

TVA Process for Production of Granular Diammonium Phosphate

R. D. YOUNG, G. C. HICKS,
and C. H. DAVIS

Tennessee Valley Authority,
Wilson Dam, Ala.

The process developed in the TVA pilot plant involves partial ammoniation of phosphoric acid in a preneutralizer and completion of ammoniation in a rotary ammoniator-granulator. Granulation is controlled by recycling product fines to the drum. Addition of excess ammonia to the drum allows reaction to an $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio of about 2.0, thereby decreasing the solubility of the ammonium phosphates and improving control of granulation. The excess ammonia is recovered by scrubbing the gases from the drum with the feed acid before preneutralization. The granular material is dried and then screened to obtain a closely sized diammonium phosphate of 18-46-0 to 21-53-0 grade. N-P-K grades, such as 18-18-18, 15-15-15, and 14-35-14, can be produced by adding other feed materials.

HIGH-ANALYSIS ammonium phosphate fertilizers are becoming more in demand as the trend toward production of higher analysis grades increases and as bulk blending increases in popularity. It is estimated that shipments of ammonium phosphates in 1960-61 was about 300,000 tons, or 28% over 1959-60, and additional plant expansion is under way or planned (3). The Tennessee Valley Authority has developed on pilot scale a new and improved process for producing granular diammonium phosphate from ammonia and phosphoric acid. Much less recycle and drying of the product are required than in other ammonium phosphate granulation processes since the heat of reaction of ammonia and acid is used to evaporate 80 to 90% of the moisture. The process can be used in a TVA-type ammoniation-granulation plant by adding a scrubber and a preneutralizer. The product is of uniform size and has very good storage and handling properties. At least three new commercial-scale plants already have been built to use this process, and other manufacturers are considering this process in their plans for entering the rapidly expanding market of granular ammonium phosphates.

In the pilot-plant work, diammonium phosphate was produced alone or with other fertilizer materials to make a variety of grades. Satisfactory results were obtained with either electric-furnace or wet-process phosphoric acid and either gaseous or liquid ammonia. The grade of the diammonium phosphate ranged from 21-53-0 to 18-46-0, depending on the amount of impurities in the acid. Grades such as 14-35-14 and 18-18-18 were made by adding

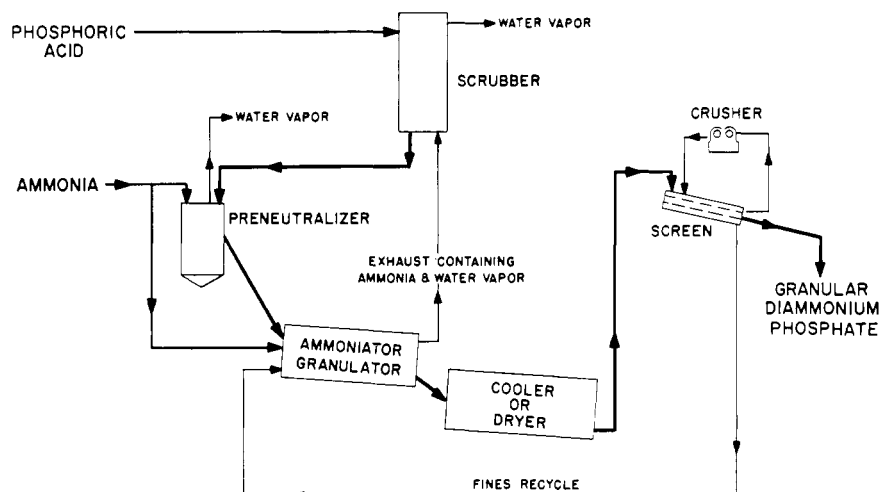


Figure 1. Flow sheet of TVA process for production of granular diammonium phosphate

potassium chloride and ammonia-ammonium nitrate solutions.

This paper describes the process and presents pilot-plant data obtained during its development.

Description of Process

A flow diagram of the process is shown in Figure 1. The process involves partial preneutralization of the acid in a tank followed by completion of the ammoniation to diammonium phosphate in an ammoniator-granulator. Excess ammonia, which must be fed to the ammoniator-granulator to produce diammonium phosphate, is recovered by scrubbing the off-gases with the acid to be used in the process. The granular product usually is dried. Cooling is not needed for diammonium phosphate; however, for products that contain other

fertilizer salts such as ammonium nitrate, cooling is needed prior to screening and storage. The product is sized, and the undersize and crushed oversize are recycled to control granulation.

