by distributors and farmers, but the cost of granulation made it uneconomical.

Granular compound fertilizers of good quality could be made by a process that involved hydrolysis with sulfuric acid followed by ammoniation, and a substantial amount of the TVA product was used in this way. However, most granulators were reluctant to provide the extra equipment that was required.

Ammonium Nitrate

A new synthetic ammonia plant was constructed and put in operation in 1942 to provide for production of materials for munitions. The main product was expected to be ammonium nitrate which at that time was used mainly as an ingredient of explosives. Before the war was over, the capacity of the several ammonium nitrate ordinance plants exceeded the need for munitions, and plans were made to divert the product to fertilizer use to help increase food production.

Ammonium nitrate was prepared for use as a munitions material by a batch 'graining' process in stationary pans with moving plows. The particle size was smaller and less uniform than today's granular fertilizer.

A program was undertaken in cooperation with the US Department of Agriculture to develop effective conditioning treatments for fertilizer use of grained ammonium nitrate and to introduce the product to farmers. The program was sufficiently successful to permit widespread use of the ammonium nitrate from munitions plants during and after the war.

After the war, TVA sought a better process for producing fertilizer-grade ammonium nitrate. At that time the prilling process was under development in Canada. TVA undertook pilot-plant studies of a continuous vacuum crystallization process. After some experimentation, conditions were found that permitted production of good-quality crystals that were mainly in the size range of 8 to 12 mesh (similar to prills). The crystals had very good storage properties when conditioned with kieselguhr.

Crystallization was selected rather than prilling mainly because of safety; prilling (and graining) involves handling highly concentrated solution at temperatures of 150^0 to 160^0C. Some serious explosions have occurred. On the other hand, the operating temperature of the crystallizer was 38^0C, and the maximum temperature in the process is about 60^0 which is attained while drying the crystals. Also, crystallization produces no fume, so control of atmospheric pollution is easier. Fume and dust from prilling towers is now a difficult problem in the fertilizer industry.

A crystallization plant was built containing five units, each rated at 105 tons per day. The crystals made in the large plant were smaller than expected, mainly in the range of 16 to 35 mesh (1.0 to 0.4mm). Considerable effort was spent in trying to increase the crystal size without much success. Crystals of the desired size (2.4 to 0.8mm) could be made only at a production rate of less than half of the rated capacity. Even then the large crystals were not satisfactory as they contained solution-filled cavities; after cooling, the solution leaked out through microscopic cracks, causing caking. The smaller crystals were sound and had satisfactory storage properties when conditioned with 4% of kaolin clay. The product was well received by farmers since it was better than the grained material they had previously received. However, when prilled ammonium nitrate became generally available, the farmers preferred it, and when bulk blending became popular, the crystalline material was unsuitable.

In 1957 a method for granulation of the crystalline material was put into practice and continued until the production of ammonium nitrate was stopped in 1965.

The reasons for the poor results with the crystallizer are not entirely clear. The capacity of the pilot plant was 50 pounds per hour, only 0.6% of the capacity of the large-scale units. This scale seems hardly adequate. Also, it is possible that not enough effort was spent on finding out how to increase the crystal size. This was partly because the product was considered acceptable at the time, and the future importance of larger, more uniform particle size was not foreseen. There were no screens for removing undersize from the dried product. A fine salt separator was installed after the plant was built to withdraw some of the suspension from a point in the crystallizer where the smaller crystals segregated and to redissolve them for return to the crystallizer. This improved the particle size, but the improvement was inadequate. Perhaps more effort should have been spent in improving the product. However, TVA felt the need for a more versatile process that would provide for making products other than straight ammonium nitrate; the granulation method filled this need.

Diammonium Phosphate

The main advantage of diammonium phosphate (DAP) is its high concentration which was recognized early in the TVA program. Production of DAP was studied in four pilot plants. Two of them, a spray tower unit and a saturator, were operated only with electric furnace acid. One of them using a crystallizer was operated first with electric furnace acid and later (with modifications) with wet-process acid. A fourth (preneutralizer-granulator) was operated only with wet-process acid.

Each of the processes showed some promise, but the crystallizer method was chosen for demonstration-scale production for reasons of economy; most of the equipment was on hand in the ammonium nitrate plant.

Initial operation (1956) of the crystallizer produced material of a rather small particle size. About 50% was smaller than 20 mesh. A screen was provided to remove minus 28 mesh fines, but it was overloaded and ineffective. Still the product had good physical properties, and the sizing was considered adequate for most of the intended uses. Later, when the need for a granular product for bulk blending became important, the sizing was improved to provide a minus 6- plus 16-mesh product. The grade of this product, produced from furnace acid, was 21-53-0.

