

ferences in storage properties were noted that could be attributed to differences between the several types of solutions that contained urea.

**Particle Strength.** The particle strengths of the pilot-plant products were compared by a procedure that involved the use of a small ball mill. The mill was a cylinder, 10 inches in diameter by 12 inches long, equipped with flights. About 1 quart of the product and 100  $\frac{5}{16}$ -inch steel balls were placed in the mill, which was rotated for 5 minutes at about 60 r.p.m. The decrease in the proportion of +28-mesh material during milling was used as a measure of the strength of the particles.

There was no appreciable difference in the strength of products made with

the different solutions except for the 5-20-20 grade. This product made with solution UC was somewhat weaker than the others probably because of the larger amount of moisture required for granulation. The particle strengths of the high-nitrogen grades generally were greater than those of the low-nitrogen grades.

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## **CALCIUM METAPHOSPHATE IN FERTILIZERS**

### **Utilization of Calcium Metaphosphate in Production of Granular Fertilizers**

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A process was developed to increase the utility of calcium metaphosphate by increasing its water solubility and granulating it with other fertilizer components. The process consists of partially hydrolyzing calcium metaphosphate in the presence of a mineral acid and ammoniating the hydrolyzate in the TVA continuous ammoniator. In pilot-plant studies, a wide variety of grades of granular fertilizers was produced using calcium metaphosphate to supply all or part of the phosphate. The products had moderately high water solubility, unusually low moisture content, and very good physical properties.

**F**ERTILIZER-GRADE CALCIUM METAPHOSPHATE [ $\text{Ca}(\text{PO}_3)_2$ ] is a vitreous material produced by the reaction of phosphate rock with phosphorus pentoxide at an elevated temperature (8, 10). Expressed on an oxide basis, the product of this reaction contains about 65% phosphorus pentoxide, 25% calcium oxide, 7% silicon dioxide, and minor amounts of aluminum, iron, and fluorine. Substantially all of the phosphate is in a citrate-soluble form, but the material dissolves very slowly in water at room temperature and little water-soluble phosphate is detected by the standard method of the Association of Official Agricultural Chemists (AOAC).

The Tennessee Valley Authority (TVA) has produced calcium metaphosphate fertilizer for test-demonstration purposes for a number of years and at present is the sole producer. As part of this test-demonstration program, agronomic studies have been made on demonstration farms in every section of the country by land grant colleges, the U. S. Department of Agriculture, and

organizations of farmers. These tests have shown calcium metaphosphate to be equal to superphosphate as a source of phosphorus for most crops on acid and neutral soils (5). The acceptance and widespread use of calcium metaphosphate have been limited, however, because of its slow solubility in water and because it cannot be used as a carrier of low-cost ammonia.

Because of the high phosphate content of calcium metaphosphate, which leads to low handling and shipping costs, TVA and others (7) have sought methods for increasing its water solubility and for using it in the manufacture of high-analysis granular fertilizers. The initial work by TVA was based on the knowledge that calcium metaphosphate can be hydrolyzed rapidly in the presence of mineral acids and thus rendered readily water soluble (2, 3, 6). Hydrolysis is used in this paper to mean any reaction of calcium metaphosphate with water or acid that converts the phosphate into a readily water-soluble form. A series of reactions takes place with formation of

complex compounds intermediate between metaphosphate and orthophosphate. Bench-scale tests showed that the hydrolyzate could be ammoniated with commercially available nitrogen solutions and potassium chloride could be added to produce fertilizers of various N:  $\text{P}_2\text{O}_5$ : $\text{K}_2\text{O}$  ratios.