In addition to utilizing the heat of reaction of ammonia and phosphoric acid to evaporate water, advantage is taken in this process of the change in solubility of ammonium phosphate with $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio (7). As shown in Figure 2, maximum solubility occurs at an $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio of about 1.45; therefore, the preneutralizer is operated at as near this point as is practical to obtain the most concentrated slurry having satisfactory fluidity. Ammoniation of the slurry in the drum to mole ratio 2.0 lowers the solubility and causes crystallization of diammonium phosphate. This decreases the amount of liquid phase present, thereby lowering

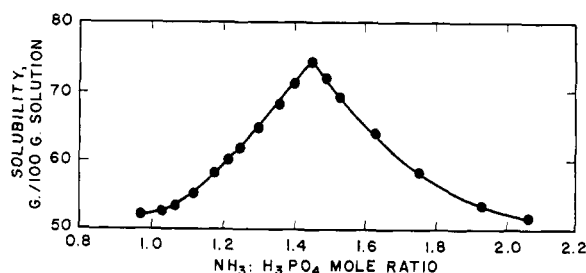


Figure 2. Effect of $\text{NH}_3\text{:H}_3\text{PO}_4$ mole ratio on solubility of ammonium phosphate at 167°F. (1)

the recycle requirement. In conventional production of granular mixed fertilizers from formulations containing phosphoric acid, the $\text{NH}_3\text{:H}_3\text{PO}_4$ mole ratio is usually limited to about 1.5 to prevent excessive loss of ammonia. At this lower mole ratio, solubility of the ammonium phosphate in the granulator is at a maximum, and excessive agglomeration is often experienced when using as little as 200 to 300 pounds of phosphoric acid per ton of product.

Description of Pilot Plant

The test work was done in the pilot plant used previously for the development of TVA continuous ammoniation process. The only modification required for the present work was the addition of a scrubber and a preneutralizer tank.

Preneutralizer. About half the total water introduced in the process was evaporated in the preneutralizer by the heat from ammoniation of the phosphoric acid. Removal of the heat and moisture in the preneutralizer was effective in reducing the recycle required to control granulation in the ammoniator-granulator. The preneutralizer consisted of a 20-inch-diameter, 5-foot-high open tank equipped with an agitator. A 2-foot liquid level was maintained in the tank. Ammonia was introduced at the bottom through a circular sparger; the sparger was made from $1/4$ -inch pipe and had perforations directed toward the center of the tank. The partially neutralized acid from the scrubber entered through an open pipe near the bottom of the tank. Type 316 stainless steel was used throughout for construction of the preneutralizer system. The tank was equipped with a hood and a fan for exhausting the moisture-laden gas to the atmosphere. This gas was not scrubbed to recover ammonia because condensation of moisture that would occur in a scrubber would result in the recycle of heat and water to the preneutralizer. The preneutralized slurry flowed by gravity through a near-vertical pipe into the ammoniator-granulator drum. This pipe was equipped with a steam jacket and connections for adding steam if required to maintain a flow of slurry.

Ammoniator-Granulator. The slurry was ammoniated to diammonium phosphate and granulated in a 3×3 feet ammoniator drum followed by a separate 2×7 feet granulator drum or in a 3×6 feet combination ammoniator-granulator with a 9-inch retaining ring 4 feet from the feed end. Drums were operated at 20 r.p.m. Equal results were obtained with either unit. Granulation was controlled primarily with recycle; the recycle requirement usually was from 1 to 3 pounds per pound of product.

Slurry from the preneutralizer usually was fed through a saw-toothed trough distributor above the rolling bed of solids in the drum. Anhydrous ammonia or ammoniating solution was fed beneath the bed in the drum through a 30-inch-long, slotted distributor of the type normally used in pilot-plant tests of the production of conventional mixed fertilizers (4). Gases from the ammoniator-granulator were drawn through the scrubber at a rate of about 350 cubic feet per minute through use of an exhaust fan. An efficient exhaust system for the drum is needed because of the large amount of water vapor evolved.

