

Pilot Plant Studies of Hydrolysis, Ammoniation, and Granulation of Calcium Metaphosphate

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A pilot plant method was developed for hydrolyzing calcium metaphosphate and utilizing the hydrolyzate as a source of P_2O_5 and as a carrier of nitrogen in the production of granular high-analysis fertilizers. Hydrolysis was carried out by slurring pulverized metaphosphate with hot water in a tank; sufficient acid was included to prevent thickening. A TVA-type ammoniator-granulator was used for ammoniation and granulation with other fertilizer ingredients. Ammonia absorption up to 3.3 pounds per unit of P_2O_5 in the hydrolyzed calcium metaphosphate was obtained, and the products had good physical properties. Methods were developed for using calcium metaphosphate to produce granular phosphates and no-nitrogen grades.

CONSIDERABLE QUANTITIES of calcium metaphosphate have been used successfully on a demonstration basis for direct application to the soil and in dry-mixed fertilizers. However, its widespread use has been limited by its low water solubility; the fact that it cannot be ammoniated, which is an economic disadvantage in the production of mixed fertilizers; and its relatively fine particle size, required for proper agronomic response but objectionable in view of current demands for fertilizers in granular form.

The Tennessee Valley Authority has attempted to overcome these disadvantages. Studies have been made also of methods for granulating calcium metaphosphate either alone or with superphosphates to give granular products with suitable agronomic response. In one process (5) calcium metaphosphate was treated with sulfuric or phosphoric acid in the first half of a TVA-type ammoniator-granulator, and ammoniation and granulation with other fertilizer ingredients were carried out in the second half. The ammoniated products had excellent physical properties, and 20 to 40% of the phosphate was water-soluble. However, no ammonia-fixing capacity was realized from the calcium metaphosphate. The degree of ammoniation that was obtained in the process did not exceed the ammonia-retaining capacity of the acid and superphosphates used in the formulations. This was an economic disadvantage.

A process has now been developed which realizes a considerable ammonia-fixing capacity from the calcium metaphosphate while retaining advantages of the previous process. The essential feature of the improved process is use of a separate hydrolysis step in which pulverized calcium metaphosphate is hydrolyzed with hot water. The resultant slurry is fed to a TVA-type ammoniator

together with dried recycle and various fertilizer materials to form granular high-analysis fertilizers. Acid is added with the water in the hydrolysis step as required to prevent thickening. The calcium metaphosphate is converted largely to water-soluble forms that will absorb ammonia. The reactions that occur in the hydrolysis and subsequent ammoniation have been studied by Brown *et al.* (1, 2). These reactions, which are somewhat complex, result in formation of several previously unrecognized water-soluble phosphates.

The present paper describes the improved process for hydrolysis of calcium metaphosphate and presents results of pilot plant tests of its use to produce several grades of high-analysis granular fertilizers. Described also are pilot plant tests in which pulverized calcium metaphosphate was granulated alone and in mixture with superphosphates to produce grades such as 0-61-0, 0-48-0, and 0-56-0. Similar tests are described in which potash was included to make no-nitrogen grades such as 0-30-30 and 0-40-20.

Hydrolysis and Ammoniation

Pilot plant tests of the hydrolysis of calcium metaphosphate with hot water and subsequent ammoniation of the hydrolyzate were preceded by small scale tests in which basic information was obtained. Most of these tests were carried out batchwise in a small vessel equipped with an agitator. When finely pulverized (-48- or -100-mesh) calcium metaphosphate was slurried with 0.75 to 1.0 pound of water per pound of P_2O_5 in the metaphosphate and heated to about 170° F., an exothermic hydrolysis reaction was initiated. The temperature of the slurry rose rapidly to between 200° and 220° F., and after about 30 minutes 90% of the P_2O_5 was water-

soluble. The hydrolyzate was viscous, and it usually solidified to form a hard but porous mass soon after agitation was stopped. However, the addition of a small amount of acid increased the fluidity of the hydrolyzate and appeared to accelerate the hydrolysis reaction. Tests indicated also that continuous hydrolysis should be feasible. The hydrolyzate from the continuous tests appeared to be more fluid than that produced in batchwise tests.

Ammoniation of the hydrolyzate in a slurry state by stirring in a beaker with aqua ammonia gave promising results; ammonia was absorbed to the extent of 3 pounds per unit of P_2O_5 in the calcium metaphosphate. The ammoniated material became dry and friable and appeared to have good granulation properties.