The potential uses of DAP were expected to be (1) for direct application, (2) for production of nongranular mixed fertilizer, (3) for liquid mixed fertilizer, (4) for incorporation in granular compound fertilizers, and (5) for bulk blending. Studies were carried out to determine the suitability for each of these uses and to provide information for the users. When it became evident that the use of DAP in bulk blending had good potential, a process was developed on a pilot-plant scale for producing a granular product from wet-process acid (18-46-0). The process was adaptable to production of either straight DAP or NPK grades. It proved to be one of TVA's most widely used processes.

Industry readily adopted the TVA granular DAP process from pilot-plant work, and construction of a larger unit by TVA therefore was not necessary. Production by industry rose sharply. In 1958, total production of ammonium phosphates was equivalent to 172,000 tons of P_2O_5. Most of it probably was monoammonium phosphate (separate data for monoammonium phosphate and DAP are not available). By 1966, production had increased to 1,376,000 tons of P_2O_5, and in 1971 it was 2,359,000 tons of P_2O_5. Most of the additional production was DAP. TVA's production was discontinued in 1969, since TVA's objectives had been fully accomplished.

Ammoniation and Granulation

The development of processes for granulation of compound fertilizers is one of TVA's best known achievements. The beginning of the development was a project to improve the efficiency of ammoniation of CSP. It was common practice to ammoniate superphosphates in mixtures, and a process to obtain more complete reaction was desired. Alternatively, it was suggested that TVA could supply ammoniated CSP to distributors who did not have ammoniation equipment. The main reasons for ammoniation were to supply nitrogen from a low-cost source and to improve the physical properties of superphosphates and mixtures containing them.

Several types of equipment were tried before the TVA continuous ammoniator evolved (7). Its essential features consisted of a rotating, nearly horizontal cylinder in which the superphosphate formed an actively moving bed, a sparger for injecting ammonia or ammoniating solution in a uniform or predetermined pattern at an appropriate point under the bed, and a flow of air through the cylinder to carry away water vapor. When properly operated, the device proved to be highly effective for attaining the maximum extent of ammonia absorption with minimum loss. Granulation was not an objective in these tests, but it was observed that the product of ammoniation of CSP with anhydrous ammonia was mainly granular, and the extent of granulation could be controlled by recycling part of the product or cooling with air flow through the ammoniator.

About this time (1954) the need for granulation of compound fertilizers in the United States was recognized by industry. The concentration of compound fertilizers had been gradually rising because of substitution of CSP for part of the single superphosphate, substitution of ammonium nitrate for ammonium sulfate, and elimination of fillers. The higher analysis mixtures had poorer physical properties. It was evident that granulation would be required to permit further increases in concentration without serious deterioration of quality.

Various modifications of the continuous ammoniator and of formulations proved effective for granulation of a wide range of NPK ratios of compound fertilizer. Ammonia - ammonium nitrate solutions were used to supply most of the nitrogen. These solutions were much cheaper per unit of nitrogen than either ammonium sulfate or solid ammonium nitrate, so there was an incentive to use as much nitrogen from this source as possible.

A basic objective in the TVA granulation process was to supply sufficient heat so that granulation would take place at low moisture content and thereby minimize or avoid the need for drying. Addition of sulfuric or phosphoric acid permitted greater use of ammoniating solutions and increased the heat of reaction.

The TVA granulation process became very popular; the majority of granulation plants in the United States (probably about 200) now use it, and it is widely used in other countries. Also, the ammoniator-granulator proved useful as a means for granulating fertilizers that did not contain superphosphate.

Superphosphoric Acid

Early in TVA's program, pilot-plant studies were made to indicate the most economical method of producing phosphoric acid from phosphorus. One of the methods involved burning phosphorus in dry air and absorbing the P_2O_5 vapor in hot concentrated phosphoric acid. The process worked best with acid concentrations in the range of 76 to 83% P_2O_5. Such acids were more concentrated than orthophosphoric acid and were called 'superphosphoric' acid (SPA). Many of the properties of SPA were investigated by TVA a early as 1938, but no use in fertilizer processes was forseen at that time.

It was not until 1956 that studies of ammoniation of SPA with addition of water to make ammonium polyphosphate solutions were started. It immediately became apparent that the ammonium polyphosphates were much more soluble than orthophosphates, and therefore, more concentrated liquid fertilizers could be produced. Also, the high concentration of SPA promised advantages in shipping costs. Accordingly, TVA offered SPA for experimental use by distributors, and in 1957, commercial use in liquid fertilizer production started. However, in the earlier years of its production, TVA had only limited success in promoting the use of SPA by liquid fertilizer manufacturers. In 1959, TVA started producing ammonium polyphosphate solution and offering it to liquid fertilizer manufacturers. This program proved much more successful, and within a few years the solution became TVA's most popular product. The grade was 11-33-0 at first; later it was changed to 10-34-0 and then to 11-37-0 as research on the solubility in the complex system advanced.