In searching for engineering equipment for carrying out such a process, tests were made in the TVA pilot-plant continuous ammoniator (4, 9). The advantage of this approach was that this type of equipment was already in use in many fertilizer plants. As adapted for use in the continuous ammoniator, the process consists of hydrolyzing part of the calcium metaphosphate in the presence of acid in the first half of the ammoniator and ammoniating the hydrolyzate with nitrogen solution in the second half. When desired, potassium chloride is added in the ammoniator. The ammoniated material is then cooled and screened to separate the product-sized fraction. The oversized fraction is crushed and recycled to the ammonia-

**Table I. Typical Analyses of Raw Materials**

Solids, Raw Material	Chemical Composition, %						Screen Analysis (Tyler Mesh), %					
	N	P <sub>2</sub> O <sub>5</sub>			H <sub>2</sub> O	K <sub>2</sub> O	+4	-4	-6	-28	-48	-100
		Total	C.I.	W.S.				+6	+28	+48	+100	
Calcium metaphosphate	...	64.0	2.0	0.5	0.1	...	0.0	0.0	29.2	30.5	13.6	13.6
Ordinary superphosphate	...	20.4	0.7	18.2	7.6	...	0.1	4.4	41.2	32.8	15.9	5.6
Potassium chloride flotation (red)	...	...	...	...	0.3	61.0	0.0	0.1	22.6	27.7	30.9	18.7
Ammonium sulfate	20.7	...	...	...	0.1	...	0.0	0.0	28.9	32.9	32.7	5.5

Nitrogen solutions (prepared in pilot plant)

Authors' Designation	Chemical Composition, %		
	NH <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	H <sub>2</sub> O
X	21.7	65.0	13.3
Z	16.6	66.8	16.6

tor along with the fines to aid in control of granulation.

The present paper describes the work carried out in the pilot plant and the formulations and conditions used in the production of a variety of grades of high-analysis granular fertilizers based on calcium metaphosphate.

**Equipment and Materials**

**Description of Pilot Plant**

The continuous ammoniation-granulation pilot plant used in this work has been described in detail in previous TVA publications (4, 9). The design and location of the distributors in the ammoniator were somewhat different than in earlier work on the production of granular fertilizers (4). A partitioned, slotted-type distributor located under the rolling bed of material was used to introduce acid in the front half of the ammoniator and to introduce ammoniating solution in the second half. A perforated-pipe distributor, fastened to the acid-ammonia distributor, was used to introduce water when needed to promote granulation. These distributors were constructed of American Iron and Steel Institute Type 316 stainless steel. Corrosion of the acid distributor was moderately severe; however, it appeared to be no worse than that experienced with the same type of acid distributors when conventional fertilizer formulations were used in the pilot plant. A perforated-pipe distributor above the bed was used to supply air for cooling when needed. Volumetric feeders were used to control the flow of solids and rotameters were used for liquids.

Most of the runs were made at a net production rate of 1 ton per hour. Throughput rates, including recycle, ranged from 1.1 to 3.1 tons per hour. The maximum capacity of the ammoniator for typical formulations is believed to be in the range of 3 to 4 tons of throughput per hour.

**Raw Materials**

Typical analyses of the raw materials used are given in Table I. Most of the work

was done with -14-mesh calcium metaphosphate from the TVA plant. The ordinary superphosphate, potassium chloride, and sulfuric acid were purchased from commercial sources. The sulfuric acid was purchased as 66° Bé. acid and used at this concentration. TVA electric-furnace phosphoric acid, when used, was at a concentration of about 78% phosphoric acid. The nitrogen solutions were prepared in the pilot plant from anhydrous liquid ammonia and solid ammonium nitrate obtained from local TVA operations.

**Discussion of Results**

Two general types of formulations were tested in the pilot plant. In one type, calcium metaphosphate was used to supply all of the phosphate. In the other, part of the phosphate was supplied as ordinary superphosphate, phosphate rock, or phosphoric acid.

**Formulations Utilizing Only Calcium Metaphosphate**

Fertilizers having 1:1:1, 1:2:1, 1:2:2, 1:4:2, and 1:4:4 N:P<sub>2</sub>O<sub>5</sub>:K<sub>2</sub>O ratios were produced from formulations in which calcium metaphosphate was the only source of phosphate. The grades of these fertilizers were 13-13-13, 11-22-11, 9-18-18, 7-28-14, and 6-24-24. Complete formulations and operational data for each of these grades are given in Table II.

