

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.

## FERTILIZER MATERIALS

# Exploratory Studies of Hydrolysis and Ammoniation of Calcium Metaphosphate

SINCE 1938, the Tennessee Valley Authority has produced a vitreous fertilizer material called calcium metaphosphate,  $\text{Ca}(\text{PO}_3)_2$  (about 65% total  $\text{P}_2\text{O}_5$ ), 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

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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TVA-type ammoniator-granulator and adding ammonia in the second half. Although 20 to 40% of the  $\text{P}_2\text{O}_5$  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  $\text{P}_2\text{O}_5$  were fixed and 30 to 50% of the  $\text{P}_2\text{O}_5$  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

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Exploratory studies were made of the hydrolysis of calcium metaphosphate (65%  $P_2O_5$ ) to obtain a product with a high degree of water solubility and a capacity for fixing ammonia. In some tests, pulverized calcium metaphosphate was hydrolyzed and ammoniated simultaneously with aqua ammonia under pressure of about 100 p.s.i. The resultant slurry contained about 4 pounds of ammonia per unit of  $P_2O_5$  and drying resulted in a product of 8-45-0 grade. Alternatively, ammonia-ammonium nitrate solution was used to produce higher nitrogen grades. About 40% of  $P_2O_5$  in the dried product was water-soluble. In other tests, pulverized calcium metaphosphate was hydrolyzed with hot water by a mixing and denning procedure under conditions simulating those encountered in a conventional superphosphate mixer and den. The product (52% available  $P_2O_5$ ) from the den was dry and friable, contained 80% of its  $P_2O_5$  in a water-soluble form, and had an ammonia-holding capacity of about 3 pounds per unit of  $P_2O_5$  when used in the TVA continuous ammoniator.

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agitator and external electrical heaters. Calcium metaphosphate ground to -100 mesh was placed in the reactor and aqua ammonia (18%  $NH_3$ ) was added. Although the reaction was exothermic, the rate was slow at low temperatures. Therefore, the reactor was heated externally until the temperature reached 150° F. The temperature continued to rise to about 250° F., at which point the material solidified. Heat was used again until the temperature was about 280° F. and until the material became sufficiently fluid to allow agitation. The maximum pressure during a test was about 100 p.s.i. After cooling, the product was removed from the reactor as a damp solid and dried in an oven at 150° F. to remove free ammonia and water. The dry products (9-48-0 grade) contained about 4.5 pounds of ammonia per unit of  $P_2O_5$ . About 97% of the  $P_2O_5$  was available; about 40% was water soluble.

A continuous process was visualized for the the reaction of calcium metaphosphate with ammoniating materials under pressure in a conventional reactor equipped with an agitator, or a long, slender reactor in which the velocity would be sufficient to prevent channeling without the use of an agitator. The latter was selected for use in pilot plant studies because it would be simpler and less expensive. The reactor (Figure 1) was about 2 inches in diameter and 40 feet long. It was made from sections of schedule 40 stainless steel (Type 316) pipe and was steam-jacketed. Water, calcium metaphosphate, and aqua ammonia or ammonia-ammonium nitrate solution were fed at controlled rates to a mixing tank; the resulting mixture was fed to the bottom of the reactor with a screw-type pump (Moyno pump equipped with a stainless steel rotor and a rubber stator). The products of the reaction, in the form of a thick slurry, were discharged at the top of the reactor through a valve with which the pressure on the system was controlled. A pressure of about 100

p.s.i.g. usually was used. From the reactor, the product slurry was passed through a cyclone vapor separator (3 gallons) where steam and excess ammonia were flashed off. The slurry was thixotropic, and agitation was used in the separator to increase its fluidity. The product from the vapor separator flowed by gravity to a collection tank. Samples of the slurry were dried in an oven at 170° F. and then analyzed.

The steam jacket was divided into three sections. However, it was not necessary to use the middle section of the jacket. In starting up, steam was fed to the top and bottom sections until the reaction started; this was indicated by a rapid rise in temperature. Thereafter, it was necessary to supply steam only to the bottom section to maintain the desired temperature. Temperature control was based on the reading of the thermocouple showing the highest temperature. The thermocouples were located near the discharge and 20 and 30 feet from the discharge. In most tests the highest temperature was at the discharge. Both aqua ammonia (12.5%  $NH_3$ ) and ammonia-ammonium nitrate solution (16.6%  $NH_3$ , 37.0% total N) were used, but no differences were noted in operation. The amount of water in the feed usually was about 2 pounds per pound of calcium metaphosphate, which preliminary tests had indicated as necessary to keep the slurry fluid enough to flow through the reactor.