Pilot Plant. In the pilot plant, calcium metaphosphate was fed continuously to a reaction vessel in which it was hydrolyzed with hot water alone or with a small amount of acid added. The hydrolyzate was fed continuously into a TVA-type continuous ammoniator, where it was ammoniated and processed with other materials to produce finished, granular products. Evaluations of the effects of variables in the hydrolysis step were based chiefly on the behavior of the hydrolyzate in the ammoniator and on analyses of the finished products.

The reaction vessel used for hydrolysis was a stainless steel cylindrical tank 14 inches in diameter with a 4-inch conical bottom. The overflow was variable from 18 to 34 inches above the bottom of the cylindrical section. As little as 12 inches of freeboard was satisfactory. This hydrolyzer was equipped with a turbine-type agitator driven by an air motor. Pulverized calcium metaphosphate was fed with a belt-type volumetric feeder. Water was metered with a constant-

level, orifice-type meter, and the acid used to maintain fluidity was fed through a similar type of meter. A steam-jacketed heat exchanger was used to heat the water when desired. The rate of feed of calcium metaphosphate was 400 to 800 pounds per hour.

The pilot plant ammoniator was 3 feet in diameter by 3 feet long. This unit and auxiliary drying and screening equipment have been described (3, 6). The hydrolyzed calcium metaphosphate was fed by gravity as a hot slurry directly to the ammoniator through a simple distributor with a serrated slot as shown in Figure 1. This distributor remained virtually free from plugging and was easily cleaned. It was positioned about 8 inches above the bed in the ammoniator and was located to distribute the hydrolyzate over the first two thirds of the length of the bed. Acid and ammonia or ammoniating solution were fed through distributors located beneath the bed. The acid distributor was a drilled pipe that extended through the first half of the ammoniator. The ammonia or solution distributor was of the slotted type (3) and extended the full length of the ammoniator.

Water and Acid Requirements. Attempts were made to operate without acid in the hydrolysis step. Frequent difficulties were experienced due to stoppages in the discharge line from the hydrolyzer and solidification in the tank. However, the addition to the hydrolysis tank of a portion of the sulfuric, phosphoric, or nitric acid, required by the formulations, ensured fluidity. Requirements of acid and water for satisfactory hydrolysis and fluidity were:

	lb./lb. P_2O_5 in Calcium Metaphosphate	
	Water	Acid
Sulfuric acid (93% H_2SO_4)	1.0-1.2	0.22
Phosphoric acid (53% P_2O_5)	1.0-1.2	0.56
Nitric acid (43% HNO_3)	1.0	0.48

When higher proportions of acid were fed to the hydrolyzer, a thicker hydrolyzate was obtained, and this was difficult to distribute. The thickening was attributed to increased evaporation of water because of higher temperatures and

to the formation of additional complex compounds. Also, the ammonia absorption by the hydrolyzed calcium metaphosphate was significantly lower when higher proportions of acid were used. For these reasons any additional acid required in the formulations was fed into the ammoniator rather than into the hydrolyzer. The amount of water was held near the values shown in the tabulation, to decrease requirements of recycle for control of granulation and to limit the amount of water to be removed in the dryer.

Effect of Particle Size of Calcium Metaphosphate. Tests in the pilot plant were made using calcium metaphosphate pulverized to -14, -35, -48, and -100 mesh. The -14-mesh material did not hydrolyze to any appreciable extent even with extended periods of treatment; difficulty due to settling of the coarser particles in the hydrolysis tank was also experienced. The -35-mesh material hydrolyzed considerably, but absorption of ammonia was not as great as with finer material. Best results were obtained with the -48- and -100-mesh metaphosphate; slightly higher degrees of ammoniation were obtained with the -100-mesh material. The choice between -48 and -100 mesh would be dictated by cost and difficulty of grinding. When -35-mesh or finer calcium metaphosphate was used, the hydrolyzate was a homogeneous, fairly viscous slurry which flowed readily by gravity through the piping and distributor.

Effect of Retention Time and Temperature in the Hydrolyzer. The nominal retention time in the hydrolyzer was varied from 6 to 30 minutes by variations in rate of feed of the calcium metaphosphate and by raising or lowering the overflow level on the hydrolyzer. The minimum practical retention time for -35-mesh or finer calcium metaphosphate appeared to be 16 to 20 minutes. This would require a tank of 225- to 250-gallon capacity (about 3 by 5 feet) for a 15-ton-per-hour granular fertilizer plant.