As was the case in previous studies with superphosphates in the continuous ammoniation-granulation process (4), the most important factor in granulating formulations containing calcium metaphosphate was the control of the liquid phase. The amount of liquid phase is determined by the proportion of moisture and soluble salts in the formulation and by the heat released in the ammoniator.

With formulations in which calcium metaphosphate was the only source of phosphate, the large amount of heat released by the hydrolysis and neutralization reactions resulted in a tendency toward too much liquid phase and,

consequently, overagglomeration. This was overcome by recycling fines to the ammoniator and, in some cases, by limiting the amount of nitrogen solution in the formulation. Because nitrogen solution is an economical source of nitrogen, as much solution was used as was consistent with reasonably low rates of recycle—i.e., rates that probably would be feasible in most existing granulation plants without major changes in equipment. Grades that contained 9 units (9%) or less of nitrogen were formulated with all of the nitrogen from solution. Grades containing more nitrogen (11-22-11 and 13-13-13) were formulated with 8 to 10 units from solution and the remainder from ammonium sulfate.

The relationship between the amount of nitrogen supplied as solution, the amount of recycle required to control granulation, and the temperature of the product from the ammoniator is shown in the following tabulation.

Grade	Nitrogen as Solution, <sup>a</sup> Units	Ammoniator Product Temperature, °F.	Recycle % of Throughput
6-24-24	6	216	31
7-28-14	7	198	43
13-13-13	8	185	60
11-22-11	9	222	60
13-13-13	10	195	66

<sup>a</sup> Solution X: 21.7% ammonia, 65.0% ammonium nitrate, and 13.3% water.

Granulation generally was satisfactory when the temperature of the product from the ammoniator was between 160° and 225° F. Difficulties due to pastiness became pronounced above 225° F., and granulation was difficult to promote below 160° F. The use of air for cooling the material in the ammoniator permitted a decrease in the proportion of recycle used in some tests.

Although substitution of solution Z (16.6% ammonia) for solution X (21.7% ammonia) decreased the temperature of the product from the ammoniator by about 15° F., it was not effective in reducing the requirement of recycle.

**Table II. Formulations and Pilot-Plant Data for Fertilizer Using Only Calcium Metaphosphate as Source of Phosphate**

Run No.	13-13-13		9-18-18	11-22-11	7-28-14	6-24-24
	AM-5/16	AM-4/25	AM-3/2	AM-5/18	AM-9/28	AM 9/16
Production rate, tons/hr.	1.0	0.98	0.96	0.99	0.95	1.0
Formulation, lb./ton product						
Calcium metaphosphate (plant size)	438	437	601	737	952	765
Sulfuric acid (94%)	262	349	266	297	236	183
Nitrogen solution	403(X)	506(X)	582(Z)	449(X)	373(X)	308(X)
Potassium chloride	432	454	651	371	497	783
Ammonium sulfate	532	335	...	297	0	0
Water	0	0	0	0	21	87
Subtotal	2067	2081	2100	2151	2079	2126
Recycle	3100	4052	3367	3049	1579	965
Total	5167	6133	5467	5200	3658	3091
Units of nitrogen from solution	8	10	9	9	7	6
Moisture content, % of feed (calculated)	1.5	1.6	2.5	1.7	2.7	4.8
Recycle, % of total feed	60.0	66.1	61.6	59.6	43.2	31.2
Availability of P <sub>2</sub> O <sub>5</sub> in metaphosphate, %	97-98	96-97	96-97	97-98	96	96
Nominal retention time, min.	8	8	8	8	...	...
Depth of bed above NH <sub>3</sub> inlets, inches	7	7	7	7	...	...
Moles H <sub>2</sub> SO <sub>4</sub> /mole Ca(PO <sub>3</sub> ) <sub>2</sub>	1.14	1.52	0.84	0.77	0.48	0.48
Moles neutralizing NH <sub>3</sub> /mole H <sub>2</sub> SO <sub>4</sub>	2.04	1.93	2.23	2.06	2.08	2.23
Ammoniator cooling air, cu. ft./ton product	0	0	0	6000	4400	2300
Loss of free ammonia, % (by gas analysis)	1.9	5.8	8.3	2.5	3.1	1.7
Temperature, ° F.						
Ammoniator product	185	195	175	222	198	216
Granulator product	178	185	162	208	186	200
Screen analysis (Tyler), %						
Granulator product						
Oversize (+6 mesh)	16.7	34.7	61.5	26.9	28.7	41.4
On-size (-6 +28 mesh)	81.7	63.6	38.3	71.4	69.0	53.1
Undersize (-28 mesh)	1.6	1.7	0.2	1.7	2.3	5.5
Cooler product						
Oversize (+6 mesh)	7.9	38.8	57.9	11.7	...	...
On-size (-6 +28 mesh)	89.9	58.4	42.1	87.9	...	...
Undersize (-28 mesh)	2.2	2.8	0.0	0.4	...	...
Chemical analysis of screened product, %						
Total N	13.3	13.0	9.6	10.6	6.9	5.9
Ammoniacal N	10.6	10.3	6.5	8.9	4.8	4.2
Total P <sub>2</sub> O <sub>5</sub>	14.6	15.5	20.8	23.4	30.2	24.8
Available P <sub>2</sub> O <sub>5</sub>	14.4	15.3	20.1	22.9	28.9	23.8
W.S. P <sub>2</sub> O <sub>5</sub>	3.8	3.6	4.2	4.3	2.5	2.7
K <sub>2</sub> O	13.0	13.6	19.1	10.6	15.8	24.3
H <sub>2</sub> O	0.2	0.3	0.7	0.3	0.6	1.0

