A Laboratory-Scale Study of the Simultaneous Ammoniation and Granulation of Triple Superphosphate

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Thirteen separate and distinct samples of triple superphosphate were examined on a laboratory scale for ammoniation-granulation performance and found to vary widely. Some variation was attributed to particle size distribution, but significant differences in inherent granulating tendency were large, and varying response to incremental amounts of water was also observed. No correlation was found between either the chemical or physical properties measured that would permit a reliable prediction of granulating tendency. Ammoniation efficiency, under conditions leading to granulation, was found to correlate with physical properties related to accessible surface area, which would affect a gas-solid or liquid-solid heterogeneous reaction. The similarity of optimum operating conditions to those in full-scale TVA granulators show the efficacy of this laboratory unit.

I$_N$ RECENT YEARS, farmers have increasingly shown their preference for fertilizers in the granular form. Manufacturers have responded by establishing ammoniation-granulation units to supply the demand.

The factors governing the choice of raw materials for the process have been availability, cost, and the fertilizer grades important in particular marketing areas. The logical application of these factors to manufacturing practice frequently means that potassium chloride is the material of choice for supplying K$_2$O in the formulation; anhydrous ammonia and nitrogen solutions are used to provide the nitrogen; and superphosphate, phosphoric acid, and triple superphosphate are the sources of available P$_2$O$_5$. Standard potassium chloride can be considered a constant, and the anhydrous-nitrogen solution ratio can be established by the neutralizing values of the phosphatic constituents plus sulfuric acid.

Differences in both granulation efficiency and ammonia absorption efficiency are dependent on the properties of the phosphate raw material and the plant operating conditions. From an economic viewpoint, granulation rate establishes the production capacity of a given plant while ammonia absorption determines the amount of low-cost ammonia that can be used in a fertilizer without serious loss, thereby significantly influencing the cost of raw materials.

Fertilizer manufacturers have reported that both ammoniation and granulation efficiency (measured by production rate of on-size fertilizer) have varied for different shipments of triple superphosphate, even though all of the other raw materials and the operating conditions have been unchanged. A study was

initiated to simulate conditions of simultaneous ammoniation-granulation on a laboratory scale; to ascertain any variation of granulation tendency of triple superphosphate if, in fact, it existed; to delineate chemical and physical properties of triple superphosphate which correlate with granulation efficiencies; and to determine the influence of operation factors on laboratory ammoniation granulation efficiency. These data would ultimately permit a rational basis for studying factors in triple superphosphate manufacture to optimize its ammoniation and granulation characteristics.

An earlier paper (3) by the authors describes construction, mode of operation, and validity of performing simultaneous ammoniation-granulation on a laboratory scale. The purpose of this paper is to report the results of a study of triple superphosphate granulation as affected by variation in raw materials and operation conditions.

Characterization of Triple Superphosphate Samples

Commercial samples of run-of-pile triple superphosphate were obtained in 100- to 400-pound quantities. The results of chemical determinations are listed in Table I, the particle-size distributions in Table II, and pore volume measurements in Table III.

Variability among Commercial Triple Superphosphates

The effect of added water on granulation has been investigated by earlier workers (1, 4, 6, 7, 10) and found to be profound. The liquid phase is pictured as agglomerating particles by virtue of

Table I. Chemical Properties of Triple Superphosphate Samples

Identi-fication No.	Total P$_2$O$_5$, %	Citrate-Insolu-ble P$_2$O$_5$, %	Free Acid as H$_3$PO$_4$, %	Mois-ture,[a] %
1	48.1	0.9	3.0	5.5
2	47.0	1.5	0.9	4.7
3	47.8	0.5	1.4	4.4
4	46.5	2.8	4.0	5.3
5	48.1	1.3	4.3	4.1
6	47.8	1.3	2.4	3.8
7	48.7	1.0	0.8	2.3
8	48.7	1.8	1.8	2.6
9	48.5	2.3	1.6	2.5
10	48.8	1.4	2.2	4.0
11	48.8	1.3	2.1	3.0
12	40.6	1.6	0.3	6.5
13	47.8	0.7	1.0	2.4

[a] Dried for 5 hours at 100° C.

cohesive forces arising from the surface tension of the liquid and capillary action between discrete particles (9). Before such agglomeration can occur, enough liquid is required first, for wetting the particles and second, for the formation of capillary bonds. It is, therefore, reasonable to expect that different samples of triple superphosphate, formed under differing conditions and possessing a characteristic surface structure and pore size distribution, would exhibit different granulating properties.