Best hydrolysis and ammoniation were obtained when the temperature in the hydrolyzer was 220° to 230° F. When sulfuric acid was used, the heat of dilu-

tion of the acid and the heat liberated by the hydrolysis reactions maintained the temperature in this range. When phosphoric or nitric acids were used, however, it was necessary to heat the feed water to the hydrolysis tank to about 160° F. to obtain hydrolysis temperatures of 220° to 230° F. Temperatures higher than about 230° F. resulted in excessive evaporation of water from the hydrolysis tank and difficulties due to thickening of the hydrolyzate.

Production of Granular Fertilizers

Several grades of granular high-analysis fertilizers were produced in the pilot plant. Shown in Table I are the formulations, operating conditions, and test data from typical runs in which small amounts of phosphoric or sulfuric acid were fed to maintain fluidity. The quantities of water and acid used were in the ranges that give satisfactory fluidity. No tests with nitric acid are shown, because the use of nitric acid usually resulted in unaccountably high loss of nitrogen. Calcium metaphosphate, fed to the hydrolyzer, supplied all or a major proportion of the phosphate in the formulations. In production of most grades, additional acid was fed in the ammoniator as required by the formulation. Recycled fines were used as a primary control of granulation; the rate ranged from 1000 to 2000 pounds per ton of net product. The net degree of ammoniation of the calcium metaphosphate ranged from 2.7 to 3.3 pounds of ammonia per unit of P_2O_5 supplied as calcium metaphosphate. [Ammoniation is calculated on the assumption of absorption of 5.8 pounds of ammonia per unit of P_2O_5 by the ordinary superphosphate, 7.2 pounds by the phosphoric acid, and the neutralization of H_2SO_4 to $(NH_4)_2SO_4$.] All the products were dried in a rotary dryer.

12-12-12 Grade. Good results were obtained with a formulation for 12-12-12 that included calcium metaphosphate (6.5 units of P_2O_5 , -100 mesh), ordinary superphosphate (5.5 units of P_2O_5), ammonium sulfate (3 units of N), nitrogen solution (9.2 units of N), and potassium chloride. For hydrolysis, 170 pounds of water at room temperature and 29 pounds of 92% sulfuric acid were used per ton of product. An additional 75 pounds of sulfuric acid were fed in the ammoniator. In one test, all of the sulfuric acid was fed to the hydrolyzer, but excessive thickening of the hydrolyzate resulted and prevented completion of the test.

The input degree of ammoniation for the calcium metaphosphate was 2.8, and the loss of ammonia as indicated by gas analysis was about 6%. Control of granulation was satisfactory with about 1150 pounds of recycle per ton of net product. About 62% of the dryer product was of the desired -6- +20-mesh size.

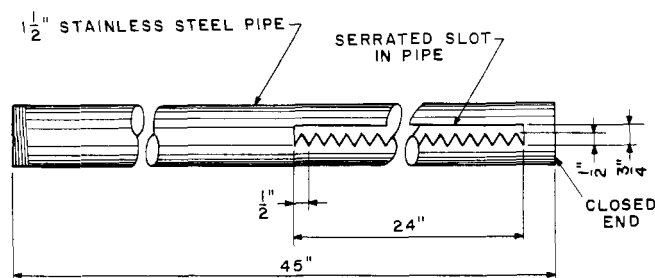


Figure 1. Distributor for feeding hydrolyzed calcium metaphosphate in pilot plant ammoniator

Table I. Production of Granular Fertilizers from Hydrolyzed Calcium Metaphosphate