Tests with solution Z generally required about 15% more recycle, presumably because of the higher water content of solution Z (16.6 vs. 13.3%). Less sulfuric acid was required with solution Z because of its lower content of free ammonia.

When the proper amount of recycle was used, granulation was such that more than 50% and sometimes as much as 80% of the product from the granulator was -6 +28 mesh in size. This high efficiency of granulation actually was not needed because of the high rates of recycle that were required. However, over-all operation of the equipment and retention of ammonia was better when the efficiency of granulation was high. As there usually was not enough oversize and fines to meet the requirement for recycle, some of the on-size product (-6 +28 mesh) was crushed and also used as recycle. In practice, it would be preferable to use a coarser screen and produce a closer-sized product. The material for recycle usually was crushed by a single pass through a hammer mill. A typical screen analysis of recycle prepared in this manner follows.

Screen Analysis (Mesh), %					
+28	-28 +50	-50 +100	-100 +150	-150 +200	-200
29.5	30.2	21.4	4.6	5.8	8.5

The input moisture for the formulations was relatively low (1.5 to 5%) and free moisture was reduced by hydrolysis of the calcium metaphosphate and evaporation in the ammoniator. Consequently, the products contained only 0.2 to 0.7% without artificial drying. The products had unusually good physical properties. The granules were tough and homogeneous; they were highly resistant to deterioration by abrasion and moisture and could be stored in open piles under humid conditions without caking.

**Loss of Ammonia.** Loss of ammonia was determined by passing a measured portion of the gas through a series of bubblers containing dilute (0.5N) sulfuric acid and titrating the resulting solution. The loss usually was 3% or less when the mole ratio of NH<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub> was not more than 2.0. The effect of increasing the NH<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub> ratio on loss of ammonia is shown by the following tabulation, which gives data from a test

in which a 13-13-13 product was made from a formulation similar to that shown for run AM-5/16 (Table II).

Sulfuric Acid Rate, lb./Ton Product	NH <sub>3</sub> :H <sub>2</sub> SO <sub>4</sub> Mole Ratio	Loss of Free Ammonia, %
250	2.0	2.5
240	2.1	6.0
230	2.2	7.2
193	2.6	9.2
169	2.9	10.6

Other factors also influenced loss of ammonia. In tests of the production of 13-13-13 grade, the loss was higher when 10 instead of 8 units of nitrogen were supplied as solution. Also, there was a tendency toward higher losses of ammonia when overagglomeration occurred or when a large amount of air was used for cooling.