Simultaneous ammoniation-granulation test runs were performed using the apparatus and procedure described previously (3). The objectives were to ascertain the variation of percentage on-size granules formed between samples of triple superphosphate with optimum water addition rates, to determine differential response to added water, and to use the data to seek correlations between

Table II. Particle-Size Distribution of Test Materials

Identification No.	(Tyler Mesh Fractions)							
	+6	−6 +10	−10 +14	−14 +20	−20 +35	−35 +65	−65 +100	−100
1	1.2	8.7	4.3	7.1	21.6	32.3	6.4	18.7
2	1.5	22.3	8.9	8.2	16.3	18.8	7.3	17.0
3	0.4	13.1	8.6	11.6	19.6	23.9	8.0	14.9
4	1.4	11.6	10.9	11.4	22.1	20.2	6.3	11.2
5	Received direct from curing pile							
6	0.6	10.5	12.0	15.7	28.2	19.7	3.8	9.8
7	2.5	7.4	5.8	6.4	16.3	21.8	9.9	29.6
8	0.0	1.6	7.8	9.5	22.8	34.3	7.5	16.5
9	2.4	9.3	8.6	9.3	21.1	26.8	7.5	14.8
10	1.0	20.2	13.6	13.6	22.2	17.2	4.0	8.3
11	1.9	18.4	9.7	8.7	20.7	22.1	6.0	11.4
12	1.3	11.7	11.7	17.7	20.6	20.6	7.8	14.8
13	1.1	13.1	10.4	10.4	19.1	20.2	8.2	17.5

Table III. Pore Volume[a] and Particle Density of −6+10 Mesh Fractions

Identification No.	Pore Volume in Pore Diameter Range, Cc./Gram		Total Pore Volume, Cc./Gram, 0.06 to 100 μ	Particle Density, Grams/Cc.
	5 to 100 μ	0.06 to 5 μ		
1	0.133	0.094	0.227	1.29
2	0.123	0.116	0.239	1.28
3	0.096	0.091	0.189	1.52
5	0.127	0.094	0.221	1.36

[a] Mercury porosity measurements made by Prado Laboratories, Cleveland, Ohio.

granulating tendency and the chemical and/or physical properties listed in Tables I, II, and III. It was assumed that the original particle-size distribution influenced the percentage on-size granules made during a run. Therefore, some samples were sieved into their various mesh fractions and then recombined in proportion to the distribution of other triple superphosphates to provide a better comparison of the inherent granulating tendency of the particles.

Granulation Results

The results (Table IV) demonstrate conclusively that triple superphosphate samples to which identical quantities of water have been added exhibit extreme variations in their granulating tendency, both in the total quantity of on-size material present in the final product and in the extent that under-size is agglomerated into the on-size range. Furthermore, when comparisons are made after preparing the same particle size distributions, the individual particles comprising a particular material differ in their tendency to granulate and in their response to water addition levels. Products 6, 11, and 12 showed that the quantity of water had little effect; Products 1, 5, and 8 were very sensitive to extra water; and Product 3 granulated well at the lower levels but progressively poorer with larger amounts.

In Table I, the principal chemical differences apparent from the analytical values are free phosphoric acid and free moisture. The values found for F, Fe, Al, and Ca were all within such a narrow range that they were omitted. Since the moisture was equilibrated to 4.5 to 5.5% before any granulation runs were made, only the free phosphoric acid remained as a significant chemical variant. Products 4 and 5 contain relatively high concentrations, but Product 3 granulates equally well while having one of the lowest free acid values. Since the granulation coefficients show much larger variation than do the analyses, one is led to the conclusion that physical factors are of greater significance.