Scrubber. The scrubber for recovery of ammonia consisted of a tower that was 2 feet in diameter and 10 feet high and contained 8 feet of wood grid-type packing. This type of scrubber was used because it was already on hand; however, any type of conventional scrubber that would not be subject to plugging by the solids in the wet-process acid probably should be suitable. Type 316 stainless steel was used in the construction of the scrubbing system. However, rubber-lined equipment or appropriate epoxy resin materials should be suitable. The acid was recirculated to the top of the tower at a rate of about 10 gallons per minute. A double-cone distributor was used to disperse the scrubbing liquor over the packing.

Drying, Cooling, and Sizing. The rotary dryer and rotary cooler were of conventional design. A countercurrent flow of air was used in each unit. However, concurrent drying probably would have been satisfactory. The dryer was 3 feet in diameter by 24 feet long and contained eight 8-inch radial flights. The temperature of the air to the dryer was 240° to 270°F. and the temperature from the dryer was 180° to 210°F. The air rate was about 1800 cubic feet per minute. The cooler was 2.5 feet in diameter by 20 feet long and usually was operated to maintain a product temperature of about 150°F. since better results were obtained with hot recycle. The product was sized on double-deck screens usually having 6- and 10-mesh openings.

Pilot-Plant Tests

Most pilot-plant tests were made with wet-process acid; in a few instances, comparison tests were made with electric-furnace acid. The production rate was

Table I. Typical Analyses of Raw Materials Used in Pilot-Plant Tests

Phosphoric Acid Type	Wet-Process (WP)			Electric Furnace (EF)
	1	2	3	
Chemical analysis, %				
Total P_2O_5	54	46	54	55
SO_3	3.0	4.8	2.0	...
CaO	0.1	0.8	0.8	...
Al_2O_3	1.5	1.4	1.0	...
Fe_2O_3	1.7	1.1	1.3	...
H_2O (calcd.)	17	26	21	24
Solid Material Type	Triple Superphosphate			Potassium Chloride
Chemical analysis, %				
Total P_2O_5	48.6			...
Available P_2O_5	48.1			...
W.S. P_2O_5	41.4			...
K_2O	...			62.0
H_2O	2.4			Nil
Screen analysis (Tyler mesh), %				
+6	0.3			0.0
-6 +10	10.5			0.3
-10 +16	13.7			0.5
-16	75.5			99.2

Table II. Results from Pilot-Plant Tests of Production of Granular Diammonium Phosphate