The reason for the popularity of the solution as compared with SPA was the relative ease of transporting and storing the solution, and the convenience and simplicity of making liquid mixed fertilizer from it.

The success of SPA and solutions made from it led to experiments in concentrating wet-process acid to the SPA range. The experiments indicated that wet-process SPA would be suitable for liquid fertilizer production. Difficulties with sludge in the acid and ammoniated solution which were serious with orthophosphoric acid were relatively minor with SPA because polyphosphates sequestered the impurities. A pilot plant was built and operated to demonstrate the feasibility of producing wet-process SPA and to provide quantities for experimental use in liquid fertilizers.

Production of SPA by industry increased rapidly. By 1971, US production was estimated at 600,000 metric tons of P_2O_5, and additional capacity is planned.

Production of solid ammonium polyphosphate was started by TVA in 1967 after successful process development in bench-scale and pilot-plant equipment. The grade of the product, initially 15-60-0, was later increased to 15-62-0. This product also has proved popular, mainly for use in liquid fertilizer manufacture. Development of a process for making a similar product from wet-process acid is in progress.

TVA also pioneered in production of suspension fertilizer which is now a fast-growing segment of the liquid fertilizer industry.

Nitric Phosphates

In 1950 an economic evaluation of phosphate fertilizer processes indicated that the most economical process for use at Muscle Shoals was one that involved dissolution of phosphate rock in nitric acid. The process then planned involved production of dicalcium phosphate and ammonium nitrate as separate products and a calcium carbonate byproduct. This arrangement reflected TVA's concern with straight fertilizers. After bench-scale studies were complete, a pilot plant was built. However, it was operated only briefly to study the separate product process, since it seemed unnecessarily complicated. Also, TVA's policy of promoting straight phosphate fertilizers had changed to acceptance of the general demand for compound fertilizers. The nitric phosphate process evolved through several pilot-plant modifications. Finally, use of the continuous ammoniator to complete ammoniation and to granulate the product completed the development of a simplified process. A 20-ton-per-hour demonstration-scale plant was built and is still in operation (8). The products, 20-20-0 and 26-13-0, are of good physical quality and are popular with distributors, including bulk blenders, who mix them with granular potash. These products also have been used in granulation processes.

Ammonium Phosphate Nitrate

Development of an ammonium phosphate nitrate (APN) process was initiated by a report that state agronomists in certain wheat-growing areas recommended a 3-1-0 ratio fertilizer which the fertilizer industry was unable to supply. Pilot-plant studies of APN processes have been reported (9) which covered several alternative methods for producing APN products. The project was later expanded to include ammonium nitrate sulfate (ANS) because of the need for a high-analysis sulfur-containing nitrogen fertilizer in some areas. Production of the APN grades 30-10-0 and 25-25-0 and ANS grade 30-0-0-5S in a demonstration-scale plant has been described (10). The products met with good reception in some market areas, and supplies of similar products are now available from industry. The demand for such products in homogeneous granular form declined after the practice of bulk blending became sufficiently widespread, as similar products could readily be provided by blending.

Sulfur-Coated Urea

The need for an economical controlled-release fertilizer has long been emphasized by agronomists. TVA's work in this field has included experimentation with various N, P, and K materials (11). As agronomic information accumulated, it appeared that a controlled-release nitrogen fertilizer would likely be more useful than controlled-release P or K materials. The most promising of several controlled-release nitrogen materials that TVA has studied is sulfur-coated urea (SCU). Processes for manufacturing SCU have been under development by TVA for 11 years. Currently, development work is in progress in a 1-ton-per-hour pilot plant. The process is considered technically successful. However, assessment of the value of SCU in agriculture and the probable market is a complex problem, and it is not yet evident what the outcome will be. Sufficient evidence has been accumulated to show that SCU would be well worth the projected additional cost in some cases. The main question is whether the demand would be sufficient to support a sufficiently large scale of production to achieve the projected cost. As with many new products, the small-scale production results in relatively high cost, and a high cost would restrict the demand.

Other Pilot Plant Projects

The above-described projects probably are sufficient to illustrate some of TVA's successes and failures in the field of development of fertilizer processes and products. Obviously the scope of this paper does not permit even a brief account of all of TVA's work in these fields. In the list given below, other major pilot-plant projects are divided into two parts, one of which was related to fertilizer and the other was not.