Caro and Freeman (2) measured pore size distribution of representative triple superphosphate samples. The authors presented evidence to show that the differences in pore size distribution between products lay in the pore volume of the 0.06- to 5-micron diameter pores and, hence, grouped samples by the pore volume found in this range. Table III shows that Products 1, 3, and 5 can be grouped on this basis, but since the total volume of Product 3 in the range measured is distinctly lower than the other samples, Products 1, 2, and 5 can be grouped on the basis of total pore volume and on particle density. Product 3 appeared dense and free of large voids when examined either by the naked eye or microscopically. Products 1 and 5 were friable, irregularly shaped, and possessed large voids. Unlike any of

magnification, appear amorphous, Product 2 exhibited extensive crystal formation. The size of these crystallites was measured by low-angle scattering of x-rays and by high magnification and found to be approximately 150 A.

Since Products 3 and 5 granulate readily and Products 1 and 2 distinctly less, it is apparent that the groupings based on the pore volume measurements are not determinant in granulation efficiency. The good response of Product 5 at similar levels of water addition is particularly striking in view of its high porosity as compared to Product 3.

In an effort to gage the influence of particle size distribution on the granulation achieved, a large amount of product was sieved into various size fractions and then each fraction granulated with ammonia and water under identical conditions. The results are listed in Table V.

The −20+35 fraction behaved like wetted sand and, considering that most of the granules formed fell in the −14+20 mesh size and that only a small amount of agglomeration would have been sufficient to achieve the on-size range, the per cent of granulation was very low. The next smaller fraction gave slightly lower results, but in this case a much larger number of particles had to cohere before reaching the on-size reaction. Granulation of the −100 mesh material was found to be very efficient, but the difficulty in handling dust precludes any possibility of exploiting the operation. While no experiments were made to ascertain optimum particle size distribution, it is interesting to note that a large portion of Product 6 fell in the −20+35 fraction and a small amount in −100 mesh. Product 6 granulated poorly and responded but slightly to extra water addition.

Effect of Operating Variables on Granulation

Before making the large number of runs that the authors have reported, it was necessary to establish realistic operating conditions. The results of the more fundamental steps in the procedure are recorded here to provide the reader with an idea of their effect and the rationale behind the somewhat arbitrary conditions finally chosen as standard.

Duration of Rolling Period. The rolling time after water addition, but before introduction of ammonia, and the rolling time after completing of ammoniation prior to air drying were tested at several levels. The granulation values given in Table VI are based on tests using 1000 grams of Product 1 at 35 r.p.m. with 4 pounds of NH_3 per unit of P_2O_5 and 100 ml. of water.

Table IV. Granulation of Triple Superphosphate Samples at Different Levels of Incremental Water[a] (Simultaneous Ammonia Addition)

Identification No.	Particle Size Distribution	H₂O Added, Grams/1000 Grams	Final On-size[b], %	Increase in On-size Granules, Grams/100 Grams
1	As received	100	44.3	23.4
		110	46.5	25.6
		120	54.8	33.9
		130	60.7	39.8
		140	77.7	56.8
	As for No. 3	100	52.5	18.9
		110	57.5	23.9
		140	71.8	38.2
	As for No. 2	100	63.4	25.0
		110	70.6	30.2
2	As received	100	56.4	16.0
		110	60.0	19.6
		120	68.3	28.1
		130	67.3	26.9
		140	72.0	31.6
2	As for No. 1	100	37.2	16.3
		110	36.6	15.7
3	As received	100	72.1	38.5
		110	88.8	55.2
		120	81.1	47.5
		130	72.7	39.1
4	As received	100	72.7	32.8
		110	79.2	39.3
		120	83.8	43.9
5	As for No. 1	100	52.3	31.4
		120	83.1	62.2
		140	83.7	62.8
6	As received	100	64.1	25.5
		110	60.9	22.3
		120	63.0	25.4
		130	59.1	20.5
7	As received	120	46.1	24.7
		140	51.2	29.8
		160	60.8	39.4
8	As received	100	33.1	15.1
		120	38.8	20.8
		140	65.0	47.0
9	As received	100	39.8	11.0
		120	47.9	19.1
		140	57.9	29.1
10	As received	100	71.8	23.8
		110	76.3	28.3
		130	83.0	35.0
11	As received	100	47.5	8.4
		110	53.1	14.0
		130	52.1	13.0
12	As received	100	55.5	13.5
		110	57.5	15.5
		130	58.5	16.5
13	As received	100	53.2	18.6
		110	49.2	15.0
		130	59.0	24.4