Grade	12-12-12	8-16-16	7-28-14	8-32-16	5-20-20
Production rate, ton/hr.	0.96	1.0	1.0	0.90	0.97
Formulation, lb./ton product					
Calcium metaphosphate, 63% P ₂ O ₅ (size in parentheses)	215(-100)	360(-35)	526(-50)	720(-100)	560(-35)
For hydrolysis					
Phosphoric acid Furnace (56.9% P ₂ O ₅)	191
Wet process (53% P ₂ O ₅)	287	...
Sulfuric acid (92% H ₂ SO ₄)	29	52	75
Water	170	234	409	542	335
Liquid ammonia	...	71	74	69	133
Nitrogen solution	448 ^a	198 ^b	204 ^b	270 ^b	...
Ammonium sulfate (20.5% N)	294	133
Ordinary superphosphate (20% P ₂ O ₅)	561	481	481	...	420
Sulfuric acid (92% H ₂ SO ₄)	75	126	60-100
Potassium chloride (60.5% K ₂ O)	394	546	457	525	687
Recycle	1150	965	910	2020	910
Moisture content, %					
Feed (calculated)	5.5	5.7	13.0	14.3	11.5
Ammoniator discharge	4.5	3.7	9.4	10.9	8.5
Dryer discharge	1.1	0.8	4.4	6.6	3.5
Screened product	0.9	0.7	4.1	6.7	3.5
Lb. neutralizing NH ₃ fed/unit P ₂ O ₅ in metaphosphate ^c	2.8	2.7	3.2	3.3	2.9-3.8
Loss, %					
Free NH ₃ by gas analysis	5.8-6.1	3.8	6.1	3.3	7.5-11.7
P ₂ O ₅ availability in metaphosphate	0	0	0	0.3	0
Temperature, ° F.					
Hydrolyzate	216	218	220	223	225
Ammoniator product	182	184	196	188	195
Granulator product	164	168	164	165	165
Dryer product	211	195	194	155	170
Screen analysis (Tyler), %					
Granulator product					
Oversize (+6 mesh)	28.2	27.5	21.6	20.2	11.9
Onsize (-6 +20 mesh)	66.8	68.8	58.4	74.2	79.2
Undersize (-20 mesh)	5.0	3.7	20.0	5.6	8.9
Dryer product					
Oversize (+6 mesh)	26.9	30.8	16.5	21.8	16.6
Onsize (-6 +20 mesh)	62.4	62.2	59.4	70.4	73.9
Undersize (-20 mesh)	10.7	7.0	24.1	7.8	9.5
Chemical analysis of screened product, %					
Total N	12.0	7.8	6.9	7.8	5.0
NH ₃ N	9.2	6.6	5.4	6.5	5.0
Total P ₂ O ₅	13.1	17.9	29.1	31.5	21.7
Available P ₂ O ₅	12.7	17.3	28.5	31.0	21.0
W.S. P ₂ O ₅	5.8	8.1	12.9	15.4	6.2
K ₂ O	12.2	15.9	14.1	15.7	19.6
CaO	10.8	...	14.4	10.0	...
SO ₃	21.6	...	6.7	1.3	...
H ₂ O	0.9	0.7	4.1	6.7	3.5

^a Nitrogen solution Type 414 (19-74-0); 41.4% total N, 19% free NH₃, 74% ammonium nitrate, 0% urea.

^b Nitrogen solution Type 410 (22-65-0); 41.0% total N, 22% free NH₃, 65% ammonium nitrate, 0% urea.

^c Assuming absorption of 5.8 pounds of NH₃ per unit of P₂O₅ by ordinary superphosphate, 7.2 pounds per unit for H₃PO₄, and neutralizing H₂SO₄ to (NH₄)₂SO₄.

8-16-16 Grade. The formulation tested for this grade consisted of calcium metaphosphate (11.2 units of P₂O₅, -35 mesh), ordinary superphosphate (4.8 units of P₂O₅), anhydrous liquid ammonia (2.6 units of N), nitrogen solution (4.1 units of N), ammonium sulfate (1.4 units of N), and potassium chloride. For hydrolysis, 50 pounds of sulfuric acid and 234 pounds of water per ton of product were used. An additional 126 pounds of 90% sulfuric acid were fed in the ammoniator. The input degree of ammoniation for the calcium metaphosphate with this formulation was 2.7 pounds of ammonia per unit of P₂O₅, and loss of free ammonia was 3.8%. Granulation was controlled easily by using a recycle rate of about 1000 pounds per ton of product. About 60% of the dryer product was -6 +20 mesh.

7-28-14 Grade. The formulation tested for 7-28-14 grade consisted of calcium metaphosphate (17.8 units of P₂O₅, -50 mesh), ordinary superphosphate (4.8 units of P₂O₅), electric-furnace phosphoric acid (5.4 units of P₂O₅ as 78% H₃PO₄), anhydrous liquid ammonia (3 units of N), nitrogen solution (4.1 units of N), and potassium chloride. All of the phosphoric acid (190 pounds) and 405 pounds of water per ton of product were fed to the hydrolyzer. The water was heated to about 160° F. to give a temperature of 220° F. in the hydrolyzer. No additional acid was fed in the ammoniator.

Granulation was good, with a recycle rate of 900 pounds per ton of product. About 60% of the product from the dryer was -6 +20 mesh. The input degree of ammoniation for the calcium metaphosphate was 3.2 pounds of ammonia per unit of P₂O₅ and the loss of ammonia was 6%. The loss of ammonia probably could have been decreased by formulating to a somewhat lower degree of ammoniation.