The test periods ranged from about 4 to 8 hours. No major operating difficulties were encountered. There was no indication of any appreciable scale formation or build-up of material on the walls of the reactor. However, after a test was completed, the reactor was drained and washed out, since periods of 16 hours or more elapsed between tests and the slurry tended to solidify on cooling. The slurry pump operated satisfactorily; however, occasional replacement of the rubber stator was required.

Tests were made of the effects of temperature, retention time, and input degree of ammoniation. The conditions of the tests and analyses of the products are presented in Table I. The effects of these variables are plotted in Figure 2. The feed rate of calcium metaphosphate ranged from 96 to 300 pounds per hour. In tests of the effect of temperature, the retention time was 13 minutes and the input degree of ammoniation was 6 pounds of ammonia per unit of  $P_2O_5$  in the feed. The amount of ammonia fixed increased from 2.3 to 4.2 pounds per unit of  $P_2O_5$  as the temperature was increased from 230° to 320° F. Availability of  $P_2O_5$  remained at about 94%, but the proportion of  $P_2O_5$  in a water-soluble form increased from 33 to 45% as the temperature was increased. The slurry thickened considerably at about 330° F., and tests at higher temperatures could not be completed because of stoppages in the reactor.

Increasing the retention time from 4 to 13 minutes, with the temperature at 320° F. and ammonia fed at a rate of 6 pounds per unit of  $P_2O_5$ , resulted in an increase in the degree of ammoniation from 3.8 to 4.2 pounds of ammonia per unit of  $P_2O_5$ , an increase in  $P_2O_5$  availability from 87 to 93%, and an increase in  $P_2O_5$  water solubility from 23 to 45%. Clogging in the reactor prevented operation at retention times longer than about 13 minutes.

In tests of the effect of ammonia input, ammonia-ammonium nitrate solution was used at rates up to 4.6 pounds of ammonia per unit of  $P_2O_5$  and aqua ammonia was used at rates from 6 to 11 pounds of ammonia per unit. The temperatures were in the range of 300° to 330° F. and the retention times were 7 to 13 minutes. As the input of ammonia was increased from 2.3 to about 6 pounds per unit of  $P_2O_5$ , the degree of ammoniation of the dried product increased from 2.3 to 4.2 pounds. As the ammonia input was increased further to 11 pounds per unit of  $P_2O_5$ ,

**Table I. Reaction of Calcium Metaphosphate with Aqua Ammonia and Ammonia-Ammonium Nitrate Solution**

Test No.	Effect of Temp.			Effect of Time				Effect of NH <sub>3</sub> :P <sub>2</sub> O <sub>5</sub> Input							
	1	2	3	4	5	6	3	8	9	10	11	12	3	13	14
Feed rate to reactor, lb./hr.															
Ca(PO <sub>3</sub> ) <sub>2</sub> <sup>a</sup>	96	96	96	300	240	180	96	168	222	166	174	111	96	132	86
Aqua ammonia <sup>b</sup>	150	144	146	456	366	276	146	...	...	...	...	...	146	234	245
Ammonia-ammonium nitrate soln. <sup>c</sup>	...	...	...	...	...	...	...	75	114	96	108	101	...	...	...
Water	87	87	89	273	218	161	89	358	377	357	420	264	89	37	0
Feed ratios															
H <sub>2</sub> O:Ca(PO <sub>3</sub> ) <sub>2</sub> wt. ratio <sup>d</sup>	2.3	2.2	2.3	2.2	2.2	2.2	2.3	2.2	1.8	2.2	2.5	2.5	2.3	1.8	2.5
Lb. NH <sub>3</sub> /unit P <sub>2</sub> O <sub>5</sub>	6.1	5.8	5.9	6.0	6.0	6.0	5.9	2.3	2.5	3.0	3.3	4.6	5.9	6.9	11.0
Reactor conditions															
Maximum temp., ° F.	230	265	320	325	315	320	320	315	330	325	330	315	320	320	300
Retention time, min.	13	13	13	4	5	6	13	7	7	7	7	9	13	13	12
Pressure at top, p.s.i.g.	105	105	105	99	130	121	105	85	85	85	77	70	105	105	110
Dried product															
Chemical compn., % by wt.															
Total P <sub>2</sub> O <sub>5</sub>	50.3	52.6	48.1	47.7	49.4	50.0	48.1	38.6	39.8	39.0	33.6	33.1	48.1	49.2	49.2
Available P <sub>2</sub> O <sub>5</sub>	47.5	48.8	44.6	41.7	43.2	44.9	44.6	37.7	38.2	37.4	...	32.0	44.6	46.6	43.2
W.S. P <sub>2</sub> O <sub>5</sub>	16.8	18.8	21.8	10.9	12.8	16.3	21.8	17.4	17.2	17.0	...	14.1	21.8	14.4	13.3
Total N	4.8	5.4	8.3	7.4	7.7	8.3	8.3	10.5	12.1	12.3	11.6	16.2	8.3	9.1	9.0
NH <sub>3</sub> N	...	...	...	...	...	...	...	7.1	8.1	8.3	7.8	10.7	...	...	...
W.S. N	3.4	4.2	6.1	3.0	3.2	4.1	6.1	...	...	...	...	...	6.1	4.0	3.9
Available P <sub>2</sub> O <sub>5</sub> , % of total P <sub>2</sub> O <sub>5</sub>	94	93	93	87	87	90	93	98	96	96	...	97	93	95	92
W.S. P <sub>2</sub> O <sub>5</sub> , % of total P <sub>2</sub> O <sub>5</sub>	33	36	45	23	26	33	45	45	43	44	...	43	45	29	27
W.S. N, % of total N	67	72	69	41	42	49	69	...	...	...	...	...	69	43	43
Lb. NH <sub>3</sub> /unit P <sub>2</sub> O <sub>5</sub>	2.3	2.5	4.2	3.8	3.8	4.0	4.2	2.3	2.5	2.7	2.9	3.8	4.2	4.5	4.4
Ammonia recovered in dried product, % of input	38	43	71	64	63	67	71	98	100	90	88	83	71	65	40