[a] The operating conditions were: ammonia addition equal to 4.0 pounds per unit of P₂O₅, added over a period of 3 minutes; speed of rotation set at 35 r.p.m., i.e., corresponding to 50% of the critical speed which is defined as the speed at which the charge can just be carried around the drum by centrifugal action. Its value is $76.5\sqrt{d}$, where d is the drum diameter in feet and has been found by Brook (1) to be optimum. The material was rolled 1 minute after water addition and before ammonia addition, 2 minutes after all the ammonia charged, and finally 10 minutes while air was passed under the bed to effect cooling and drying. Total triple superphosphate charged was 1000 grams. All samples were equilibrated to an original water content of 4.5 to 5.5.

[b] On-size granules in this table refer to the −6+20 mesh fraction, plus two thirds of the small proportion of +6 mesh material.

Table V. Granulation of Separate Mesh Fractions

Screen Mesh Fraction	Granulation, %
−20+35	45
−35+65	39
−100	79

Table VI. Effect of Duration of Rolling Period on Granulation

Rolling Period, Min.		Increase in On-size Granules, Grams/100 Grams
Before ammoniation	After ammoniation	
0	2	24.9
1	2	29.0
3	2	36.6
1	0	29.9
1	2	29.0
1	4	31.2
1	8	33.5

Table VII. Effect of Quantity of Material Charged on Granulation

Charge, Grams	Increase in On-size Granules, Grams/100 Grams
500	30.5
1000	40.4
1500	36.8
2000	34.5

Table VIII. Granulation of Triple Superphosphate with External Heating

Product No.[a]	H₂O Added, Ml./1000 Grams	Increase in On-size Granules, Grams/1000 Grams
1	95	25.7
1	103	40.7
1	112	66.9
1	120	67.8
2	100	23.1
2	110	25.8
2	120	35.4
2	130	Over-granulated

[a] Particle sizes as received.

Table IX. Ammoniation Results of Various Triple Superphosphate Samples

Product No.	Ammoniation Achieved, Pounds/Unit P₂O₅	Efficiency, %
1	3.86	96
2	3.52	88
3	3.52	88
4	3.20	80
5	3.88	97
6	3.78	94.5
8	3.94	98.5
9	3.82	95.5
10	3.50	87.5
11	3.56	89
12	3.54	88.5
13	3.70	92.5

It is evident that the rolling period before ammoniation must be controlled closely if reproducibility is to be obtained. Rolling after ammoniation is less critical probably because water evaporation at 100+° C. has reduced the liquid phase below the effective granulating level.

Influence of Quantity of Material Charged to the Granulation. The optimum charge for granulation of run-of-pile triple superphosphate was determined in the series of trials shown in Table VII. The use of 1000 grams was found to be convenient and, at the

same time, close to maximum yield of on-size material. In the drum, measuring 14 inches in diameter and 6 inches from front to back face, this charge fills the unit so that 10% of the cross sectional area is occupied. Product 4 was used at 35 r.p.m. with 4 pounds of NH_3 per unit P_2O_5 and 10 ml. of H_2O per 100 grams of triple superphosphate.

Granulation with Water and External Heating with No Ammoniation

Considerable tonnage of run-of-pile triple superphosphate is also granulated without ammoniation for direct application and bulk blending. In this process it is also important that the raw material feed granulates quickly in order to realize operating economies. A series of runs was made to determine the way different samples performed. Granulation was effected by distributing the chosen quantity of water onto the rolling bed and then applying the heat from two Meker burners to the exterior of the drum until the bed temperature reached 90° C. (1.5 to 2 minutes). Rolling was continued 3 minutes, and then air was distributed through the rolling bed for a further 10 minutes. The results are tabulated in Table VIII.

It is immediately evident that both the relative granulating tendency and the response to incremental water are very different. At the same level of water addition, the granulation is somewhat higher than occurred with simultaneous ammoniation, this increase being particularly true in the case of Product 1. Any process changes in the production of triple superphosphate that can be found to exploit the observed differential granulation behavior would yield a superior product for use in granular manufacture.

Ammoniation Efficiency of Various Run-of-Pile Triple Superphosphate Materials

The gaseous ammonia added to triple superphosphate forms a mixture of ammonium and calcium phosphates (3, 5, 11). An ammoniation rate of 3.8 to 4.0 pounds of NH_3 per unit is considered to be the practical upper limit.

