between plant operation and laboratory-scale apparatus. There have been more than 250 runs made in our equipment in an endeavor to understand better the nature of the materials to be ammoniated and granulated, and the factors affecting granulation and ammoniation. These results will be reported at a later date.

Conclusion

The laboratory ammoniator–granulator which has been built and tested permits determination of granulation efficiency and ammonia absorption under controlled conditions with small quantities of raw materials.

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FERTILIZER TECHNOLOGY

Application of Slurry-Type Processes in the TVA Ammoniator-Granulator

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Pilot-plant studies were made of several processes for the production of granular, high-analysis fertilizers in which reaction slurries or liquids comprised a major proportion of the feed to a TVA-type ammoniator-granulator. Processing was characterized by relatively high recycle ratios (1 : 1 to 5 : 1), since recycle was used as the primary control of granulation. Data are presented to show the effects of process variables on recycle requirements, flexibility of control of operation, and quality of granules. Variables studied included formulations, methods of slurry distribution, size and temperature of recycle, size range of granulator discharge, and special drying, crushing, and screening procedures.

SINCE ITS development, about 10 years ago, the Tennessee Valley Authority (TVA) continuous ammoniator has met wide acceptance in the fertilizer industry. There are now more than 150 ammoniators of this type in use in plants in 37 states. It is estimated that over two thirds of the granular fertilizer used in the United States in the past few years was produced in these units.

More recently, pilot-plant work with the TVA-type ammoniator has shown that it can be used to advantage as an acidulating drum in the production of superphosphates (*4*) and for processing slurries of fertilizer materials (*2*). There is at present limited commercial application of these processes.

This article discusses the use of the ammoniator in slurry-type processes, which are of interest because of the generally lower cost of raw materials and the variety of higher analysis grades that can be produced. The material covered does not entail a complete description of any one process, but includes general considerations based on observations and data obtained in pilot-plant work on several slurry-type processes.

Pilot-plant studies that form the basis for this paper include the following.

Utilization of Calcium Metaphosphate. In this work a slurry of hydrolyzed calcium metaphosphate was ammoniated and granulated with other fertilizer materials to produce a variety of grades of granular fertilizers (*5*).

Nitric Phosphates. Extraction slurry of nitric and sulfuric or phosphoric acids and phosphate rock was ammoniated and granulated with other fertilizer materials in the continuous ammoniator (*2*).

Preneutralization Studies. This work included prereaction of sulfuric acid, wet-process and furnace phosphoric acids, and nitric acid with ammonia and/or nitrogen solutions in an open tank followed by completion of ammoniation and granulation with other fertilizer materials in the TVA-type ammoniator-granulator. This would be considered as a partial slurry-type operation, since solid fertilizer materials usually comprise a considerable portion of the formulations.

Production of Granular Diammonium Phosphate. This process recently developed by TVA utilizes a preneutralizer and continuous ammoniator. Excess ammonia fed to the drum to produce diammonium phosphate is recovered by scrubbing the exhaust gases with the phosphoric acid used in the process. Straight diammonium phosphate as well as several N–P–K grades can be produced (*3*).

Equipment Requirements and Processing Characteristics

Conventional ammoniation-granulation plants require additional equipment for utilizing slurry-type processes. Changes in and additions to the plant are comparatively minor for use of a preneutralizer and are at present included in several plants. For separate process application, such as the production of nitric phosphates and granular diammonium phosphate, more equipment is required. In the nitric phosphate process (*2*), a two-stage extraction unit is required. Auxiliary equipment for feeding phosphate rock and acid and facilities for storage of the nitric acid also are required. The process for granular diammonium phosphate (*3*) requires a preneutralizer and a scrubber for recovery of ammonia as the main additional equipment.

The slurry-type processes are characterized by the need for high recycle ratios (usually 1:1 to 5:1) for control of granulation. This results from the use of formulations containing relatively large proportions of water and, in most instances, the formation of large proportions of soluble salts. The high heat of reaction from increased use of acid and ammonia in some of these processes also contributes to the formation of the liquid phase.

The use of high recycle ratios is undesirable, chiefly because it reduces the net production capacity of the equipment and increases the amount that must be conveyed, dried, crushed, and screened. For these reasons, every effort is made to decrease the requirement of recycle, particularly in plants that were not designed for handling large amounts of recycle.

The work carried out by TVA has shown that there are several ways of decreasing recycle required in slurry-type processes that utilize a TVA-type continuous ammoniator-granulator.