In many tests, fuming from the ammoniator exhaust stack was more severe than when the same grades were made with superphosphates. In a few runs,

a small impingement device was used in series with one of the bubbles in the sampling system mentioned above. A sample of the exhaust gas was passed through the impinger at a rate of about 1 cubic foot per minute; the impinger collected practically all of the visible portion of the fume. Analyses of the solutions from the impinger and bubbler indicated that the fume was mostly ammonium chloride. No appreciable amount of nitrate nitrogen was detected in these solutions. The indicated loss of ammonia was about one and one-half times as great when the visible portion of the fume was removed by the impinger.

Loss of total nitrogen as indicated by product analyses for several runs was in the range of 2 to 4% of the input nitrogen.

**Water Solubility.** The proportion of the phosphate that was in a water-soluble form varied from about 20 to 40% in most of the products. The water-soluble phosphate was determined by an AOAC procedure that involves washing a 1-gram sample on filter paper (7). Steps were taken to assure hydrolysis of nonorthophosphate in the solution to the ortho form before analysis. A systematic study of the factors affecting

water solubility was not made because solubilities in this range were considered sufficiently high for most purposes. However, it was found that the water solubility was proportional to the  $H_2SO_4:Ca(PO_3)_2$  ratio. This relationship is illustrated by the data from a special test on 13-13-13, which are tabulated below.

$H_2SO_4:Ca(PO_3)_2$ Mole Ratio	Water Solubility of $P_2O_5$ , % of Total $P_2O_5$
1.16	34
1.11	32
1.06	29
0.89	27
0.78	25

Other factors, such as the moisture content of the feed materials and the temperature in the ammoniator, undoubtedly affected the water solubility also.

The water solubility of most of the products increased during curing, presumably because of slow continued hydrolysis of calcium metaphosphate. Reanalysis of several samples of 13-13-13 product, in which approximately 30% of the phosphate was water soluble at the time of production, showed an increase in water solubility to a range of 40 to 60% after 6 to 10 weeks of storage.

The largest increase occurred in a product in which -100-mesh calcium metaphosphate rather than the usual -14-mesh material had been used. The use of the more finely ground calcium metaphosphate apparently had no other effect on the properties of the product or on the operation of the plant.

**Solubility Studies** The rate of solution in water of the phosphate in several pilot-plant products and in plant-grade calcium metaphosphate was studied. The primary purpose of these tests was to obtain solubility data which may correlate with agronomic tests. The method used involved agitating the sample in an excess of water for 1 month. The proportions of phosphate which had gone into solution in both ortho and nonortho forms by the end of 1 hour, 1 week, and 1 month were determined by analyzing aliquots of the liquid phase. The tests were made at room temperature (70° to 80° F.).

At the end of 1 month, about 80 to 90% of the phosphate in the mixed fertilizers had gone into solution, while only 40% of that in the calcium metaphosphate was in solution after 1 month. At the end of a month, about one third to one half of the phosphate which had been solubilized was in the ortho form

**Table III. Formulations and Pilot-Plant Data for Fertilizers Using Calcium Metaphosphate Together with Other Phosphatic Materials**