For the purpose of standardizing a laboratory procedure, it was considered reasonable to add 4.0 pounds per unit and then calculate the efficiency of absorption from the ammonia absorbed and the amount added. The efficiency is then used as a measure of the ability of one sample or another to absorb ammonia during granulation. The operating procedures and method of calculating have been described earlier (3). The time of addition was within 10 seconds of 3 minutes, and the results in Table IX are those obtained under identical condition of moisture addition and other granulating variables.

Significant variations between samples are evident, and these low values would be detrimental in complete fertilizer manufacture. In contrast to the poor correlation between pore size distribution and granulation efficiency, ammoniation relates well to these measurements. The large pore volume in the 5- to 100-micron diameter region of Products 1 and 5 and low particle density (Table III) coincide with high ammonia absorption. The effect of low pore volume and high density of Product 3 as well as its lack of voids in visual examination also agree well with the low ammoniation efficiency.

Although further porosimeter measurements were not available, it was possible by visual means to see that one could correlate high ammoniation efficiency with a sponge rubber porous irregular structure as compared to the more dense, less porous, and more regular shape. The latter type particle is normally obtained by working in some manner the freshly prepared triple superphosphate or by using a more dilute phosphoric acid in the triple mixing process.

Effect of Water Level on Ammoniation

Kumagai (8) investigated the effect of initial moisture content of ordinary triple superphosphate on the ammonia absorption efficiency. The authors were interested in the effect of the water level under granulating conditions, i.e., with higher moisture levels than in the previous study and with the water added just prior to the ammoniation rather than by equilibration. Ammonia was added at the level of 4.0 pounds per unit to the same triple superphosphate sample (porous and of low density, Product 1), and the time of addition was maintained at 3 minutes in all cases. Other operating variables were invariant. The results (Table X) demonstrated that the efficiency passed through a maximum at water levels below those necessary for optimum granulation, but the difference between the efficiencies was not very large. This suggests the utility of determining ammoniation and granulation properties simultaneously in a way directly analogous to plant conditions.

Level of Ammonia Addition and Efficiency

The same material was used as in the previous test, but the water added was constant at 100 ml. per 1000 grams of triple superphosphate; the time of addition was fixed at 3 minutes, and other operating variables were constant. The data in Table XI demonstrate the extent to which ammonia addition is practical. An efficiency of 95 to 100% was possible in the region of 3.7 to 4.0 pounds per

Table X. Effect of Water Level on Ammoniation[a]

Water Added, Cc./1000 Grams	Ammoniation Achieved, Pounds/Unit P_2O_5	Efficiency, %
0	3.66	91.5
20	3.68	92
40	3.92	98
60	3.96	99
80	3.74	93.5
100	3.76	96
120	3.80	95
140	3.74	93.5

[a] In all cases, 4.0 pounds of ammonia was added per unit of P_2O_5.

Table XI. Effect of Quantity of Ammonia

NH_3 Added, Pounds/Unit P_2O_5	Ammoniation Achieved, Pounds/Unit P_2O_5	Efficiency, %
3.7	3.70	100
4.0	3.76	94
4.3	3.78	88
4.6	3.79	82.5
4.9	3.60	73.5

Table XII. Effect of Rate of Addition of Ammonia

NH_3 Added, Unit/Pounds P_2O_5	Time of Addition, Sec.	Ammoniation Achieved, Pounds/Unit P_2O_5	Efficiency, %
4.0	105	3.64	91.0
	185	3.76	94.0
	260	3.78	94.5
	345	3.90	97.5
4.9	170	3.60	73.5
	380	4.06	83.0

Table XIII. Effect of Particle Size on Ammoniation

Size	NH_3 Added, Pounds/Unit P_2O_5	Ammoniation Achieved, Pounds/Unit P_2O_5	Efficiency, %
−20+35	4.73	4.18	88.5
−35+65	4.73	4.57	96.5
−100	4.73[a]	2.76	58.5
+10	4.00	3.28	82.0
−20+35	4.00	4.00	100
−65	4.00	4.00	100

[a] Over-granulated.

unit level of ammonia addition, but successively higher additions of ammonia did not even raise the level of ammoniation achieved during the fixed time of addition. The poor absorption of ammonia at the highest rates of addition was undoubtedly due to the high velocity of gaseous ammonia through the bed permitting its escape before contacting any particles of the material being tested.