8-32-16 Grade. Tests were made of a 1:4:2 ratio grade in which no ordinary superphosphate was included. Prior to the tests it was uncertain whether a grade as high as 8-32-16 could be produced because of uncertainties as to the extent of dilution of the calcium metaphosphate by hydrolysis and the degree of ammoniation that could be obtained. The formulation consisted of calcium metaphosphate (24 units of P₂O₅, -100 mesh), wet-process phosphoric acid (8 units of P₂O₅ as 53% P₂O₅), anhydrous liquid ammonia (2.8 units of N), nitrogen solution (5.3 units of N), and potassium chloride. All of the phosphoric acid was fed to the hydrolyzer together with about 500 pounds of water per ton of product. The water was heated to about 150° F. to give a hydrolysis temperature of 210° to 225° F. The amount of sulfuric acid fed in the ammoniator was varied from a maximum of 120 pounds per ton of product to zero by appropriate adjustment in the formulation. This re-

sulted in a range of input degrees of ammoniation for the calcium metaphosphate from 2.1 to 3.3 pounds of ammonia per unit of P_2O_5 .

Over-all operation and control of granulation were good both with and without the use of sulfuric acid in the ammoniator. Recycle required for control of granulation was about 1 ton per ton of product. The data in Table I are for a test without addition of acid in the ammoniator. Temperature in the ammoniator was satisfactorily high (190° F.) without use of acid. About 70% of the product of the dryer was -6 +20 mesh, and the granules were unusually well rounded and uniform. The loss of ammonia with an input degree of ammoniation of 3.3 was 3%. In tests with coarser, -48-mesh calcium metaphosphate, the loss of ammonia was 5 to 6%.

Very moderate conditions of drying (product temperature of 150° to 155° F.) were used in the test shown in Table I; this resulted in high moisture content of 6.5 to 7% for the screened product. In other tests of this grade, drying at a product temperature of 200° F. gave 2% or lower moisture. Chemical analyses showed that drying to 2% moisture would give an 8-32-16 grade.

5-20-20 Grade. The formulation for this grade consisted of calcium metaphosphate (16 units of P_2O_5 , -35 mesh), ordinary superphosphate (4 units of P_2O_5), anhydrous liquid ammonia (5 units of N), and potassium chloride. The calcium metaphosphate was hydrolyzed with 335 pounds of water and 75 pounds of 90% sulfuric acid per ton of product. From 60 to 100 pounds of additional sulfuric acid per ton of product were fed in the ammoniator to give a range of ammoniation of the calcium metaphosphate from 2.9 to 3.8 pounds of ammonia per unit of P_2O_5 . Loss of ammonia ranged from 7 to 11%. This is believed to be due to the use of coarse calcium metaphosphate. The temperature in the ammoniator was 190° to 200° F., and granulation was good with a recycle rate of about 900 pounds per ton of product. About 75% of the product from the dryer was -6 +20 mesh.

Chemical and Physical Properties of Products. Chemical analyses of products from the pilot plant tests indicated that the effective grade of the calcium metaphosphate in the formulations ranged from 52 to 58% available P_2O_5 as compared to 63% in original calcium metaphosphate. The variation in effective grade apparently resulted from variations in the degree of hydrolysis and hydration of the calcium metaphosphate. Therefore, some experience with the various formulations would be required to formulate accurately.

The water solubilities of P_2O_5 in the granular products of the several grades are tabulated:

Table II. Production of Granular Phosphates and No-Nitrogen Grades from Calcium Metaphosphate

Grade	0-61-0	0-56-0	0-48-0	0-30-30	0-40-20
Production rate, ton/hr.	0.80	0.91	1.0	1.0	1.0
Formulation, lb./ton product					
Calcium metaphosphate (63% P_2O_5)	1989 ^a	1155 ^b	1314 ^b	701 ^b	1102 ^b
High-analysis superphosphate (54% P_2O_5)	...	820
Ordinary superphosphate (20% P_2O_5)	712
Phosphoric acid (78% H_3PO_4)	275	216
Calcined dolomite (59% CaO, 38% MgO)	83	54
Potassium chloride (61% K_2O)	990	669
Steam	...	253	250	255	255
Water	220-250	59	35
Recycle	400	600	500	400	400
Temperature, ° F.					
Calcium metaphosphate preheat	210
Reaction drum	180-200	200	195	222	218
Dryer product	152	174	192	191	196
Moisture content, %					
Granulator discharge	2.4	2.9	3.7	3.1	2.8
Dryer discharge	0.9	1.3	1.2	0.8	0.5
Screened product	0.9	1.4	1.0	0.5	0.2
Screen analysis (Tyler) of dryer product, %					
+6	10.2	2.6	10.0	10.2	32.4
-6 +20	77.4	65.2	78.2	77.1	58.4
-20	12.4	32.2	11.8	12.7	9.2
Onsize after crushing oversize, %	83	67	85	84	79
Chemical analysis of product, wt. %					
Total P_2O_5	62.8	58.3	49.5	30.5	42.3
Available P_2O_5	61.6	56.5	48.9	30.1	41.9
W.S. P_2O_5	9.8	27.3	10.2	7.1	7.5
Free acid P_2O_5	...	0.2	...	0.1	0.07
K_2O	31.4	21.6
F	...	0.5
CaO	...	23.7	27.1
H_2O	0.9	1.4	...	0.5	0.2