<sup>a</sup> 64% P<sub>2</sub>O<sub>5</sub>, 26.5% CaO; -100 mesh (Tyler).  
<sup>b</sup> 12.5% NH<sub>3</sub>, 87.5% H<sub>2</sub>O.  
<sup>c</sup> 16.6% NH<sub>3</sub>, 66.8% NH<sub>4</sub>NO<sub>3</sub>, and 16.6% H<sub>2</sub>O.  
<sup>d</sup> Includes water in ammoniating media.

**Table II. Hydrolysis of Calcium Metaphosphate with Hot Water-Denning Process**

H <sub>2</sub> O:Ca(PO <sub>3</sub> ) <sub>2</sub> <sup>a</sup> Wt. Ratio	Denning		Product from Den					Product Cured 7 Days at 210° F.				
	Retention time, min.	Max. temp., ° F.	P <sub>2</sub> O <sub>5</sub> , %		W.S. of total	H <sub>2</sub> O, % <sup>c</sup>	P <sub>2</sub> O <sub>5</sub> , %		W.S. of total	H <sub>2</sub> O, % <sup>c</sup>		
			Total	Avail. <sup>b</sup>			Total	Avail. <sup>b</sup>				
-200-MESH CALCIUM METAPHOSPHATE <sup>d</sup>												
0.65	30	230	46.6	46.0	36.0	78	14.7	...	...	...	...	...
0.50	29	243	49.5	48.8	39.4	80	9.1	50.4	49.9	41.8	83	6.6
0.50	36	242	50.1	49.5	39.2	78	7.6	...	...	...	...	...
0.33	25	263	53.4	52.7	41.2	77	1.6	...	...	...	...	...
0.33	46	259	52.4	51.8	41.5	79	2.6	52.6	52.1	44.2	84	0.7
0.33	46	275	54.5	53.8	41.6	76	2.4	52.7	52.1	43.7	83	0.5
0.33	180	262	53.5	52.9	41.3	77	1.8	...	...	...	...	...
0.25	38	270	54.4	53.8	38.2	71	1.3	...	...	...	...	...
-16-MESH CALCIUM METAPHOSPHATE <sup>e</sup>												
0.33	66	218	54.8	54.1	28.4	52	7.0	...	...	...	...	...
0.33	75	215	53.2	52.6	32.9	62	6.5	...	...	...	...	...
0.33	135	229	53.4	52.9	36.9	69	3.2	52.4	52.0	45.1	86	0.7