Effect of Length of Time Used for Ammonia Addition

The interval for ammonia addition is usually controlled in a large scale

operation by the design and size of the plant and by the rate of production. To ascertain how much ammonia would be absorbed under granulation conditions but with low gas flows, ammonia at levels of 4.0 and 4.9 pounds per unit were added over varying lengths of time. The results (Table XII) show that longer times gave higher efficiencies, but at the high rate of addition, a maximum absorption value just over 4 pounds per unit occurs in the apparatus using Product 1. The operating conditions not listed in the table were maintained constant, and the water level used was 100 ml. per 1000 grams of triple superphosphate.

Effect of Particle Size

A portion of run-of-pile triple superphosphate (Product 1) was separated into its constituent particle size fractions, and the fractions were ammoniated at two levels of ammonia addition with constant amounts of water added. The efficiency results appear in Table XIII.

The medium-sized particles exhibited high ammonia absorption, whereas the larger particles did not. This lower absorption of the large particles can be caused by the short reaction time employed (3 minutes). The time necessary for diffusion of gases into the interstices of the particle, over the relatively short reaction time employed may explain the lower absorption into these larger particles. Should the chemical reaction of ammonia with monocalcium phosphate cause complete blocking of ink-bottle pores, suggested by Caro and Freeman (2) as existing in triple superphosphate, one would expect reduced absorption. Also, there is a greater probability of pores that are blocked off from any exterior surface in large particles which would reduce contact of solid with gas. The low efficiency of the -100 mesh size was due to the rapid granulation which occurred, giving subsequent isolation of a large portion of the material from further possibility of contact with ammonia gas. It is evident that the particle size distribution

present in the granulation is more important to ammoniation efficiency than the particle sizes charged in the dry state.

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PHOSPHORUS STATUS OF CROPS

Phosphorus Fractions in High and Low Phosphate Plants

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Lima bean plants were grown in nutrient solutions at low and high levels of phosphate addition. Comparable samples of leaflet-blades and petioles were collected for fresh-freezing and for oven-drying. The fresh-frozen samples were analyzed for orthophosphate, organic phosphate soluble in trichloroacetic acid, and acid-insoluble phosphate. Dried materials were analyzed for acetic acid–soluble phosphate and insoluble phosphate. The results indicate that much of the organic phosphate is broken down as a consequence of the drying process; nevertheless, the use of dried samples for assessing the phosphorus status of the plant would seem to be as adequate as the use of fresh materials, under ordinary conditions. For fresh-frozen material, the differences in phosphate supply produce little variation in acid-insoluble organic phosphate; intermediate variation in acid-soluble organic phosphate; and a very large variation in orthophosphate, with the orthophosphate reflecting the external phosphate most closely.

CHEMICAL ANALYSIS of plant parts as a means of evaluating the nutritional status of field crops has generally involved oven-dried materials. Although the advantages of dried over fresh materials have been well appreciated (17), it is also true that during the process of drying a considerable number of chemical transformations involving some of the essential elements will occur, resulting in a loss of some information. As the first step in an attempt to discover which phosphorus compound or fraction present in fresh material is best correlated with the adequacy of the phosphate supply to the plant, the amounts of phosphorus in the three conventional phosphate fractions (orthophosphate, acid-soluble organic phosphate, and acid-insoluble phosphate) were determined on fresh-frozen parts of high- and low phosphate lima bean plants. For comparison, analyses of oven-dried plant parts were also run.

Methods and Materials

Growing of Plants. Lima bean seeds

(*Phaseolus limensis*, var. Fordhook concentrated), which had been dusted with Arasan, dieldrin, and Delsan, were planted in vermiculite on November 7, 1958, and watered daily with distilled water. On November 20, healthy seedlings were selected and set out (cotyledons attached), five per 20-liter container, in nutrient solutions at four phosphate concentrations. All solutions at the time of transplanting contained the following concentrations of mineral nutrients: 3 mmoles KNO_3, 1 mmole $MgSO_4$, 0.5 mmole $NaCl$, 0.5 mmole