	12-12-12	5-20-20	6-24-12	8-16-16	6-24-24	0-23-23
Run No.	AM-4/27	AM-3/9-5	AM-4/4	AM-3/9-8	AM-11/8	AM-1/26
Production rate, tons/hr.	1.03	3.0	1.0	1.0	0.94	1.1
Formulation, lb./ton product						
Calcium metaphosphate (plant size)	221	510	577	303	545	507
Sulfuric acid (94%)	223	127	110	111	...	318
Phosphoric acid (78%)	...	...	...	...	356	...
Nitrogen solution	445(X)	297(Z)	343(Z)	425(Z)	327(X)	...
Potassium chloride	391	662	396	531	872	756
Phosphate rock (CSP dust)	...	...	...	...	...	433
Ammonium sulfate	319	...	...	...	...	...
Ordinary superphosphate	480	460	631	695	...	...
Water	0	20	8	20	25	268
Subtotal	2079	2076	2065	2085	2125	2282
Recycle	1359	153	278	502	532	...
Total	3438	2229	2343	2587	2657	2282
Moisture content, % of feed (calculated)	3.6	4.8	5.2	6.0	5.8	12.6
Recycle, % of total feed	39.5	7.0	11.9	19.4	20.0	...
Moles $H_2SO_4$ /mole $Ca(PO_3)_2$	1.91	0.46	0.36	1.0	1.02	0.84
Lb. neutralizing $NH_3$ /unit available $P_2O_5$ in ordinary superphosphate	5.1	1.7	3.4	5.1	...	...
Ammoniator cooling air, cu. ft./ton product	4000	0	0	0	0	0
Loss of free ammonia, % (by gas analysis)	7.7	0.5	2.1	4.8	1.6	...
Temperature, °F.						
Ammoniator product	192	200	164	160	165	160
Granulator product	177	184	148	144	145	141
Screen analysis (Tyler), %						
Cooler product						
Oversize (+6 mesh)	45	12	45	28	22	14 (dryer)
On-size (-6 +28 mesh)	54	84	58	68	74	86 (dryer)
Undersize (-28 mesh)	0	4	2	4	4	0 (dryer)
On-size recovery after crushing oversize	88	93	87	89	94	97
Chemical analysis of screened product, %						
Total N	12.0	5.0	6.4	7.8	6.5	...
Ammoniacal N	9.4	3.4	4.4	5.0	4.6	...
Total $P_2O_5$	12.6	22.4	25.3	18.3	27.6	25.3
Available $P_2O_5$	12.3	21.9	24.7	17.7	26.5	22.8
W.S. $P_2O_5$	4.1	5.3	5.7	4.8	11.0	8.6
$K_2O$	12.5	20.1	11.9	15.9	25.7	22.8
$H_2O$	1.1	1.2	2.5	2.7	1.2	0.2

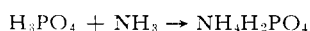
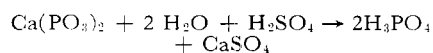
in the case of the mixed fertilizers but only one fourth of the soluble phosphate was ortho in the test with calcium metaphosphate.

#### Chemical Composition of Products.

Estimates of the compositions of 13-13-13 and 9-18-18 products, based on calculations made from chemical analyses and on petrographic studies, are given below.

Chemical Component	Estimated % of Product Weight in Grades	
	13-13-13	9-18-18
Ca(PO <sub>3</sub> ) <sub>2</sub>	12.5	19
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	9	8.5
CaHPO <sub>4</sub>	Nil	1
NH <sub>4</sub> NO <sub>3</sub>	Trace	Trace
NH <sub>4</sub> Cl	9	11.5
KNO <sub>3</sub>	17	21.5
KCl	9	12.5
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	34	12
CaSO <sub>4</sub>	4	6

The only water-soluble phosphate identified in the petrographic analysis was monoammonium phosphate. However, chemical analyses indicate that some water-soluble phosphate was present in a nonortho form. The water-insoluble phosphate was present as unreacted calcium metaphosphate. These observations indicate that the main chemical reactions involving calcium metaphosphate that take place in the process can be expressed by the following equations:



Essentially no ammonium nitrate was present, which indicated substantially complete reaction with potassium chloride to form potassium nitrate and ammonium chloride.

#### Formulations Utilizing Supplementary Phosphoric Components

Grades in which ordinary superphosphate was used as a supplementary source of phosphate were 12-12-12, 8-16-16, 6-24-12, and 5-20-20. Formulations and operating data from typical tests are shown in Table III. The following tabulation shows the proportion of phosphate supplied from each source and the source of nitrogen in each grade.

Grade	Units of P <sub>2</sub> O <sub>5</sub> from		Units of N from	
	Calcium metaphosphate	Ordinary superphosphate	Solution	Ammonium sulfate
12-12-12	7	5	9(X)	3
8-16-16	9	7	8(Z)	0
6-24-12	18	6	6(Z)	0
5-20-20	15	5	5(Z)	0

Sulfuric acid was used at rates of 110 and 130 pounds per ton of product, respectively, when producing the 6-24-12 and 5-20-20 grades. These rates were about the minimum that would give sufficient heat of reaction for good granulation. When producing the

8-16-16 and 12-12-12 grades, the acid rates were 111 and 223 pounds per ton of product, respectively, and were the minimum that could be used without excessive losses of free ammonia.