Evaporation of moisture through efficient use of heat of reaction.

Change in formulation.

Control of moisture content, size, and temperature of recycle material.

Effective distribution of slurry.

Heat of Reaction. A considerable proportion of the moisture in formulations can be removed by efficient use of the heat of chemical reaction when acids are neutralized with ammonia or ammoniating solutions. This can be done effectively in some instances through use of a preneutralizer. The preneutralizer serves the twofold purpose of removing a large part of the water and heat of reaction before the feed materials reach the ammoniator drum. Also, in almost all processes, a considerable proportion of water can be evaporated in the ammoniator-granulator.

Maximum use of heat of reaction for removal of moisture in the preneutralizer is limited by loss of ammonia and decomposition of nitrates and by decreased fluidity of the slurry. It also is limited in the drum by loss of ammonia and increased plasticity of formulations that contain a considerable proportion of ammonium nitrate. The authors have found it necessary to maintain the temperature in the preneutralizer not higher than 240° to 275° F. in most applications to prevent such difficulties. A convenient method for control of the temperature is through the addition of water directly to the preneutralizer for evaporative cooling. Maximum allowable temperature in the drum depends largely upon the proportion of ammonium nitrate and other soluble salts. For diammonium phosphate and many N–P–K grades using the preneutralizer, temperatures of 190° to 220° F. in the ammoniator drum have been best. For other grades, such as 12–12–12 nitric phosphate, best ammoniation-granulation was at lower temperatures in the range of 150° to 160° F.

An example of effective utilization of heat of reaction for removal of moisture was in the work on production of granular diammonium phosphate. In the pilot plant, more than 90% of the water in the feed materials was removed by the heat of reaction. In typical tests, about 50% of the input water was removed in the preneutralizer and 40 to 43% in the ammoniator. In this process, full use of heat of reaction in the ammoniator-granulator can be realized because of the limited plasticity and solubility of the diammonium phosphate and because a scrubber is used to recover ammonia evolved from the drum.

Formulation. The recycle requirement often can be decreased by changing the formulation to decrease input moisture or to provide more heat of reaction for evaporation of moisture. Also, it can be decreased by decreasing the heat of reaction when liquid phase is due principally to the presence of large quantities of highly soluble salts such as ammonium nitrate. Changes in formulation may result in higher formulation costs which must be weighed against the higher net production capacity that is obtained. In pilot-plant work on nitric phosphates, inclusion of ordinary superphosphate in a 12–12–12 formulation greatly reduced the recycle ratio by decreasing the input moisture. This is shown in the following tabulation.

Units P_2O_5		Recycle Ratio Required, Lb./Lb. Product
From ordinary superphosphate	From phosphate rock in extraction slurry	
0	12	3.4
3.5	8.5	2.5
6	6	1.6

In plants that produce ordinary superphosphate, the net production could be practically doubled without a great increase in formulation cost by supplying six units of the P_2O_5 as the comparatively cheap, captive ordinary superphosphate.

When potash is included in formulations of slurry-type processes to produce N–P–K grades, the recycle ratio that is required is not nearly as high as for N–P grades. With one formulation for a 19–49–0 ammonium phosphate, the recycle ratio was 2.6; when 450 pounds of potassium chloride were included to produce a 14–35–14, the recycle ratio was only 1.3. Potash is considerably more effective than an equal weight of recycled fines in controlling granulation. Its effectiveness results not only from its physical nature and dryness, but also from chemical reaction to form salts that decrease the solution phase in the granulator.

Moisture, Size, and Temperature of Recycle. Recycle of low moisture content decreases the amount of recycle required. This is shown by the water balances given below for formulations with low and high ammonium nitrate contents. These formulations require, respectively, about 5 and 3% of moisture for good granulation. In the first case, the recycle ratio increased from 2.3 to 3.0 as the moisture content of the recycle increased from 1 to 2%. In the second case, the same increase in moisture content increased the recycle ratio from 5 to 10.

Conditions	Low Ammonium Nitrate Formulation		High Ammonium Nitrate Formulation		
Moisture content of raw material, %	13		8		
Moisture for granulation, %	5		3		
Moisture content of recycle, %	1	2	0.5	1	2
Recycle ratio required	2.3	3.0	2	5	10

In practice, the effect often is much more pronounced than that indicated by a moisture balance. Sometimes it may be advisable to dry the product more than is necessary for good storage and handling properties in order to decrease the recycle requirement to a reasonable level.