^a 40% - 100 mesh.

^b Regular, 100% - 14-mesh size.

Grade	W.S. P_2O_5 , % of Total
12-12-12	48-50
8-16-16	47
7-28-14	45-47
8-32-16	50-52
5-20-20	30

These water solubilities, except for a somewhat lower value for 5-20-20, are as high as are usually obtained with the same or equivalent grades when only ordinary and triple superphosphates are used.

The granular ammoniated products, particularly those with higher degrees of ammoniation, were found by petrographic studies to contain substantial proportions of calcium diammonium pyrophosphate [$Ca(NH_4)_2P_2O_7 \cdot H_2O$]. This is one of the phosphatic compounds recently identified in ammoniation products of hydrolyzed calcium metaphosphate at TVA's research laboratories (7). Agronomic tests are being made to determine whether such materials have unique agronomic properties.

All of the products had good physical appearance, and the granules were strong and generally well rounded. In tests made to evaluate bag-storage properties, the products were stored in five-ply paper bags having one asphalt-laminated ply. The test bags were placed in the bottom

four positions in stacks 12 bags high. The bags were inspected at 1-, 3-, and 6-month intervals to determine the degree of bag set and caking. These tests indicated that the storage properties of the products were at least as good as those of conventional products of equal moisture contents. Good storage without addition of a conditioning agent prior to bagging was obtained with the 12-12-12 grade dried to 0.5% moisture content, the 7-28-14 and 8-16-16 grades dried to about 1%, and the 5-20-20 grade dried to about 3%. Conditioner was required, however, when the moisture content of the 12-12-12 was about 1% and that of the 7-28-14 was about 3%. The 8-16-16 and 5-20-20 were not tested at higher moisture contents. The 8-32-16 grade was tested only at the relatively high moisture content of about 6%, and the results showed that greater drying of this grade would be required, even if conditioners were used.

General Considerations. A potential difficulty which must be avoided in application of this process is excessive thickening and setting up of the hydrolyzate in the hydrolysis tank and feed lines. In the pilot plant this difficulty was practically eliminated by using the proportions of water and acid given in this report. It was necessary, however,

to empty the hydrolysis tank quickly if operation were discontinued for any appreciable length of time to avoid solidification. In regular operation, it would be desirable to discharge the contents of the hydrolyzer to the ammoniator before a scheduled shutdown, and to provide for dumping the contents of the hydrolyzer to a salvage pit in emergency shutdowns when the ammoniator could not be operated. The hydrolyzate should form a solid mass that could be crushed and utilized. In the pilot plant the solidified material, particularly when only water was used for hydrolysis, was porous and friable, resembling superphosphate.

A simple distributor of the type used in the pilot plant for feeding the hydrolyzate (Figure 1) should be satisfactory for use in large scale application.

It appeared that the input degree of ammoniation of the calcium metaphosphate should be held to about 2.7 to 3.0 pounds of ammonia per unit of P_2O_5 for best results. In a few tests, good absorption was obtained with degrees of ammoniation as high as 3.3.

Granular Phosphates and No-Nitrogen Grades

Methods were developed for granulating calcium metaphosphate alone and in admixture with superphosphates to produce partially water-soluble granular phosphates and with potassium chloride to produce no-nitrogen (PK) grades. The most satisfactory procedure for granulating calcium metaphosphate alone involved heating the material to 200° F. and feeding it to the granulation drum, where it was partially hydrolyzed by spraying with hot water. When superphosphates were used as supplementary material, granulation was accomplished by feeding steam beneath the bed and sprays of water above the bed; the calcium metaphosphate was not preheated. The latter procedure was used when potassium chloride was fed with calcium metaphosphate to produce granular no-nitrogen grades. Data from typical tests of the various grades are given in Table II.