Grade Test no.	18-46-0 1	16-48-0 2	16-48-0 3	21-53-0 4	16-48-0 5	14-35-14 6	18-18-18 7	15-15-15 8
Production rate, ton/hr.	0.5	0.5	1.0	0.5	1.0	0.75	1.0	1.0
Type of acid	WP-2	WP-2	WP-3	EF	EF	WP-1	WP-1	WP-3
% P ₂ O ₅	46.3	46.5	54.0	54.5	54.8	52.4	53.6	54.0
% H ₂ O	25.8	25.5	21.0	23.4	25.4	19.4	17.3	21.0
Feed rates, lb./ton								
To scrubber								
Phosphoric acid	1994	2056	1493	1870	1497	1381	662	565
Water	355	...	334	96	...	654
To preneutralizer								
Liquid ammonia	278	336	253	334	249	272	...	285
Sulfuric acid, 66° Bé.	103	594
Water (with liquid NH ₃)	...	259	...	485	309	336	127	149
Solution 448 ^a	589	...
Scrubber effluent	2291	2029	1808	1905	1464	1457	672	1229
To granulator								
Solution 448 ^a	232	...
Ammonia (L, liquid; G, gas)	191(L)	86(G)	147(L)	194(L)	148(L)	101(L)	...	80(L)
Sulfuric acid, 66° Bé.	94
Preneutralizer slurry	2264	2271	1730	2297	1710	1713	1397	1774
Potassium chloride	501	565	496
Triple superphosphate	372	...	403
Recycle	4236	9237	6110	5763	5682	3154	4055	3669
Equivalent acid concentration, %								
P ₂ O ₅	39	41	44	44	45	40	45	22
Scrubber conditions								
Temperature, ° F.								
Inlet gas	120	110	121	120	116	133	96	100
Liquor	138	128	139	150	170	175	118	110
Composition of effluent, %								
Total N	1.2	0.2	1.4	1.8	3.5	2.3	1.3	1.30
Total P ₂ O ₅	40.3	47.1	44.6	54.5	56.1	49.7	52.9	24.8
H ₂ O	34.0	24.6	33.6	22.4	19.2	20.7	16.8	61.9
NH ₃ loss, %	0.1	0.0	1.2 ^b	0.2	0.8	0.4	0.2	1.9 ^b
Scrubber efficiency, %	98	...	86	98	94	...	98	71
Preneutralizer conditions								
Temperature, ° F.	237	238	242	240	240	239	272	225
pH	5.5	5.9	5.9	5.6	6.1	5.5	5.0	6.0
Composition of effluent, %								
Total N	10.4	12.2	12.6	13.0	14.0	12.0	19.7	13.4
Total P ₂ O ₅	40.8	42.1	46.6	45.2	48.0	42.3	24.7	17.2
H ₂ O	22.0	17.8	17.1	21.8	16.8	20.3	13.5	27.8
NH ₃ :H ₃ PO ₄ mole ratio	1.29	1.47	1.37	1.46	1.47	1.44	...	1.37
NH ₃ loss, % of total feed	2.8	4.1	4.8	3.1	2.8	5.8	2.0	4.5
Granulation conditions								
Recycle								
Lb./lb. product	2.1	4.6	3.1	2.9	2.8	1.6	2.0	1.8
Temperature, ° F.	97	117	109	93	111	130	100	85
Input moisture content, %								
Including recycle	8.7	4.8	4.8	6.2	4.6	7.1	3.7	9.0
Excluding recycle	20.3	16.5	13.1	20.1	13.2	15.0	9.3	20.5
Ammoniator temperature, ° F.	188	164	183
Granulator product								
Temperature, ° F.	165	151	182	140	174	165	162	154
Moisture content, %	4.1	2.6	3.4	2.1	2.7	3.7	1.6	6.6
NH ₃ :H ₃ PO ₄ mole ratio	2.03	1.76	...	1.98	...	1.98
Screen analysis, %								
+6 mesh	1.2	28.1	7.3	25.2	39.5	15.3	30.4	43.9
-6 +10 mesh	56.0	46.7	30.0	9.1	15.7	40.9	17.5	28.6
-10 +16 mesh	40.3	18.7	45.7	26.5	20.2	31.0	13.8	7.2
-16 mesh	2.5	6.5	17.0	39.2	24.6	12.8	38.3	20.3
NH ₃ evolved from granulator, % of total	5.7	0.1	9.0	8.6	13.7	...	12.3	7.1
Dryer product								
Temperature, ° F.	180	210	183	180	196	184	208	190
NH ₃ loss, % of total	2.8	0.8	0.6	3.5	1.4	2.8	2.1	0.8
Moisture content, %	1.8	1.8	2.1	0.6	1.9	1.6	0.5	3.6
NH ₃ :H ₃ PO ₄ mole ratio	2.01	1.76	...	2.00	...	1.96
Screened product								
Chemical analysis, %								
Total N	18.5	16.8	15.8	20.9	15.8	14.7	17.2	14.2
Total P ₂ O ₅	47.0	48.8	50.6	53.4	51.8	38.1	19.0	15.5
Available P ₂ O ₅	50.3	...	51.1
K ₂ O	13.6	18.6	15.4
H ₂ O	1.7	1.6	2.2	0.5	1.9	1.7	0.5	2.8
NH ₃ :H ₃ PO ₄ mole ratio	2.00	1.75	...	1.98	...	1.96

^a 25% NH₃, 69% NH₄NO₃, 6% H₂O.

^b High loss of ammonia due to collapsed packing in scrubber.

0.5 to 1.0 ton per hour. Typical analyses of the raw materials are shown in Table I, and operating data and results of typical tests are shown in Table II.

Ammonium Phosphates. Granular diammonium phosphate was produced from wet-process phosphoric acid by ammoniation of the acid to an $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio of 2.0. The grade ranged from 18-46-0 to 19-49-0 depending on the purity of the acid used. The acid was preneutralized with anhydrous liquid ammonia to an $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio between 1.26 and 1.47. Best operation of the preneutralizer was obtained with a mole ratio of 1.35 and a temperature of about 240° F. Under these conditions, loss of ammonia from the preneutralizer was low ranging from 2 to 3% of the total amount fed to process. The slurry contained 18 to 22% H_2O and was fluid enough to flow readily to the ammoniator-granulator by gravity. Operation at a mole ratio of about 1.45, which would result in maximum solubility, was not practical because loss of ammonia was high.