<sup>a</sup> 65.5% P<sub>2</sub>O<sub>5</sub>, 25.8% CaO.  
<sup>b</sup> P<sub>2</sub>O<sub>5</sub> availability was 99% in all tests.  
<sup>c</sup> A.O.A.C. vacuum desiccation method.  
<sup>d</sup> 88% -200 mesh (Tyler).  
<sup>e</sup> 99% -16 mesh, 81% -48 mesh, 16% -100 mesh (Tyler).

the degree of ammoniation increased only to 4.4 pounds. P<sub>2</sub>O<sub>5</sub> availability was about 97% for products from tests in which the input degree of ammoniation was 2.3 to 4.6 pounds of ammonia per unit of P<sub>2</sub>O<sub>5</sub>. When the rates were higher, availability was lower (92 to 95%). The P<sub>2</sub>O<sub>5</sub> water solubility was about 44% at input degrees of ammoniation of up to about 6 pounds per unit of P<sub>2</sub>O<sub>5</sub>; at higher rates the water solubility decreased.

The data indicate that about 4 pounds of ammonia can be fixed per unit of P<sub>2</sub>O<sub>5</sub> without significant loss of P<sub>2</sub>O<sub>5</sub> availability. In the system such as

described, it would be necessary to feed about 20% excess ammonia. However, it should be feasible to recover the ammonia by scrubbing with water and recycling the aqua ammonia to the reactor. If an ammonia recovery system is not used, about 2.5 pounds of ammonia can be fixed without excessive loss of ammonia.

The grade of the dried products ranged from about 5-48-0 to 9-43-0 when aqua ammonia was used and from 10-37-0 to 16-32-0 when ammonia-ammonium nitrate solution was used.

Petrographic examinations of products made at 230°, 265°, and 320° F. (tests

1, 2, and 3, Table I) showed that calcium diammonium pyrophosphate [Ca(NH<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O] was a major phase. This is one of the phosphatic compounds recently identified in ammoniation products of hydrolysis of calcium metaphosphate (7). Other compounds found were monoammonium phosphate and calcium phosphate more basic than dicalcium phosphate.

The water solubility of the nitrogen in the dried products was determined by extraction of a 1-gram sample with 250 ml. of water at room temperature for 1 hour. In products made with aqua ammonia, about 30 to 60% of the nitro-

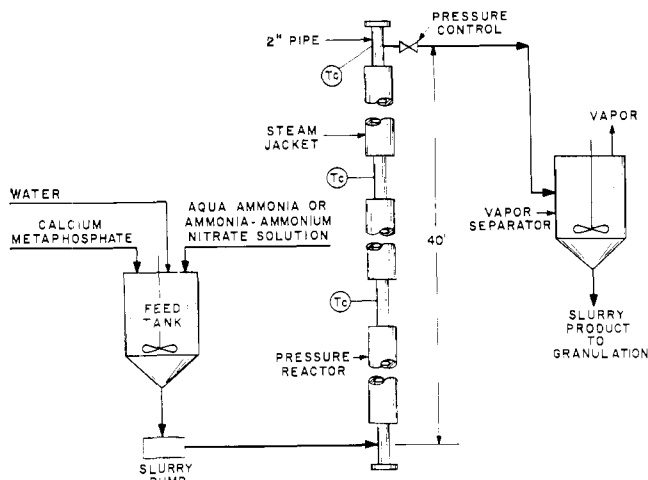


Figure 1. Equipment for reaction of calcium metaphosphate with aqua ammonia or ammonia-ammonium nitrate solution

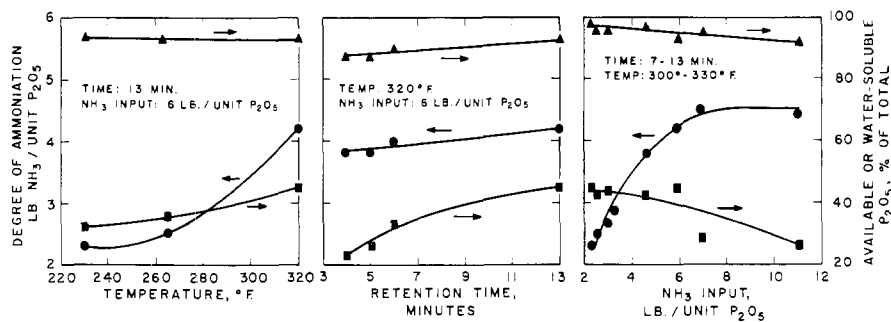


Figure 2. Effect of temperature, time, and ammonia input

● Degree of ammoniation ■  $P_2O_5$  water solubility ▲  $P_2O_5$  availability

gen was water insoluble. Products made with ammonia-ammonium nitrate solution contained less of their nitrogen in a water-insoluble form, since a large proportion of total nitrogen was present as ammonium nitrate. Greenhouse tests indicated that the water-insoluble form of nitrogen in these products was just as effective as standard water-soluble nitrogen fertilizers.