0-61-0 Grade. This grade was made by granulation of calcium metaphosphate alone. Best results were obtained when the particle size of the calcium metaphosphate was somewhat finer than the regular plant product. A screen analysis of material that proved satisfactory is given below, together with that for the regular size.

Material	Screen Analysis (Tyler), %			
	-14	+48	+100	-100
For granulation	0-1	35-40	17-20	40-45
Regular size	0-2	55-60	25-30	15-20

The calcium metaphosphate was preheated so that it was fed to the drum at 200° to 220° F. Water heated to 160°

to 190° F. was sprayed onto the bed through two solid-cone nozzles located about 8 inches above the bed. The sprays were positioned 6 inches apart and were located to cover about two thirds of the length of the drum. No distributors were used beneath the bed. A better rolling action was obtained by changing the retaining ring at the discharge end of the drum to lower the bed depth from 8 to about 4 inches. Best granulation was obtained with a water rate of 230 to 250 pounds per ton of product.

A product of good quality was obtained by either cooling or drying the granulated material. In the best tests, 80% or more of the product was -6 +20 mesh. About 15% of the phosphate in the product granules was water-soluble. The moisture content of the cooled product was 1.6% and that of the dried product was less than 1%. The unconditioned products behaved very satisfactorily in bulk and bag storage. Agronomic tests showed that the granules, which consisted of small particles of unreacted calcium metaphosphate cemented together with water-soluble products of hydrolysis, gave results equal to those obtained with regular-size (-14-mesh) calcium metaphosphate.

Attempts to granulate calcium metaphosphate alone by using steam beneath the bed as the source of heat were unsuccessful. The main difficulty encountered was inadequate means for controlling the extent of hydrolysis at the proper level to promote granulation without causing excessive stickiness and overagglomeration.

0-56-0 Grade. Granular phosphate containing 56.5% available P_2O_5 , about half of which was water-soluble, was produced successfully in the rotary granulator by partial hydrolysis of regular-size calcium metaphosphate admixed with cured high-analysis (54%) superphosphate (4). Calcium metaphosphate was used to supply 20 units of P_2O_5 and high-analysis superphosphate to supply 36 units. Steam was fed beneath the bed at a rate of about 250 pounds per ton of product, which was sufficient to heat the material in the drum to 200° F. Hot water was sprayed on top of the bed at a rate of about 60 pounds per ton of product for control of granulation. Good granulation, which resulted in about 65% -6 +20 mesh, was obtained. The product granules, which were dried to about 1.5% moisture, remained free from caking in bulk storage and in bags. After 6 months of storage in bags there was a noticeable weakening of the bags (five-ply paper with one asphalt ply); however, this was overcome by using bags with a polyethylene inner coating or by dusting the product with about 1.5% of calcined dolomite prior to bagging.

0-48-0 Grade. A granular phosphate of 0-48-0 grade was produced by partial hydrolysis of regular-size calcium metaphosphate admixed with ordinary (20%)

superphosphate. The formulation contained 41 units of P_2O_5 as calcium metaphosphate and 7 units as ordinary superphosphate. Steam was fed beneath the bed at a rate of 250 pounds per ton of product and water was sprayed above the bed at a rate of 40 to 60 pounds per ton. The purpose of the steam was to give a temperature of 200° to 220° F. in the drum and to hydrolyze the calcium metaphosphate partially. The water rate was varied for control of granulation. Good granulation was obtained and control was easy; about 78% of the product from the dryer was -6 +20 mesh. The product, which contained 1% moisture, remained in very good condition in the storage pile. Bag-storage tests of unconditioned product showed very little caking, but the bags were attacked somewhat in 3 months. Treating with a neutralizing agent such as calcined dolomite, lime, or ammonia probably would prevent this attack.