The temperature in the preneutralizer was controlled by evaporation of water and was maintained at 240° to 245° F.; attempts to operate at higher temperatures resulted in excessive thickening of the slurry. To maintain a temperature of 240° F., the total amount of water required was equivalent to the use of acid containing 39 to 43% P_2O_5 . Since the tests usually were made with merchant-grade acid that contained about 54% P_2O_5 , water was added either to the scrubber or with the ammonia fed to the preneutralizer. Some difficulty was experienced with the freezing out of solids in the vicinity of the ammonia distributors in the preneutralizer. Without premixing of the ammonia and water, freezing occurred during startup when the preneutralizer was cold or during operation when there was not enough agitation of the slurry in the preneutralizer. Freezing did not occur when water was added with the ammonia.

In a granulation plant integrated with a plant producing wet-process phosphoric acid, acid containing about 40% P_2O_5 would be fed and water, as such, would not be added with the ammonia. It would be desirable, therefore, when starting, to use an ammonia vaporizer to prevent freezing in the preneutralizer and to add some water to the preneutralizer to ensure a fluid slurry until operating conditions have been established.

The slurry from the preneutralizer was distributed over a bed of recycled fines in the ammoniator where ammoniation to diammonium phosphate was completed with anhydrous liquid ammonia. With slurry at a temperature of about 240° F. and containing 18 to 22% moisture, good granulation was

obtained with recycle ratios of 2.1 to 2.5 pounds per pound of product. The temperature of the product leaving the ammoniator was 180° to 200° F., and the moisture content was 2.5 to 4.5%. The temperature of the product leaving the separate granulator or the combination ammoniator-granulator was 150° to 180° F. Better results were obtained with higher temperatures because more water was evaporated and the bed was drier. Higher temperatures were obtained when using hot recycle (150° F.). They also could have been obtained by using gaseous instead of liquid anhydrous ammonia. Operation also was improved and greater moisture evaporation obtained throughout the process when granulation was controlled so that less than 10% of the product from the granulator was +6 mesh in size and about 50% was -10 mesh in size. With this control of granulation, most of the recycle was obtained directly from the screens as -10-mesh material.

Control of the operation to obtain the desired mole ratios in the preneutralizer and in the ammoniator-granulator was based primarily on measurement of the pH of the preneutralizer effluent, which usually was held in the pH range of 5.5 to 5.7. Appropriate adjustments in feed of ammonia to the drum were made on the basis of any change in pH of the preneutralized slurry. Measurements of the loss of ammonia from the preneutralizer and drum were used as secondary aids to control. Some success also was obtained in the use of a rapid double titration procedure for direct determination of the $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio on samples of the slurry and product. In this procedure, an estimated 1 to 2 grams of slurry or product was added to 100 ml. of water and titrated with 0.5*N* hydrochloric acid to the methyl orange end point (*A*). Then, phenolphthalein indicator was added for a second titration with 0.5*N* sodium hydroxide (*B*). The $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio was determined by dividing the sum of the titers (*A* + *B*) by the second titer (*B*).

The recycle requirement was 2.1 to 2.5 pounds per pound of product when the concentration of the acid to the preneutralizer was equivalent to about 40% P_2O_5 . A limited study was made to determine the effect of using more dilute acid on the requirement of recycle. Gaseous instead of liquid anhydrous ammonia was fed to the preneutralizer to provide more heat of reaction and thereby increase evaporation of water. When the acid concentration was 37 instead of 40%, the recycle ratio was 3.5. When the concentration of the acid was further decreased to 34, 33, and 32% P_2O_5 , the recycle ratio increased to about 5, 6, and 8, respectively. These values are only approximations because, with these high recycle ratios, the drying

and crushing equipment became overloaded before steady conditions could be attained.

Ammonia in the off-gas from the ammoniator-granulator varied from 6 to 15% of the total to the process, and most of it (90% or more) was recovered by scrubbing with the acid which later was fed to the preneutralizer. Ammonia loss from the scrubber was less than 0.5% of the total to the process.

Loss of ammonia during drying was 2 to 3% at 180° F. and 4% at 210° F. In this process, the load on the dryer is low because about 90% of the input moisture is removed by the heat of reaction in the preneutralizer and ammoniator-granulator.