Formulations containing calcium metaphosphate and ordinary superphosphate granulated more readily than the same grades formulated with ordinary and concentrated superphosphates.

Granulation was such that 87 to 93% of the product was of the desired particle size range (-6 +28 mesh) after the oversize was crushed. Considerably lower recycle rates were required for control of granulation than were required when all of the phosphate was supplied as calcium metaphosphate. No recycle was required for control of granulation of the 5-20-20 and 6-24-12 grades. The recycle rates required for the 8-16-16 and 12-12-12 grades were about 20 and 40% of the throughputs, respectively.

Although none of the products were dried artificially, the moisture contents ranged from 1.1 to 2.7%. The particles were well-rounded, homogeneous, and unusually resistant to deterioration by abrasion or humid conditions.

Phosphoric acid was used instead of sulfuric acid in the production of a 6-24-24 grade. In this formulation, 18 units of phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>) were supplied as calcium metaphosphate and sufficient phosphoric acid was used to provide a NH<sub>3</sub>:H<sub>3</sub>PO<sub>4</sub> mole ratio of 1.5. The recycle rate was about 20%. Operation was very good; only 1.6% of the free ammonia was lost, and 74% of the product from the cooler was -6 +28 mesh in size. After crushing the oversize material, 88% of the total product was of this size. Data are given in Table III (run AM-11/8).

A granular 0-23-23 fertilizer (no nitrogen) was made from calcium metaphosphate, phosphate rock, potassium chloride, and sulfuric acid. About one third of the phosphate was supplied as pulverized phosphate rock (90%-100 mesh). The proportion of acid was slightly higher than normally used in the production of ordinary superphosphate. Water and steam were added under the bed to promote granulation, and the product was dried to ensure good storage

properties. However, drying may not have been necessary. The dried product (0.2% water) consisted of tough, well-formed granules and was free from caking in open-pile storage. The over-all availability of the phosphate was 92% and the net conversion of the phosphate

supplied as phosphate rock was about 80% after curing for 5 days. Analyses of undried product that had been cured for 1 week at 150° F. indicated 95% net conversion of the phosphate supplied as phosphate rock. The complete formulation and operational data are given in Table III (run AM-1/26).

#### Bag-Storage Tests

Bag-storage properties of most of the pilot-plant products were evaluated in long-term storage tests. The products were bagged in six-ply, multiwall paper bags that had either one or two asphalt-laminated plies. The bags were stacked 12 high in a ventilated, unheated building. After 3 months of storage the degree of bag set was judged as zero, light, medium, or hard from the hand pressure required to compress the bag. Each bag then was dropped four times, once on each face and side, on a concrete floor from a height of 3 feet, and the proportion of +2-mesh lumps was determined as a further measure of caking.

Tests were made of uncured and cured products with and without addition of a conditioning agent such as kaolin clay or diatomaceous earth. To simulate curing in large storage piles, some of the products were cured at 110° F. for 7 days in heated, wooden bins. The cured products were passed through a 4-mesh screen to break up any lumps that had formed, and then were bagged with and without the addition of a conditioning agent.

Results of the inspections after 3 months of storage are summarized in Table IV. Products that had not been cured or conditioned showed hard bag sets and, in most cases, excessive lumps after the drop test. Curing for 7 days or coating with a conditioning agent was effective in reducing caking, but the products still had medium to hard bag sets before dropping. Best results were obtained when the products were cured and then conditioned. When this was done, there was, at the most, only light bag set and there were no lumps after the drop test.

The results on the 9-18-18 product indicate, also, that curing for only 1 day was almost as beneficial as curing for 7 days. There were no significant differences between results with bags having one and two asphalt-laminated plies or with kaolin and diatomaceous earth as conditioning agents.