Fertilizer-Related Pilot-Plant Projects

Potassium Metaphosphate
Blast Furnace Process for Producing Phosphoric Acid
Fused Calcium Magnesium Phosphate
Thermal Fixation of Atmospheric Nitrogen
Ammonium 'Metaphosphate' from Phosphorus, Air, and Ammonia
Oxidation of Phosphorus with Steam
Production of Ammonia Synthesis and Carbon Monoxide Conversion Catalysts
Utilization of High-Alumina Phosphate Ores
Utilization of Ferrophosphorus
Agglomeration of Phosphate Ore for Furnace Charge
Improved Processes for Producing Wet-Process Phosphoric Acid
Dewatering Phosphate Tailings (Slime)
Electric Furnace for Smelting Phosphate Fines
Fluorine Recovery Processes
Pan Granulation of Urea, Ammonium Nitrate, and Other High-Nitrogen Fertilizers

Urea - Ammonium Phosphates
Utilization of Byproduct Gypsum
Production of Ammonium Polyphosphate from Orthophosphoric Acid
Granulation of Ammonium Sulfate

Pilot-Plant Projects Not Directly Related to Fertilizer

Coal Carbonization
Feed-Grade Dicalcium Phosphate
Conversion of White Phosphorus to Red Phosphorus
Alumina from Clay
Aluminum-Silicon Alloy from Clay
Magnesium from Olivine
Organic Phosphorus Compounds
Recovery of Uranium from High-Alumina Phosphate Ore
Feed-Grade Molasses by Wood Hydrolysis
Recovery of Sulfur Dioxide from Stack Gas
Extraction of Manganese from Low-Grade Ores

Ingredients of a Successful Research and Development Program

There is a tendency for a chemical research and development organization to concentrate its efforts on lowering the production cost of fertilizers. However, production costs are often less than half of the total cost of fertilizer applied to the soil. Manderson (12) estimated that the production cost of nitrogen fertilizers, including return on investment, ranged from 27 to 42% of the total cost. The nitrogen fertilizers considered were anhydrous ammonia, urea, ammonium nitrate, and nitrogen solution. Distribution and marketing costs, including storage, transportation, handling, distribution, retailing, and application costs were 58 to 73% of the total. So possible savings in distribution and marketing costs often outweigh any likely saving in production cost.

It follows that it may be unwise to start a major new project on the basis of a prospective saving of a small percentage of production cost alone, particularly if the project involves a new product that may require new methods of distribution or application.

The saving in cost due to increasing the concentration of fertilizers is widely recognized and can readily be calculated for specific cases. Some other possible savings are less obvious and not so easily evaluated. For instance, bulk blending combines the functions of mixing and retailing and thereby saves one step in the distribution process and usually saves one physical movement. The resulting savings have been variously estimated at 10 to 20% of the delivered cost under US conditions (13). A similar saving is inherent in the liquid mixed fertilizer distribution system.

Savings in application costs are not easy to estimate when the farmer applies his fertilizer. Much depends on the size of the farm, on what value the farmer places on his time, and on what equipment he has or is willing to buy. With contract application, which is becoming common in the United States, the costs are more definite. For application of about 300 kg per hectare of granular fertilizer, the charge may be about $1.50 per hectare or about $5 per metric ton. Application of 150 kg of anhydrous ammonia per hectare may cost $4.30 per hectare or nearly $29 per ton. However, charges for contract application do not always reflect actual costs, as retailers may offer contract application below cost or without profit in order to promote sale of fertilizers. Various estimates of the actual cost plus a reasonable profit range up to $10 per ton for bulk dry granular fertilizer and up to $33 per ton for anhydrous ammonia. Obviously the costs depend on rate of application per hectare, size of farm, distance from the retailer's store, and other factors. Combinations of fertilizer application with irrigation, or fertilizer with pesticides, offer savings that can be calculated under specific conditions.

Bulk distribution saves costs of bags and bagging. Storage and handling of liquids are less expensive than for solids, in TVA's experience. Pipeline transportation of liquids may bring about further savings.

In each of the above examples, savings in distribution and marketing costs are only possible when suitable materials are available. For instance, bulk blending requires closely sized, strong, granular materials that can be shipped and stored in bulk and applied with mechanical spreaders.

The success of DAP was largely due to its suitability for bulk blending and resultant savings in distribution and marketing, although the development of a relatively simple, economical production process was a factor. Calcium metaphosphate was not very successful in spite of its high concentration because it did not fit in well with any distribution and marketing system.

TVA's experience indicates that there is little demand by farmers for straight phosphate fertilizer. During the first decade of the TVA program, straight phosphate fertilizer was distributed to farmers free of charge (except for transportation costs) either through the TVA test-demonstration program or through the Agricultural Adjustment Administration (a US Department of Agriculture agency). Farmers in these programs agreed not to use the fertilizer on row crops; it was used in soil conservation programs on pasture, hay crops, or on small grains in rotation with legumes.

As a Government soil conservation program, the use of straight phosphate (with lime and potash when needed) was presumably appropriate at the time when nitrogen fertilizer and mixed fertilizer were quite expensive. It did not become popular as a commercial farming practice.