The product slurry from the vapor separator contained about 50 to 60% water. Tests of processing the slurry into a granular fertilizer were outside the scope of this work. However, there should be no problem in feeding the slurry to a rotary drum for granulation with recycle fines and other fertilizer materials.

#### Hydrolysis with a Hot Water-Denning Process

In earlier work by TVA (8), when finely ground calcium metaphosphate was mixed with water (0.6 lb.  $H_2O$ /lb. calcium metaphosphate) and heated to about 170° F., an exothermic hydrolysis reaction was initiated. The

temperature of the slurry rose to about 220° F. and, after 30 minutes, about 90% of the  $P_2O_5$  was in a water-soluble form. The hydrolyzate solidified to form a hard, porous mass. To prevent difficulties with thickening and setting up of the hydrolyzate, which was to be used directly in the TVA continuous ammoniator for the production of high-analysis granular fertilizers, some mineral acid was added with the water.

The observations of this earlier work suggested the possibility of producing a dry, porous product by hydrolyzing calcium metaphosphate in conventional superphosphate manufacturing equipment such as a cone mixer and a den. The product could be stored until needed for the production of high-analysis mixed fertilizers or for direct application. To test this method in laboratory equipment, a 600-ml. insulated beaker was used as a combination mixer and den. A propeller-type stirrer was used for agitation during the mixing step. The procedure for making a test was as follows: The beaker and insulation were heated to about 200° to 250° F. Boiling water was added to the beaker, and the agitator was started. About

300 grams of ground calcium metaphosphate were added to the beaker, and agitation was continued long enough to obtain thorough mixing. The mixture was fluid during the mixing time (15 seconds to 2 minutes). The agitator was removed, and the hydrolysis reaction was continued in the beaker to simulate denning. The reaction gave off heat which converted some of the water to steam and caused bloating of the mixture similar to that which occurs in the manufacture of superphosphate.

Results of the laboratory tests are shown in Table II. With finely ground calcium metaphosphate (88%, -200 mesh), about 80% of the  $P_2O_5$  in the denned products was in a water-soluble form when 0.33 to 0.65 pound of water was used per pound of metaphosphate. The maximum temperatures were developed in 20 to 35 minutes, and denning for an additional hour or two had no significant effect on water solubility; however, a further increase in water solubility to about 84% resulted when the products were cured at 210° F. for 7 days. When the initial water to calcium metaphosphate weight ratio was 0.50, the maximum temperature was about 240° F.; the products contained 8% or more moisture and appeared wet. When the water to calcium metaphosphate ratio was decreased to 0.33, the maximum temperature increased to about 270° F.; the products contained about 2% moisture and appeared dry. Decreasing the amount of water to 0.25 pound per pound of calcium metaphosphate resulted in a decrease in the proportion of water-soluble  $P_2O_5$  to about 71%.

In tests with coarser calcium metaphosphate (ground to pass 16 mesh), the rate of hydrolysis was slower, the maximum temperature was lower, and the proportion of  $P_2O_5$  in a water-soluble form increased with increase in retention time. In these tests, increasing the retention time in the den from 66 to 135 minutes increased the proportion of  $P_2O_5$  in a water-soluble form from 52 to 69%. Curing for 7 days at 210° F. resulted in an increase in water solubility to 86%. These results indicate that there would be no advantage in using finely ground calcium metaphosphate if time for curing is provided.

The  $P_2O_5$  availability was 99% in all tests. The products contained from 51 to 54% available  $P_2O_5$  when 0.25 to 0.33 pound of water per pound of calcium metaphosphate was used. Microscopic examination of the products indicated that the major phase was crystalline monocalcium phosphate monohydrate. Residual calcium metaphosphate was a minor phase.