Test 1 (Table II) was typical of the production of granular diammonium phosphate of 18-46-0 grade from wet-process acid. All the acid and sufficient water to give an equivalent acid concentration of 39% P_2O_5 were fed to the scrubber. About 39% of the water in the feed to the preneutralizer was evaporated, and the slurry from the preneutralizer to the ammoniator-granulator contained 22% water. The recycle ratio was 2.1, and the moisture content of the granulated product before drying was 4.1%. About 56% of the product was -6 +10 mesh in size, and part of it had to be crushed and returned as recycle. Loss of ammonia amounted to 5.7% of the total to the process: 0.1% from the scrubber, 2.8% from the preneutralizer, and 2.8% from the dryer.

Wet-process acid also was used in two formulations for the production of 16-48-0 ammonium phosphate. In one formulation, all the P_2O_5 was supplied as acid, but the acid was only partially ammoniated; the $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio was about 1.7 instead of 2.0. In the other, part of the P_2O_5 was supplied as triple superphosphate and the remainder as acid. The acid was ammoniated fully, and the superphosphate was ammoniated presumably to the normal degree of about 3.8 pounds of ammonia per unit of available P_2O_5 .

The conditions used in producing 16-48-0 with all the P_2O_5 supplied as acid (test 2) were about the same as were used in making 18-46-0 except that the amount of ammonia fed to the ammoniator-granulator was limited to give an $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio of about 1.7 instead of 2.0. Because of the higher solubility of ammonium phosphate at the lower mole ratio (Figure 2), over twice as much recycle was required to prevent excessive agglomeration as when producing the 18-46-0 grade (4.6 *vs.* 2.1 pound per pound of product). Very little ammonia was evolved from the ammoniator-granulator, and scrubbing to recover ammonia was not required.

The formulation for 16-48-0 containing part of the P_2O_5 as triple superphosphate was tested because less recycle

would be required (test 3). In this test, 9 units of P_2O_5 were supplied as triple superphosphate. The presence of the superphosphate reduced the liquid phase in the granulator not only by replacing a liquid with a solid but also by permitting ammoniation of the phosphoric acid to a mole ratio of near 2, the region of minimum solubility. As a result, excellent granulation was obtained with a recycle ratio of about 3 instead of 4.6, and over-all control of granulation was significantly improved. The high loss of ammonia from the scrubber for this test (Table II) was a result of collapsed packing.

A few tests were made with electric-furnace acid; the grades of the products were 21-53-0 and 16-48-0. In making the 21-53-0 product (test 4), the acid was preneutralized to an $NH_3:H_3PO_4$ mole ratio of 1.46. The temperature of the slurry (240° F.) and the moisture content (22%) were about the same as when wet-process acid was used to make the 18-46-0 product (test 1). However, about one third more recycle (2.9 *vs.* 2.1 pound per pound of product) was required to control granulation. Loss of ammonia from the preneutralizer was 3.1% of the total fed to the process.

In making the 16-48-0 grade (test 5) with electric-furnace acid, a part of the P_2O_5 was supplied as triple superphosphate. The recycle requirement was about the same as in the test of a similar formulation (test 3) with wet-process acid described above. In both tests with furnace acid, there was considerably more oversize (+6 mesh) and less onsize material in the products from the granulator than when using wet-process acid.

Ammonium Phosphate with Potash. A granular 14-35-14 grade of fertilizer was produced from wet-process acid, ammonia, and fine sized potassium chloride (90% -28 mesh). The operating procedure was identical to that used in 18-46-0, except that the required amount of potassium chloride was added with the other materials to the ammoniator-granulator. In test 6, good granulation was obtained with a recycle ratio of 1.6 as compared with 2.1 to 2.5 when making the 18-46-0. The results showed that the net production capacity of the plant would be considerably higher when making potash grades because of the lower recycle requirement. In a similar test of the production of 10-25-25, there was not enough liquid phase for granulation because of the large amount of nongranular potassium chloride used. Reducing the recycle ratio to 0.2 pound per pound of product and diluting the slurry to 29% water did not significantly improve granulation. No data for this test are given in the tables. Good granulation of such grades probably could be obtained with the use of granular potassium chloride (2).