In recent years, most of TVA's fertilizer materials have been sold to distributors who agree to evaluate their usefulness both for application as such and in mixtures. The newer materials are sold at a small discount to stimulate experimentation; materials of proved usefulness are sold at the market price of equivalent commercial products. Under these conditions, we find that most of our products are used in mixed fertilizers - bulk blends, liquid mixes, or granular compounds. In fact, most of our present products contain both nitrogen and phosphorus.

From the foregoing discussion it is evident that evaluation of a new fertilizer material is a complex process, involving all of the steps that the new material will go through after production until it is placed in the soil. Even then, evaluation must continue to determine whether the agronomic effectiveness of the new material is equal to or perchance greater than standard materials. When considering a new product, we need to ask: Who will use this product? How will he use it? Why should he use it in preference to present materials? What advantages will he gain? What difficulties will he encounter? How can they be solved? The answers to these questions may require a substantial amount of experimental work.

It follows that a research and development organization is more likely to be successful if it is thoroughly familiar with all steps in the distribution and marketing process. It is helpful, of course, if the organization has specialists in all fertilizer-related fields - agronomists, soil chemists, economists, agricultural engineers, and marketing specialists. It does not work very well, in my opinion, for each specialist to rely entirely on other specialists for ideas and guidance in their field. I believe that key personnel directing a fertilizer research and development program should have a general understanding of all fertilizer-related subjects. Some of this understanding can be gained by discussions with other specialists. It is particularly effective to plan tours to observe mixing plant practice, fertilizer application techniques, agronomic tests, and transportation and handling techniques. The tours should provide opportunities, not only for observation, but also for an exchange of viewpoints which can be very useful in promoting ideas for new or improved products that will fill the needs of the users. As practices and needs change rapidly, such tours should be frequent. International meetings like the present one with associated factory or field tours are very helpful, not only for the papers presented, but also for the individual or group discussions.

It is not always possible to foresee the best use pattern for a new product. For instance, TVA felt that SPA should be shipped to liquid fertilizer manufacturers who would produce ammonium polyphosphate solution. This scheme would take advantage of the high concentration of SPA (76% P_2O_5) to reduce transportation costs. However, at first, TVA had only limited success in promoting the sale of SPA. So TVA offered the ammonium polyphosphate solutions (10-34-0 and 11-37-0) for sale. These products met with excellent reception and soon became the most popular of TVA materials. Similar materials soon became available from industry. It appeared that many small liquid mixed fertilizer plants found it uneconomical to install the equipment necessary to convert SPA to the ammoniated solution; the additional freight on the solution was offset by the lower capital and operating cost of the plant. It may be concluded that marketing plans should be flexible enough to permit adaptation to the needs of the users in case these needs have not been correctly foreseen.

Naturally it would be helpful if the future needs of the users could be foreseen. For instance, if TVA had foreseen the trend toward granulation sooner, we might not have put so much effort on fused tricalcium phosphate and calcium metaphosphate, products that are ineffective in granular form. Likewise, if we had foreseen the abrupt change in the sulfur situation from scarcity to surplus, we might have put less effort on nitric phosphate processes. However, the best forecasts are often faulty, so while it is useful to make forecasts of trends in technology and markets, it seems best not to put too much faith in them.

I have often felt that there is a need for more emphasis on product development as opposed to process development. For instance, at the Second Interregional Fertilizer Symposium in Kiev, there were six papers on urea production processes. All of them stressed process improvements; improved or simplified equipment, better conversion, and better utilization of heat or energy. None of the papers dealt with improvement of the final product. The discussion at the meeting confirmed that there was a need for improving the final product. While process development is effective in lowering production costs, the success of a product depends on its suitability to the needs of the users.

Development of process and product should be thorough and on an adequate scale. What constitutes an adequate scale may depend on the type of process. In TVA's experience with granulation processes, a scale of 0.5 to 1.0 ton per hour is necessary to provide reliable data for design of full-scale plants. Experiments with smaller scale equipment can be useful in identifying promising approaches at minimum cost, but should not be relied on for design data. Ammonium nitrate crystallization is an example of a process in which the scale of the pilot-plant work was inadequate. In the final analysis the failure of the process was due to failure to provide product quality to meet the needs of the users. If the scale and extent of the pilot-plant work had been adequate, presumably either means for producing better quality product would have been found or the process would have been abandoned in favor of some other method.

Pilot plant projects should be preceded by small-scale studies that develop information on the chemistry of the process. As much of the necessary information as possible should be obtained in laboratory or bench-scale equipment to avoid unnecessary expense. It is often helpful to continue laboratory-scale studies concurrently with pilot-plant work to investigate problems that arise in the pilot plant. Concurrently with the development work, products from small-scale tests provide materials for agronomic evaluation in pot tests, and pilot-plant products provide larger quantities for field tests. Also, concurrent tests should be made of the physical properties that are important in storage, handling, transportation, and application.