Particle size of recycle is very important. Better control of granulation and lower recycle requirements result from the use of fine rather than coarse material, probably because much greater surface area is afforded by the finer material and the smaller particles have to grow more when coated with or agglomerated with slurry to become oversize. The lower moisture content of the finer material that usually results at the same condition of drying is important to a lesser extent. The importance of particle size of recycle is shown by material containing about 50% +12 mesh which required a recycle ratio of 5.2 as compared with 3.4 when material with only about 10% +12 mesh was used. These data were from tests of the production of 12–12–12 nitric phosphate. The practice that is often employed of returning product size material as recycle is not efficient. Screening of recycle at 10- or 12-mesh and recrushing the oversize would be advisable. Also, it is beneficial to adjust granulation to produce directly as much as possible of fine material required for recycle.

The effect of temperature of recycle has been found to be different for different formulations. Whether it is best to use cooled or hot recycle depends on the formulation being used and, especially, on the amount of highly soluble salts, such as ammonium nitrate present. It is best to use hot recycle to maintain a higher temperature in the ammoniator and evaporate more water when producing diammonium phosphate or nitric phosphate grades such as 6-12-12, which contain little or no ammonium nitrate. On the other hand, cooled recycle is better for production of fertilizers such as 12-12-12 by the nitric phosphate process or 20-10-10 by preneutralization to decrease the temperature and, therefore, the liquid phase. In producing diammonium phosphate in the pilot plant, the use of recycle at 160° F. instead of at 100° F. decreased the recycle ratio from 3.3 to 2.6 by increasing the amount of water evaporated from the granulator.

Distribution of Slurry. Effective distribution of slurry in the ammoniator is important in obtaining good operation with minimum recycle. Distribution is equally important in decreasing the proportion of oversize material and in obtaining good ammoniation. Distribution of slurry will be discussed at greater length in connection with design and operation of the ammoniator and accessory equipment.

Design Features and Operating Techniques

Feeding and Metering Equipment. There are no particular problems in control of feeding solids in the slurry-type operations. However, the use of considerably higher proportions of acids and nitrogen solutions makes accurate metering of these liquids important. The magnetic-type flowmeter, which is now quite widely used, especially for wet-process acid, gives very dependable results and accurate metering of practically all types of liquids.

Reaction Vessels and Preneutralizers. The main additional equipment required for the slurry-type processes consists of the reaction tanks for extraction slurry or a preneutralizer for reacting the large proportions of acids and ammoniating solution or ammonia. The following features appear important from pilot-plant experience.

Size of Tanks. Retention time is important for extractors and at least two stages may be required. Surface area for evaporation of water as well as volumetric considerations is quite important in the preneutralizer because of the large quantity of water evaporated. Generally 15 to 40 minutes' retention for extraction and 6 to 10 minutes for preneutralization is satisfactory. In the pilot plant, up to 300 pounds of water were evaporated in the preneutralizer per hour per square foot of surface. Large-scale design probably should be based on not more than about 200 pounds per hour per square foot, however. Ammonia loading of 35 to 50 pounds of ammonia per hour per cubic foot of preneutralizer liquid was found to be satisfactory in pilot-plant work, and rates in this range would be recommended for large-scale units.

Adequate freeboard is quite important in extraction tanks and preneutralizers for control of foaming and splashing. Freeboard of 25 to 50% should be satisfactory in most cases.

Agitation. Turbine-type agitators generally are best for viscous slurries and for ammoniation. In some cases, when very thick slurries are being handled, two turbines on a single drive shaft may be required.

Maximum dispersion of reactants by use of well designed spargers for acid and ammonia is important in the preneutralizer for efficient ammoniation and decreased fuming. Separate circular drilled pipe spargers for acid and ammonia were found to give good results in the pilot plant.

A good exhaust system is needed for removal of fumes and the large quantity of water vapor from a preneutralizer.

Gravity feed from extractors or the preneutralizer to the ammoniator avoids pumping a hot, abrasive slurry and metering of reaction slurry. The feed line to the ammoniator should be as short and straight as practical and should be steam jacketed, for some applications, to avoid loss of heat.

Ammoniator. The recent trend in the design of TVA-type continuous ammoniators has been toward longer units; drums 12 to 16 feet long are fairly common. These drums generally are designed for carrying out the ammoniation in the first half to two thirds of the length, with a granulating section at the discharge end. For slurry-type processes, the separate granulating section may not be necessary and the greater length might be more effectively used for greater length of slurry and ammonia distributors. Drums with a 1:2 diameter to length ratio, such as a 7 × 14 or 8 × 16 foot drum, are quite common and should be of suitable size for slurry-type processes. Units of this size should permit a total throughput of 40 to 50 tons per hour and have a net production rate of about 15 tons per hour when the recycle ratio is about 2:1.