1:1:1 Ratio Products. Two formu-

lations were tested for the production of 1:1:1 ratio fertilizers. In production of an 18-18-18 grade, nitrogen was supplied as ammonia-ammonium nitrate solution (solution 448, 25-69-0); only a small proportion of sulfuric acid was needed to fix the excess free ammonia. In the other formulation, all the nitrogen was supplied as ammonia; therefore, it was necessary to use a much larger proportion of sulfuric acid to fix the excess ammonia, and the higher ammonium sulfate content of the product reduced the grade to 15-15-15.

In making the 18-18-18 product (test 7), wet-process phosphoric acid was fed to the scrubber and then to the preneutralizer where the sulfuric acid (66° Bé.) was introduced. Sufficient ammoniating solution was added to the preneutralizer to neutralize the sulfuric acid and ammoniate the phosphoric acid to an $NH_3:H_3PO_4$ mole ratio of about 1.35. The remainder of the ammoniating solution was added in the ammoniator-granulator to give an $NH_3:H_3PO_4$ mole ratio of 2. Because of the presence of ammonium nitrate, the slurry leaving the preneutralizer was sufficiently fluid at a moisture content of 14% and a temperature of 272° F. to feed to the granulator. Since less water was needed to obtain a fluid slurry than when using ammonia in production of 18-46-0, phosphoric acid containing 45% P_2O_5 instead of about 40% could be used and operation of the ammoniator-granulator was satisfactory with a recycle ratio of 2.0. Loss of ammonia from the preneutralizer was 2.0% of the total to the process.

In the formulation of the 15-15-15 grade (test 8), about 700 pounds of 66° Bé. sulfuric acid was required per ton of product. About 85% of this acid was fed to the preneutralizer and the remainder was added in the ammoniator-granulator. As with other formulations, phosphoric acid was fed first to the scrubber and then to the preneutralizer. Sufficient ammonia was fed to the preneutralizer to neutralize the sulfuric acid and to give an $NH_3:H_3PO_4$ mole ratio of 1.37. Because of the low solubility of the ammonium sulfate, it was necessary that the slurry contain about 28% water for satisfactory fluidity. Also, more than the usual amount of water had to be added to the preneutralizer because of the increased evaporation resulting from the heat of neutralization of the sulfuric acid. Consequently, the water added was sufficient to dilute the phosphoric acid to 22% P_2O_5 . Loss of ammonia from the preneutralizer was 4.5% of the total fed to the process. The loss of ammonia from the scrubber (1.9%) was unusually high because the packing had collapsed. With a recycle ratio of 1.8, 44% of the granulator product was oversize (+6 mesh). Although the onsize fraction (36% -6

+16 mesh) was sufficient for this recycle ratio, a decrease in the proportion of oversize would be desirable to reduce the load on crushing equipment. This probably could be accomplished by adjustments in the recycle ratio or in the proportioning of sulfuric acid between the preneutralizer and the ammoniator.

Storage Properties

The bag-storage properties of the pilot-plant products were evaluated by tests made with 50- and 80-pound multiwall paper bags having two asphalt-laminated plies. Test bags were placed under a weight equivalent to from 15 to 20 bags of fertilizer. The temperature of the products on bagging ranged from 80° to 120° F. Bags were inspected after 1 and 3 months of storage to determine bag set and degree of caking. Moisture contents of the test materials were determined by the A. O. A. C. vacuum desiccation method. Some products were conditioned for storage by coating with 2 to 3% by weight of a calcined dolomite or a kaolin clay. However, for the 18-18-18 product, which contained ammonium nitrate, a calcined fuller's earth instead of dolomite was used. Generally, the kaolin clay was not quite as effective as the other conditioning agents.

The 18-46-0, 19-49-0, and 16-48-0 products made with wet-process phosphoric acid and containing up to about 2% moisture stored satisfactorily for 3 months without conditioning. The 14-35-14 product containing about 1.7% moisture required conditioning to prevent caking, and the 18-18-18 product, which was made with both potassium chloride and ammonium nitrate, required conditioning even though it was dried to 0.5% moisture. Limited tests of products made with electric-furnace acid showed that for satisfactory storage they required more drying than did products made with wet-process acid. For example, ammonium phosphates of 21-53-0 grade containing as little as 0.2% moisture and 16-48-0 grade containing 2% moisture required conditioning to prevent caking during only 1 month of storage. Tests of longer duration with the various products are in progress.