The course of a development project naturally is influenced by the project leader. Project leaders vary in their strong and weak points, ingenuity, aggressiveness, and general approach. I have often wondered what would have happened to a project if it had been assigned to a different project leader. When a project is not going well, it may be helpful to reassign it to other people. Naturally this should be done tactfully so as to avoid openly labelling the project leader as a failure. There are many ways that new talents and viewpoints can be brought to bear on problems without abruptly changing the leadership.

Much has been said and written about mathematical design of an experimental program to obtain maximum information with a limited number of experiments and to permit computer evaluation of results. Presumably there are fields in which such experimental designs are useful. In my experience I have not encountered a development project in which a rigid mathematical design was helpful. On the contrary, there have been cases in which an experimental design delayed progress, frustrated the project personnel, and obscured an understanding of the process. In my opinion it is usually best to plan each experiment or series of experiments after the results of the last experiments have been collected and evaluated. This method helps the experimenter to gain a true understanding of the process, which is necessary for a successful outcome.

A recent report 'Success or Failure in Industrial Innovation' (14) describes a study of 29 pairs of new processes or products. Each pair consisted of one success and one failure of competing developments. For instance, two urea processes were compared.

The main conclusions were summarized in the order of their importance.

1. Successful innovators have a much better understanding of user needs, although they differed in the methods by which they acquired this understanding.
2. Successful innovators pay more attention to marketing, including market research, user education, and anticipation of customer problems.
3. Successful innovators perform their development work more efficiently than failures, but not necessarily more quickly.
4. Successful innovators make more effective use of outside technology and scientific advice; they have better contacts with the scientific community not in general but in the specific area concerned.
5. The responsible individuals in the successful attempts usually are more senior and have greater authority than their counterparts who fail.

TVA's experience tends to confirm the above conclusions. We might add that a proper understanding of the user's needs is helpful only when the users agree or can be convinced that their needs have been correctly assessed. The ultimate users of fertilizers are mainly farmers. Farmers in some areas tend to be conservative and not easily convinced that they should change their practices. TVA's test-demonstration program is helpful in showing farmers the advantages of new products and practices.

Farmers have diverse needs, varying with crops, soils, and climate. Most of TVA's fertilizers go to distributors, many of whom have small local plants (blending, liquid mixing, or granulation). These local distributors are familiar with the needs of the farmers in their area. In this case the users of TVA's products are the distributors, and an important factor is the versatility of the products to enable distributors to supply diverse needs in many areas.

Translation of Pilot Plant Results to Large-Scale Operations

The step from a pilot plant development to a full-scale operation is particularly important because mistakes at this stage can be quite expensive. Close cooperation between the pilot plant group, the design engineers, and the operating people is very helpful. Problems may arise in design that have been overlooked in the pilot plant, and may require further pilot-plant studies. In fact, it is useful to keep the pilot plant available for possible studies of problems that may arise during operation of the full-scale plant.

In our experience, most of the problems that cause trouble in the full-scale plant are mechanical difficulties that are not closely connected with the process. Most of these problems are in the transport of materials from one step of the process to another by conveyors, elevators, chutes, hoppers, and pumps.

In general, large-scale operations seem to produce a disproportionately large amount of fume and dust. In granulation processes, recycle rates tend to be somewhat larger than in the pilot plant.

A pilot plant usually is closely supervised by technically trained personnel, whereas most full-scale plants are not. For this reason it is desirable that automatic controls be employed more extensively in a full-scale plant. Operating instructions should be as explicit and complete as possible, and should cover all foreseeable contingencies. Pilot-plant engineers should participate in start-up operations and continue to assist until routine operation is established. After the preliminary operations it may become necessary to revise the operating instructions.

Conclusions

New processes and new products are most likely to be successful when they serve the needs of the users. Consequently, a fertilizer research and development organization is most likely to be successful when it is most fully informed about all phases of fertilizer production, distribution, and use. Savings in distribution and application costs for a new product can far exceed savings in production costs and, in some cases, can justify increased production costs. Conversely, difficulties in distribution and use can cause the product to be a failure even if the production cost is low.

Particular emphasis should be placed on quality of the final product as viewed from the needs of the user. As the user's needs change, up-to-date information on needs is essential, and future projections are helpful if reliable.

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DISCUSSION

DR. TRAVIS P. HIGNETT (Tennessee Valley Authority, U.S.A.) : In introducing my paper I shall not review the various TVA projects which I discussed. Instead, I shall emphasize the conclusions that I have drawn from these and other projects.