The 0-23-23 product (Table III), which was formulated with raw phosphate rock and with sulfuric acid in slight excess of that used in superphosphate manufacture, showed only light bag set and no lumps after 3 months of storage without curing or conditioning. However, the bags were seriously attacked, presumably by free acid in the

fertilizer. This product was dried to 0.2% moisture prior to storage. Conditioning with limestone or calcined dolomite, although not tested, probably would have eliminated bag rot.

Microscopic and petrographic studies of several of the products formulated with calcium metaphosphate as the sole source of phosphate showed that, during storage, the granules develop dense surface coverings of monoammonium phosphate crystals in the form of radiating needles. Where caking occurred, it was due to intergrowth of these crystals between granules. The curing period prior to bagging apparently provided time for development of these surface crystals and thereby decreased the amount of intergrowth that occurred in subsequent storage.

### Conclusions

The process described in this paper is a feasible method of utilizing calcium

metaphosphate in the production of a wide variety of high-analysis granular fertilizers. The water solubility of the calcium metaphosphate was increased to a range of 20 to 40% and unusually tough granules were produced. Efficient granulation was obtained at relatively low moisture content. The low moisture input and the water utilized in the hydrolysis of the calcium metaphosphate resulted in unusually dry products, which had superior storage properties. The process can be carried out in facilities now installed in many fertilizer plants without major changes in equipment.

The disadvantage of the process is the relatively large amount of acid required to fix free ammonia. As presently developed, the process does not permit ammoniation of the hydrolyzate to a degree which exceeds the ammonia-retaining capacity of the acid used in the hydrolysis. Further studies designed to increase the ammonia-retention ca-

capacity of the hydrolyzate are in progress.

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Table IV. Results of Bag-Storage Tests

Grade	Run No. <sup>b</sup>	Days Cured <sup>c</sup>	Moisture Content, % H <sub>2</sub> O	Condition after 3 Months			
				Unconditioned		Conditioned <sup>a</sup>	
				Bag set	Lumps <sup>d</sup>	Bag set	Lumps <sup>d</sup>
Products with Calcium Metaphosphate as Sole Source of Phosphate							
13-13-13	AM-4/25	0	0.2	Hard	15	Hard	0
		7	...	Hard	0	Light	0
9-18-18	AM-2/9 <sup>e</sup>	0	0.9	Hard	22	Hard	7
		1	...	Hard	0	Light	0
		7	...	Medium	0	None	0
11-22-11	AM-5/18	0	0.3	...	...	...	...
		7	...	Medium	0	Light	0
Products with Calcium Metaphosphate and Ordinary Superphosphate as Source of Phosphate							
12-12-12	AM-4/27	0	1.1	Hard	4	Medium	0
		7	...	Medium	0	Light	0
5-20-20	AM-3/9-5	0	1.1	Hard	0	Light	0
		7	...	Hard	1	None	0
6-24-12	AM-4/4	0	2.2	Hard	12	Hard	2
		7	...	Medium	0	Light	0

<sup>a</sup> 9-18-18 product was conditioned with 5% kaolin; all others were conditioned with 2.5% kaolin.

<sup>b</sup> For formulations and production data, see Tables II and III.

<sup>c</sup> Cured in steam-heated bin at 110° F.

<sup>d</sup> Per cent plus 2-mesh lumps after dropping four times from 3-foot level, once on each face and side of bag.

<sup>e</sup> Similar to run AM-3/2 (Table II).

## PHOSPHORUS AVAILABILITY

### Effect of Preparation Method and Water Solubility of Nitric Phosphates on Uptake by Millet in Greenhouse Culture

NITRIC PHOSPHATES are a group of fertilizers produced by the reaction of rock phosphate and nitric acid, either alone or in mixtures with sulfuric or phosphoric acid, followed by ammonia-

tion and other process steps (7). The production processes are technologically attractive (8) because they permit the formation of polynutrient fertilizers in one integrated continuous operation.

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The resultant fertilizer is an intimate mixture of fine-grained compounds that shows little tendency toward segregation of nutrients. However, the water solubility of the phosphorus is notably lower