0-30-30 and 0-40-20 Grades. Granular no-nitrogen fertilizers of 0-30-30 and 0-40-20 grades were produced by partial hydrolysis of calcium metaphosphate in admixture with potassium chloride. Initial tests with steam beneath the bed and sprays of water on the bed failed to give sufficient plasticity for good granulation. In later tests, phosphoric acid and calcined dolomite (CaO-MgO mixture) were fed as supplementary materials; the additional heat and plasticity due to reaction of the dolomite and acid resulted in good granulation. The use of granular potash resulted in better granulation than was obtained with nongranular potash. The formulation for the 0-30-30 grade was:

Calcium metaphosphate	22 units
Phosphoric acid	8 units
Calcined dolomite	80 lb./ton of product
Potassium chloride (granular)	30 units
Steam (beneath bed)	250 lb./ton of product

The granules were not strong or well formed as discharged from the granulator. However, after passing through the dryer they were satisfactory. About 77% of the product from the dryer was -6 +20 mesh. The free acid content was only 0.1%, which indicated efficient neutralization of the acid by the dolomite. The product did not cake in bag storage, and in bulk storage only light surface crust developed. However, bag rot occurred despite the low free acid content. Dusting of the granules with 2.5% of a neutralizing conditioner such as calcined dolomite prevented the bag rot.

The 0-40-20 grade was produced with a formulation very much like that for the 0-30-30. The main difference was that only about 6 units of P_2O_5 as phosphoric acid were required to give the necessary heat and plasticity for good granulation.

This product also required a neutralizing conditioner to prevent bag rot.

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CELLULOSIC WASTES AS FERTILIZERS

Microbial Decomposition and Nitrogen Availability of Reacted Sawdust, Bagasse, and Coffee Grounds

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The Fersolin process for making sawdust and other cellulosic wastes useful for supplementing soil organic matter decreases decomposability, adds plant nutrients, and avoids microbial competition for available nitrogen. Microbial and chemical studies showed carbon-nitrogen transformations of Fersolins added to soil were less decomposable than the corresponding raw materials. Bagasse, most decomposable, gave a product showing greatest resistance increase. Reacted sawdust was most resistant. Coffee Fersolin showed a decrease in decomposability, but was less resistant than reacted bagasse or sawdust. The imparted resistance is desirable for increasing persistence in the soil as well as decreasing nitrogen demands. All the reacted products carried nitrogen in excess of the requirements of microorganisms involved in their decomposition.

TREATMENT OF SAWDUST or other cellulosic wastes with dilute sulfuric acid at high temperature decreases hydrolyzable carbohydrates and increases nonhydrolyzable lignin or ligninlike substances, giving a product more suitable for use on the soil. Wood wastes and similar residues treated by the Fersolin process (8) or a modification thereof (9), because of conversion of much of the cellulose to resistant complexes, are less readily decomposable than the raw materials. This decreases or eliminates the microbial demand for available nitrogen when such organic products are added to the soil, imparts desirable lasting qualities, and prolongs physical effects. After the heat treatment, ammonia is added to neutralize the acid, and the processed material carries more than enough nitrogen for its own decomposition. Some of the nitrogen is in organic combination. Use of phosphoric acid with the sulfuric in the primary treatment, or nutrient fortification of the product with mineral fertilizer, can enhance value and economic feasibility.

An economical method has been developed for conversion of fine sawmill wastes into a useful agricultural product. The process, described by Farber and Hind (10), consists of treatment with mineral acids, addition of plant nutrients, heating, and conditioning. The finished product, generally identified as Fersolin, is an efficient fertilizer carrier and physical soil conditioner.

Appropriate analyses and soil microbial studies of raw and reacted sawdust, raw and reacted bagasse, and spent and reacted spent coffee grounds were made to evaluate these materials on the basis of their reactions under controlled conditions in the laboratory.

Materials

The soil used was collected from an area mapped as Salinas fine sandy loam, noncalcareous phase. A bulk sample representing the 0- to 6-inch horizon was passed through a 10-mesh sieve and stored in large tightly covered cans.

One-hundred-pound samples of raw and reacted sawdust, coffee grounds, and bagasse were individually well mixed and 5-pound representative subsamples were taken with a sample splitter. About 1 pound of each subsample was ground

through a No. 800 screen (approximately 60-mesh) on a Weber mill for an analytical sample and for use in the microbial studies, where fine materials are required to ensure adequate mixing with small quantities of soil and reasonable agreement between replicate treatments.

Methods

Moisture was determined as loss in weight by drying samples at 105° C. for 24 hours.

Moisture capacity of the soil and organic materials was calculated from the amount of water retained by samples in Gooch crucibles wetted from below by immersion, and then allowed to drain to constant weight in a moisture-saturated atmosphere.

Exchange capacity and exchangeable cations were determined by the ammonium acetate method. This and other methods not specifically outlined are described in procedures used by the Oregon State College soil testing laboratory (7).

Ash was determined by ignition at 900° C.; total carbon, by dry combustion at 950° C.; total nitrogen, by the Kjeldahl method modified to include nitrates. Ammonium nitrogen was de-

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