My first conclusion is that it is seldom worthwhile to devote a major effort to developing a new process for the sole purposes of reducing manufacturing costs, because even a substantial percentage reduction in manufacturing costs often represents only a minor percentage of total cost, which include the cost of raw materials, transportation, storage, handling and transportation of intermediates and finished products, distribution and application on the farm. All these costs put together usually far outweigh manufacturing costs. This is not to say that research on reducing manufacturing costs should be neglected. More worthwhile benefits can often result from improving product quality or lowering distribution costs. And I should like to emphasize that this conclusion refers particularly to the present state of the fertilizer industry. We all know of the remarkable and spectacular lowering of manufacturing costs that has taken place over the last 50 years, starting for instance with the Haber-Bosch process for fixing ammonia and subsequent improvements; this has certainly been worthwhile but has not left us with very much to improve on. I suppose every research and development organization dreams of such an achievement. I think most of us will have to be satisfied with smaller improvements and less spectacular developments. Improved processes that improve the quality of the product are well worthwhile. Products of an improved quality result in decreased distribution costs and increased demand; increased demand keeps the factory working full time which is a major economic advantage. Conversely, reduction of manufacturing cost at the expense of quality can cause increased costs in distribution and application, and farmer dissatisfaction. It is small solace to know that one has developed a low cost manufacturing process if the product is so unattractive that the factory is idle much of the time for lack of orders.

A major conclusion of my paper is that a research and development organization is the more likely to be successful, the more it is aware of the needs of the users and opportunities and pitfalls of the entire marketing and distribution chain. In considering a new product, one should always ask: who will use this product? How will he use it? Why should he use it in preference to present materials? What difficulties may be encountered? How can they be solved? What opportunities does the new product offer for decreasing distribution, marketing and application costs. The answers to these questions may require extensive research and study but this is more likely to pay off than process research. The average farmer does not want triple superphosphate or single superphosphate or urea, ammonium polyphosphate or phosphonitrilic hexanamid. What the farmer does want is a good crop and to get it he needs a fertilizer programme that supplies with maximum economy and convenience the elements needed in the proportions needed for his particular crop, soil and climate. So the success of individual materials will depend on how well they fit in to a system that will satisfy his needs. As farmers' needs vary widely both as to N, P and K requirements and the need for some or all the other essential elements, flexibility is necessary in manufacturing and distribution systems in order to satisfy all these diverse needs. As far as we can, we should base new process and product development on future rather than present needs. A major new development usually requires several years from its inception in the laboratory to commercial realisation. We must try to foresee conditions at least this far in advance. Unfortunately our vision of the future is imperfect so it is as well to re-assess our view frequently during the course of a development project. Also our judgement of the needs of the industry and the farmer may be faulty. The best insurance against disastrous failure is through pilot scale trials at every stage the new product must go through from factory to harvest. At each step we should solicit comments and evaluation from those who handle, transport, blend, market, apply and use the product. Some future trends seem obvious, that there will be a growing need for compound fertilizers of varying N, P and K ratios, secondary elements and micro nutrients will be needed for optimum results in an increasing number of cases and combinations. Labour will continue to become more expensive both in the factory, distribution chain and on the farm, so that those fertilizer products will be the most popular that require the least labour and be most convenient in handling, transportation and application. Increasing emphasis will be placed on the health and safety of factory workers and of the public and control of pollution of air, water and environment, will continue to be stressed and stricter regulations may be expected. Process and product development should take these points into account. Thank you.

MR. S.J. PORTER (Fisons Limited, U.K.) : The interests of the Tennessee Valley Authority in concentrated superphosphates and in calcium metaphosphate were still active in 1950 and the story of developments before and since that time, is most interesting. There are certain technical questions perhaps worth asking.

On page 7 we are told that TVA decided to crystallize ammonium nitrate, rather than prilling or graining, mainly because of safety. There have been mishaps in concentrating AN solution prior to crystallization, and I wonder what strength solution was used in the TVA crystallizers. Strong AN melts have been safely prilled in enormous quantities over the years. Surely the point is not that one operation is inherently safer than another but that ammonium nitrate solutions must be maintained in any process in a state of temperature, concentration and pH within the envelope of known safe conditions?

Then on page 8 in reference to diammonium phosphate we are told "later, when the need for a granular product for bulk blending became important, the sizing was improved". I enquire whether this refers to crystallizer operation producing a larger particle size or to the granulation of the crystalline product?