The speed of the drum is important for proper bed action to allow good granulation and efficient ammonia absorption. A relationship that has been found to be very convenient for determining the desirable speed of rotation for any size of ammoniator from a 1-foot diameter laboratory unit to a plant-scale unit is based on critical speed. This relationship was reported by Brook (*7*) in a discussion of fertilizer granulation in England. Critical speed is the speed at which typical granular material would barely be carried over the top point in a clean, open drum. It can be determined by the relationship:

$$\frac{76.5}{\sqrt{D}} = \text{revolutions per minute for 100\% critical speed}$$

D = drum diameter, feet

For ammoniation-granulation work, the best operating range ordinarily is 35 to 45% of critical speed. With submerged distributors about 35% is best; when a slurry is being granulated by coating on recycle without ammoniation, the higher speed gives better bed action. For a 7-foot diameter drum, this calculation would indicate a speed of about 10 r.p.m. for 35% of critical speed, or 14 r.p.m. for 45% of critical speed. A drum speed of 10 to 12 r.p.m. probably would be best for most purposes. Increased difficulty in supporting submerged distributors and somewhat increased power for operation may result at the higher speeds; many plant-scale units use a lower range of about 25% of critical speed for these reasons.

Because of the somewhat wet and sticky bed in the drum, an efficient scraper is important in a slurry-type operation. A reciprocating scraper similar to that at present used in a few plants should be quite helpful. This type of scraper consists of separate blades, or teeth, on a beam that moves back and forth at 5 to 10 cycles per minute to shave or cut the material from the walls of the drum. Use of such a scraper instead of the usual stationary type reduces the load on the drive for the drum and is more efficient in preventing build-up on the drum walls because of its more positive cleaning action.

In the authors' pilot-plant work, the depth of bed was about one fourth the diameter of the drum. Improved granulation without sacrifice in ammoniation efficiency has been reported for proportionately shallower bed depths in ammoniators for slurry processes in Europe; plant-scale units with bed depths of only about 12 inches were used successfully.

Distributors for ammonia or ammoniating solution of the usual slotted type, or the somewhat simpler drilled, pipe-type distributor submerged in the bed, were satisfactory in pilot-plant work. As would be recommended for any type of ammoniation work, these distributors should be as long as practical. The authors have tested both the "humped" distribution pattern as recommended in the original TVA ammoniator design and linear distribution. There was an indication of somewhat higher degree of ammoniation and lower loss of ammonia with linear distribution which is opposite to that obtained in ammoniation of superphosphate. For best results, the ammonia distributor should extend some distance beyond the last point of slurry distribution.

Because of the nature of the slurries, distribution beneath the bed is impractical. Efficient distribution of the slurry on top of the bed is important. Uniform distribution of the slurry over the greater part of the length of the bed is desirable. Excessive feed of slurry in one area causes increased agglomeration with excessive oversize and can result in poor ammoniation. Several types of distributors were tested in pilot-plant work. The main points for consideration are that the distributor should be simple, free from restrictions that would lead to plugging with solids, and easily cleaned, preferably during operation. Of the several types of distributors tested in the pilot plant, the best results were obtained with a saw-toothed distributor or an atomizing nozzle using compressed air.

The saw-toothed distributor (Figure 1) consisted essentially of a 1 $^1/_2$-inch stainless steel pipe, closed at one end, with a serrated or "saw-toothed" slot along one side. The slurry flowed by gravity into the open end of the pipe and was divided into a number of individual streams as it flowed over the saw-toothed weir. The saw-toothed weir was located about an inch outboard from the wall of the pipe for best results, and a cover plate was included to prevent solids from falling into the open slot.

The spray nozzle (Figure 2) consisted of a $^1/_4$-inch open pipe nipple for slurry and a flattened pipe nipple for compressed air, which was fastened in a position to cause the stream of air to impinge on the slurry as it flowed from the $^1/_4$-inch open pipe. After some adjustments in position and angle of the slurry and air supply nipples, a fixed arrangement was devised which gave a good spray pattern and was comparatively free from operating difficulty. A short metal deflector plate below the slurry nipple improved atomization of the slurry and decreased the amount of air required for good operation.