Bulk-storage tests were made of 18-46-0 and 19-49-0 products containing 1 to 1.5% moisture. Materials from the dryer were screened while hot and put into 1-ton piles at temperatures of 160° to 180° F. After 1 week of storage, the products were free flowing. The tests indicated that it should not be necessary to cool products of this type below 160° to 180° F. for satisfactory bulk storage. Products to be bagged usually are cooled to at least 130° F. to prevent weakening of the bags.

Conclusions

The TVA process for the production of granular diammonium phosphate can be used in conventional ammoniation-granulation plants with the addition of only a preneutralizer tank and an ammonia scrubber. Recycle requirement for grades such as 18-46-0 and 21-53-0 is relatively low, about 2.5 pounds per pound of product, because the process takes advantage of the change in solubility of ammonium phosphate with the $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio to assist in control of granulation. The preneutralizer is operated near the $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio giving maximum solubility of ammonium phosphate to obtain the most concentrated slurry with satisfactory fluidity, and the am-

moniator-granulator is operated at an $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio giving low solubility to further reduce the amount of liquid phase present. With operation of the preneutralizer at an $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio of about 1.4, the temperature of the slurry can be as high as 245°F . without excessive loss of ammonia, and effective use can be made of the heat of reaction to evaporate water. The process also is applicable to the production of N-P-K fertilizers.

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FERTILIZER MATERIALS ANALYSIS

Determination of Calcium in Phosphate Materials by Titration with EDTA in the Presence of Calcein Indicator

H. G. GRAHAM, Jr., T. C. McRIGHT, and E. D. FREDERICK
Tennessee Valley Authority,
Wilson Dam, Ala.

A routine analytical control procedure was developed for the determination of calcium in phosphate materials by an EDTA method. Interferences from P, Fe, Al, or Mn and from ions of salts of acids or bases used to decompose the samples were avoided by addition of triethanolamine and/or dilution of the aliquot to be titrated. Continuous stirring and back titration with a standard calcium carbonate solution were also employed. The indicator was a mixture of Calcein and thymolphthalein; the titration was carried out at pH 12.0 or above. With the phosphates tested, the procedure appeared to be about as accurate as the calcium oxalate-potassium permanganate method and required less than half the time.

THE DETERMINATION of calcium is required in many phases of the manufacture of phosphorus or phosphates from natural ores. In nature, phosphorus usually occurs as calcium phosphate associated with various contaminants. The proportion of calcium in these ores affects the process used to recover the phosphate. In the wet process for making phosphoric acid, calcium oxide in the ore reacts with sulfuric acid, and this affects the amount of acid consumed. In the electric furnace process for making phosphorus or phosphoric acid, silica must be added to the phosphate to combine with the calcium oxide present to form a calcium silicate slag which can be removed from the furnace. Many phosphate fertilizers and food-grade phosphates contain calcium. The proportions of calcium to phosphorus in these materials affect the manufacturing processes used, as well as the quality of the products. Therefore, improvements in the analytical method for determining calcium in

phosphate materials contribute to more efficient phosphate manufacturing processes.

The calcium oxalate-potassium permanganate method is used ordinarily to determine calcium in phosphate materials. This method involves time-consuming steps of precipitating and filtering calcium oxalate to separate the calcium from the phosphorus. But the direct determination of calcium in the presence of phosphates would significantly reduce the time required for such a determination. In view of this, the application of an EDTA (the disodium salt of ethylenedinitrilotetraacetic acid) method for this purpose was investigated.

Within the last two decades, the use of EDTA in the determination of calcium has gained wide acceptance because of the accuracy, speed, and convenience with which such an analysis can be made. The development of EDTA methods has been summarized by Borchert (7), Reilley *et al.* (13), Verma and Theratit (15), and Welcher (16).

The theories upon which these methods are based, together with the factors affecting the methods, have been discussed in detail by Flaschka (7, 8) and Reilley *et al.* (13). In general, EDTA methods involve the stoichiometric formation of a complex between the calcium ions and the EDTA in the presence of an indicator which is specific for free calcium ions under the titration conditions. Obviously, the indicator must exhibit a definite color change when all the calcium ions have been complexed by the EDTA; yet the indicator must not form such a stable complex with the calcium that the calcium cannot be removed by the EDTA.

The feasibility of applying an EDTA method to analysis of calcium in phosphate materials used in production of phosphorus and phosphate fertilizers was investigated. The materials tested were:

Phosphate rock (consisting mostly of colophane but containing some clay, silica, and limestone as impurities).