On page 18 we are told "a scale of 0.5 - 1.0 ton per hour is necessary to provide reliable data for design of full-scale plants. Experiments with smaller scale equipment can be useful in identifying promising approaches at minimum cost, but should not be relied on for design data." Fisons has successful experience over a period of 20 years with pilot plants smaller than this. The first granulation pilot plant which I knew in Fisons (in the middle of the 1950s) had a capacity, working continuously, of 0.05 ton per hour. From this we obtained information on which we successfully modified nine granulating plants with capacities rated, for the compounds in use in those days, of from 12 to 20 tons per hour. Although this experience was successful we were not entirely convinced of the wisdom of relying on such a large step in scale-up and we did provide for ourselves (by adaptation of an old production unit) another pilot plant whose capacity could be varied in the range 0.5 to 2 tons per hour. Whilst this was being built we checked a second 0.05 ton per hour pilot plant against the day-to-day operation of the 20 tons per hour unit in our nearby factory in Ipswich. We found on a carefully measured run complete correspondence between the conditions predicted from the granulation of a given formulation in the pilot plant and those obtaining in normal production operation of the full-scale plant. The small plant did not "feel", or in all cases behave, mechanically like the big plant and some difficulty could have been experienced in simulating the granulation conditions with more difficult formulations. The larger pilot plant was completely industrial in its design and behaviour but it was run most of the time at its minimum rate to economise in space for storage, and in labour and equipment for material handling. Operation at 0.5 ton per hour was still costly in this way. More recently an opportunity has come to make a fresh start with a new pilot granulating plant and having regard to all our experience over the last 20 years (and the four different embodiments of granulation pilot plants which we have used), we have opted for a versatile equipment with a capacity of 0.2 ton per hour, able to operate at rates down to 0.1 ton per hour while still maintaining a reasonable depth of material in the rotating equipment. This has been checked out against full-scale equipment and found to be satisfactory. Its "feel" is sufficiently like the full-scale plant to make it useful for training purposes.

The trend in the work of the TVA from straight P to NP systems is natural. I find it interesting that no work is reported on potash sources. Presumably this is because of the prevalence of the blending system in America but I should be interested to hear any comment.

Now on the philosophy of fertilizer process development, I find myself in agreement with the author. The criterion for success or failure of a product is its cost to the farmer applied to the soil. I make this point "to the farmer" because this is what determines whether the product will be bought. The customer is not concerned about the manufacturing cost, but only about the price. The cost to the farmer depends enormously on the local and national situation and this must be taken into account. It is dangerous to take a manufacturing pattern from one country and assume that it will be appropriate for another.

I cannot but agree with Mr. Hignett's views on the need for a combined view, in product and process development, of manufacturing and distribution and marketing aspects. We at Levington would go further than this. The combined view should embrace also the farm handling and spreading characteristics of the product, as well as its performance in use. This philosophy is embodied in our organization as well as in our work. The basic scientists, the chemical engineers, the handling and spreading specialists, and the agronomists, are in daily contact. In this way we seek to avoid the production of fertilizers whose appeal, be it on quality or on cost, is to the producer rather than to the user. I must admit that there is sometimes considerable difficulty in reconciling conflicting views and it would be interesting to hear if this also occurs at TVA and how conflicts are resolved there in the absence of an overriding commercial constraint.

DR. HIGNETT : In any process one must stay within the constraints of safe operation. There have, however, been some rather disastrous accidents and we were perhaps unduly influenced by the Texas City disaster when we were considering the safety of the process but that was TVA's view.

Mr. Porter asked how the sizing of DAP was improved. We did improve the sizing by making larger crystals and by installing better screens for separating the small crystals most of which were redissolved and returned to the crystallizer. There was some demand at that time for small crystals for use in liquid fertilizers so not all of the crystals were returned to the crystallizer.

On the question of the size of pilot plant I am not sure that I can come up with a good answer except to point out that in the TVA processes that we have been concerned with there were usually chemical reactions occurring in the ammoniator at the same time as granulation took place; it is necessary therefore and in fact it was our aim to use chemical heat of reaction to granulate and this rather limited the type of equipment that we could use to one which had not too much heat loss. Later on we also used to feed completely liquid feed, i.e. slurry for DAP process or for nitrophosphate process and still later concentrated solutions of ammonium nitrate or urea and the granulation took place in three types of equipment, the rotary drum, the pan and the pugmill. I am not sure whether this diversity of types of operation explains our need for larger pilot plants or whether we shall have to admit that Fisons is cleverer than we are.

Finally on potash materials, it is true that most of our work did not involve incorporation of potash in granular material. Although some of the pilot plant work did, the full scale work did not and this is mainly because of the manufacturing system in which most of the potash is added by manufacturers or blenders. In the U.S. at the present time probably as much as 60% of compound fertilizers are blends and 20% are liquid mixed fertilizers and in each of those cases the blender or liquid mixers add the potash to the basic materials. I quite agree with Mr. Porter that it is dangerous to take a manufacturing pattern in one country and assume that it will be appropriate for another and I hope that you did not infer that from anything in my paper.

And finally I did not wish to imply that we stopped our evaluation when the material was sold to the farmer. In fact I think I did mention specifically the cost of application and convenience to the farmer as some of the quality factors that might be overriding and of course agronomic efficiency.