A few exploratory tests of the process were carried out on a pilot plant scale using a TVA-type cone mixer and a

**Table III. Ammoniation of Hydrolyzate<sup>a</sup> from Denning Process**

Test No.	Max. Reactor Temp., ° F. <sup>b</sup>	Product				Degree of ammoniation, lb. NH <sub>3</sub> /unit total P <sub>2</sub> O <sub>5</sub>
		Compn., % by wt.		% of total P <sub>2</sub> O <sub>5</sub>		
		Total N	Total P <sub>2</sub> O <sub>5</sub>	Avail.	W.S.	
HYDROLYZATE CRUSHED TO -6 MESH						
50	95	1.1	52.6	99	72	0.5
51	148	7.0	50.8	99	42	3.4
52	225	7.4	50.8	99	40	3.5
53	347	7.8	50.7	99	43	3.7
HYDROLYZATE CRUSHED TO -20 MESH						
54	120	7.5	50.6	99	44	3.6
55	164	7.8	50.5	99	42	3.7
56	315	8.4	49.8	98	42	4.1

<sup>a</sup> 53.4% total P<sub>2</sub>O<sub>5</sub>, 52.7% available P<sub>2</sub>O<sub>5</sub>; 77% of total P<sub>2</sub>O<sub>5</sub> was water soluble.

<sup>b</sup> Tests made at 100 to 150 p.s.i. and retention time of 7 to 9 minutes.

continuous den of the Broadfield type (7); the retention time in the continuous den was about 50 minutes. About 1000 pounds per hour of calcium metaphosphate (-100 mesh) and 450 pounds per hour of hot water (210° F.) were fed to the cone mixer. The temperature of the mixture as discharged from the cone was 150° F.; the temperature increased during denning to 230° F. The product from the continuous den contained 52% available P<sub>2</sub>O<sub>5</sub> and 5% moisture. About 67% of the P<sub>2</sub>O<sub>5</sub> was water soluble. On curing for 3 days in a box den, the water solubility increased to 77%. The product was too hard to be cut from the continuous den with the usual type of rotary cutter (7). It is likely that a product with satisfactory cutting properties could be produced with adjustments in the proportion of water and denning time. However, further studies would be needed to establish this point.

#### Ammoniation of Hydrolyzed Calcium Metaphosphate

Bench scale and pilot plant tests were made of ammoniation of the hydrolyzate from the denning process. The bench scale tests, which were designed to determine the approximate maximum ammonia-holding capacity, were made in a 2-liter pressure reactor equipped with an agitator. Two sizes of uncured hydrolyzate (-6 and -20 mesh;

water solubility of P<sub>2</sub>O<sub>5</sub>, 77%) were tested. About 100 grams of hydrolyzate were reacted with an excess of anhydrous gaseous ammonia at pressures of about 100 to 155 p.s.i.g. The reaction was continued until the temperature reached a maximum and began to decrease, which indicated that no further reaction was likely. The retention time was 7 to 9 minutes. The reactor was preheated in some tests to vary the temperature of reaction. The products were dry and hard and had a slight odor of ammonia. They were heated in an oven at 125° F. for about 16 hours to remove excess ammonia and moisture.

The data of Table III show that, with -6-mesh hydrolyzate, increasing the temperature of ammoniation from 95° to 148° F. increased the degree of ammoniation in the product from 0.5 to 3.4 pounds of ammonia per unit of total P<sub>2</sub>O<sub>5</sub>. A further increase to 347° F. increased ammonia retention to 3.7 pounds per unit of P<sub>2</sub>O<sub>5</sub>. Decreasing the particle size of the hydrolyzate to -20 mesh increased the degree of ammoniation about 10%. The grade of the product with the highest degree of ammoniation was about 8-49-0. The availability of the P<sub>2</sub>O<sub>5</sub> was 98 to 99% in all tests. About 42% of the P<sub>2</sub>O<sub>5</sub> in the ammoniated product was in a water-soluble form.

The pilot plant tests were carried out in a TVA-type continuous ammoniator which was 3 feet in diameter by 3 feet long (2). Hydrolyzate from the den

having a P<sub>2</sub>O<sub>5</sub> water solubility of 79% was used. This material was ground to -20 mesh and fed to the ammoniator where it was ammoniated and granulated along with other fertilizer ingredients. In these tests, about 3 pounds of ammonia were fixed per unit of P<sub>2</sub>O<sub>5</sub> without excessive loss of ammonia. This is about 75% of the amount of ammonia fixed in the pressure reactor. In similar tests with superphosphates, the amount of ammonia fixed in the continuous ammoniator also was about 75% of that fixed in the pressure reactor. In the continuous ammoniator tests, about 3.8 pounds of ammonia were fixed per unit of P<sub>2</sub>O<sub>5</sub> in triple superphosphate and about 3.3 pounds were fixed in high-analysis superphosphate made from superphosphoric acid (3).

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