In the slurry-type processes, a considerably larger amount of water usually is evaporated in the ammoniator than in the applications using predominantly solid feed materials. In pilot-plant work on production of granular diammonium phosphate, as much as 300 pounds of water per ton of product were evaporated by the heat of reaction in the ammoniator. For good removal of this large amount of moisture, an efficient exhaust system of greater than usual capacity is needed.

When using high recycle ratios (2:1 or higher), pilot-plant experience showed that it is best to maintain granulation somewhat on the "fine" side. The purpose is to maintain a range of particle size so that most of the recycle requirement can be obtained by screening at 10- or 12-mesh undersize. If the usual range of good granulation is maintained, with a high percentage of onsize material, there will likely be only a small percentage of fines, and much of the recycle will have to be provided by crushing oversize and product size material or by using the less effective coarser material. One of the hardest jobs the authors have had is convincing the operators of the advantage of operating the ammoniator-granulator on the fine side, since the material as discharged from the drum does not have the good appearance usually associated with high granulation efficiency. The following size distribution for granulation of diammonium phosphate is typical of desirable operation: 6% +6 mesh, 32% −6 +12 mesh, and 62% −12 mesh. This operation required a recycle ratio of about 2.5:1; therefore, only about 28% of the throughput can be taken as product and about 72% must be returned as recycle. With the range of granulation shown, most of the recycle is provided by the −12-mesh undersize with only a small amount of the throughput (6%) to be crushed. Another important factor is that the increased surface area of the finer material improves ammoniation and increases the rate of moisture removal in drum and dryer. The importance of this control on the granulation range has been demonstrated many times in the pilot plant.

Balancing out the operation to provide consistently the necessary recycle and take-off of product is a problem in the higher recycle operations. Several schemes for balancing recycle with production have been employed in plant-scale units. These include:

Variable size of openings in the undersize screen.

Adjustable gates to return all or part of the undersize from various screen sections as recycle.

Surge bin for recycle (kept at fairly steady level; not exactly a balancing method).

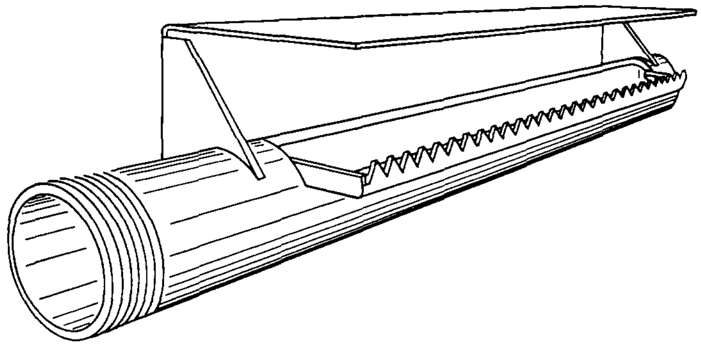

Figure 1. Modified "saw-tooth" distributor

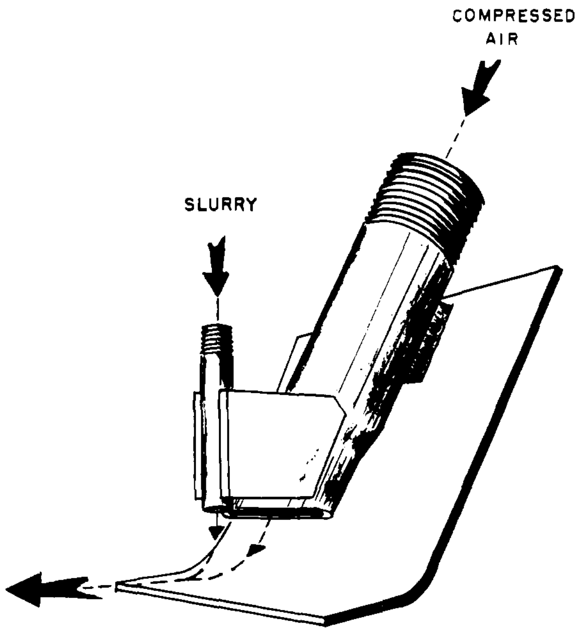

Figure 2. Slurry spray nozzle

Weigh spans on product and recycle belts (excess product crushed and returned with recycle).

Dryer and Cooler. No special features of dryer or cooler design are required; however, it is important to ensure adequate capacity for these units. They must be sized on the basis of total throughput, which may be two to five times net production. If drying is not adequate, a gradual increase in moisture content of recycle can result; this leads to higher and higher recycle requirements and ultimate failure. Both cocurrent and countercurrent drying were tested in the pilot plant, the former being preferable in some applications and the latter in others. In general, fertilizers having a high proportion of ammonium nitrate or other highly soluble salts have less tendency to soften and stick in the dryer, if countercurrent drying is used. As was pointed out earlier, control of granulation to minimize oversize is quite important. This is particularly true for good dryer performance, since the oversize is difficult to dry and usually contains considerably more moisture after drying than the product and undersize. The +6 mesh oversize has been found to contain as much as 2% moisture when the sized product had only 1% and the undersize about 0.6%. If granulation cannot be controlled to give a low proportion of oversize, accumulation of moisture in the recycle will result. One method that has been used to overcome this effect is to return crushed oversize to the dryer to allow more thorough drying.

The use of hot recycle is a definite advantage in the production of grades of fairly high recycle for which higher temperature in the ammoniator is desirable. If the plant is designed for such application, it would be advantageous to screen the product directly from the dryer to allow return of hot recycle, with cooling being confined to the sized product fraction.

Crushing and Screening. Efficient and comparatively trouble-free performances of crushing and screening equipment are very important. It is highly desirable to prevent excessive oversize and thereby avoid an unduly high crushing load for the higher recycle processes and to prevent an increase in moisture content of the recycle. The most satisfactory type of crusher the authors have tested in the pilot plant is a chain mill. This type of equipment is comparatively free from build-up of solids, is partially self-cleaning, and produces a substantial proportion of very fine material, which is desirable as recycle.

One advantage of the generally higher recycle requirements of slurry-type processes is that the product can be sized closely to produce very uniform granules of about 6 to 10 mesh. If no product is needed from the crushed oversize fraction, it should not be returned to the product screen, since the presence of irregular crushed particles in the product is undesirable. A second undersize screen in the crushing circuit can be used to provide fines for recycle from the oversize. If the proportion of oversize is small, the crushed material could be returned as recycle without screening. In general, the screen capacity should be at least 2 sq. feet of screen surface for each hourly ton of throughput for the process.

Conclusions

Slurry-type processes have several important advantages: Lower formulation costs can be realized through use of cheaper raw materials, higher analysis grades can be produced, and the closely sized, well shaped granular products have excellent physical properties. Despite the lower net production because of high recycle rates and the need for additional equipment and more extensive process control, it is expected that the use of such processes will continue to increase. Pilot-plant work has shown that the TVA-type ammoniator-granulator is readily adaptable to use in slurry-type processes.

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FERTILIZER MATERIALS

Exploratory Studies of Hydrolysis and Ammoniation of Calcium Metaphosphate

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Since 1938, the Tennessee Valley Authority has produced a vitreous fertilizer material called calcium metaphosphate, $Ca(PO_3)_2$ (about 65% total P_2O_5), by reacting phosphorus pentoxide with phosphate rock (*5*, *6*). Acceptance of calcium metaphosphate, however, has been limited because of its low water solubility and because, when used in the production of compound fertilizers, it cannot be used to fix ammonia, the cheapest source of nitrogen. Several methods for increasing the water solubility of calcium metaphosphate and adapting it to ammoniation have been studied. In one reported process (*4*), ground calcium metaphosphate was hydrolyzed partially by treating it with sulfuric acid or phosphoric acid in the feed end of a TVA-type ammoniator-granulator and adding ammonia in the second half. Although 20 to 40% of the P_2O_5 in the calcium metaphosphate was converted to a water-soluble form, no ammonia-fixing capacity was realized from the calcium metaphosphate; the ammonia retained in the product was calculated to be the amount that would combine with the acid in the formulation. In another process, pulverized calcium metaphosphate was hydrolyzed with water and acid in an open tank and the resulting slurry was ammoniated and granulated with other fertilizer ingredients (*8*). About 3 pounds of ammonia per unit of P_2O_5 were fixed and 30 to 50% of the P_2O_5 in the product was water soluble.

The present paper describes two other processes for hydrolyzing and ammoniating calcium metaphosphate. One involves simultaneous hydrolysis and ammoniation in a slurry process by reaction under pressure with ammoniating materials. The other involves hydrolysis with hot water in a denning process to obtain a solid product that can be ammoniated.

Hydrolysis and Ammoniation under Pressure

Bench scale tests indicated that pulverized calcium metaphosphate could be hydrolyzed and ammoniated simultaneously by reaction with aqua ammonia under pressure. The reaction was carried out in a 2-liter pressure vessel equipped with a propeller-type