

Development of a One-Step Process for Production of Granular Triple Superphosphate

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A simple, one-step continuous process for the production of granular triple superphosphate was developed in pilot-plant tests in which acidulation and granulation were carried out simultaneously in a rotary drum mixer such as the TVA continuous ammoniator. Wet-process of furnace phosphoric acid and steam were fed through perforated pipe distributors under the rolling bed of material in the drum. No drying was required. Product made at normal acidulation (mole ratio phosphorus pentoxide to calcium oxide of 0.94) had high conversion after only 1 to 2 weeks of curing, could be ammoniated efficiently, and did not cake in storage. The process offers advantages of low costs of equipment and processing. It should be useful to those who have continuous ammoniators and wish to diversify their production, as well as to superphosphate producers who wish to produce a granular product.

GRANULATION OF MIXED FERTILIZERS has led to an increased interest in the granulation of superphosphates. Granular superphosphates are used for direct application, blending with other dry ingredients, and as an aid to granulation in the production of mixed goods.

Two processes currently are used for the production of granular superphosphate. In one process, nongranular superphosphate, after curing for several weeks, is reclaimed from the storage pile and granulated with water or steam or both. This process is costly because extra handling is involved and the granules must be dried. In another process (4), granular triple superphosphate is produced by acidulating phosphate rock with phosphoric acid in a slurry state and then mixing the slurry with dried recycle product in a pugmill.

Because of the increased interest in granular superphosphates, the Tennessee Valley Authority has made pilot-plant studies directed toward simplification of their production. These studies have led to the development of a process in which acidulation and granulation are carried out simultaneously in a rotary drum mixer such as the TVA continuous ammoniator. This paper describes the results on the production of granular triple superphosphate, sometimes referred to as concentrated, double, or treble superphosphate. Work on granular ordinary and enriched superphosphates is still in progress.

Description and Operation of Pilot Plant

The pilot plant used in this work was the same as used in the development of processes for the production of granular high-analysis fertilizers (2). The

only significant change required in the equipment to make it suitable for use in producing granular triple superphosphate was the installation of ducts for the removal of fluorine fumes from the granulator, crusher, and screens, and the addition of a cage mill following the roll crusher.

Phosphate rock and recycle from the product screens were fed into the acidulating drum (continuous ammoniator) by means of volumetric feeders. Phosphoric acid and steam were fed under the rolling bed of material through perforated pipe distributors. The steam was used to maintain the required temperature and moisture level in the acidulating drum. The granular acidulate discharged from the acidulating drum into the rotary granulator where the loose agglomerates of granules formed during acidulation were separated and the granules made more nearly round. The product from the granulator was cooled in a rotary cooler and then screened. In passing through the cooler, the surface moisture on the granules decreased and their tendency to adhere to equipment and cake in the storage pile was reduced. The oversize from the screens was crushed and returned along with the fines to the acidulating drum to aid in control of granulation.

In early tests, only relatively small proportions of acid and phosphate rock were fed together with cured triple superphosphate primarily to granulate the superphosphate (3). The acid and rock comprised from 10 to 33% of the feed materials. Results of these early tests showed high degrees of conversion of the phosphate in the rock to an available form and good granulation when steam was introduced through a dis-

tributor located underneath the bed. The fresh superphosphate appeared to be a very good binding material, and the heat of reaction was beneficial to granulation.

In later work the cured superphosphate was eliminated, and fresh process fines were used as recycle. Tests were made with both electric-furnace and wet-process phosphoric acids. There were considerable differences in the processing characteristics with the two types of acid. Pilot-plant operation with both types of acids is discussed.

Operation Using Wet-Process Phosphoric Acid

For good mixing of phosphate rock and acid and good granulation, a free-flowing bed of solids in the acidulating drum was necessary. To maintain this condition, the temperature and moisture content were controlled by the addition of steam and recycled fines. When wet-process acid was used, steam and recycled fines were not entirely effective, and the material in the drum was subject to excessive wetting and overagglomeration. This condition could be overcome by preheating the acid. Preheating the acid served two functions in control of granulation: it increased the temperature of the material in the drum and thereby allowed greater evaporation of moisture, and it decreased the time that the acidulate (triple superphosphate) remained in a fluid or plastic state during mixing (7). A rapid transition to a friable, solid state decreased the proportion of liquid phase in the drum and thereby reduced the tendency toward overagglomeration.

Test Results. The phosphate rock was land pebble ground to about 75% -200 mesh; the phosphoric acid was manufactured from Florida phosphate. Chemical analyses of the rock and the acid are given below.

per ton of product. The acid was preheated to about 200° F. in a double-pipe heat exchanger. The temperature of the material as discharged from the acidulating drum averaged 216° F. Granulation was consistently

granulation, it was important to maintain the temperature of the material leaving the acidulation drum above 210° F. and the moisture content in the order of 6 to 6.5%. Under these conditions the material from the cooler contained 5 to 5.5% moisture. When the temperature dropped below 210° F., the material in the acidulation drum became sticky and overagglomeration resulted. The usefulness of steam to control the temperature was limited because it also affected the moisture content.

Systematic studies were not made of the effects of acid concentration and rock composition on granulation. Exploratory tests indicated, however, that either decreasing the acid concentration or increasing the grade of the rock made control of granulation more difficult. Previous work has shown that both of these factors influence the length of the time the superphosphate remains in the fluid state (7).

Tests were made in which the phosphorus pentoxide to calcium oxide mole ratio was varied from 0.86 to 0.98 by varying the proportion of wet-process phosphoric acid. Data showing conversion of phosphorus pentoxide from rock to an available form after 2 weeks of pile curing at room temperature are given below for each ratio tested.

$P_2O_5:CaO$ Mole Ratio	Lb. P_2O_5 from Acid/Lb. P_2O_5 from Rock	Conversion, %
0.86	2.14	87
0.87	2.17	87
0.89	2.23	87
0.91	2.29	90
0.92	2.32	91
0.94	2.42	94
0.98	2.60	94

Conversion was not increased by increasing the acidulation mole ratio above about 0.94. Generally, control of granulation was more difficult with ratios above 0.94 because of the increased proportion of acid. The conversions tabulated above are believed to be equal to or higher than those obtained in conventional processes using wet-process acid at the same acidulation ratios.

Metering of Acids. Metering of wet-process acid at a steady, dependable rate was a problem in the early work. However, the metering problem was overcome by using a shop-fabricated, acid-metering wheel similar to Rotodip commercial-type meters. The device consisted essentially of a series of buckets, or dippers, attached to a wheel that rotated in a vertical plane in the feed tank. A constant level sufficient to submerge the bottom dipper was maintained in the tank. As the wheel rotated, each dipper picked up a constant volume of acid which spilled into a collecting funnel as the dipper passed

	Composition, %					
	P_2O_5	Al_2O_3	Fe_2O_3	SO_3	CaO	F
Acid	53.6	0.9	1.2	2.9	0.05	0.8
Rock	32.2	1.7	2.1	...	46.3	3.6

Data from typical tests are given in Table I.

Table I. Data for Pilot-Plant Tests of Production of Granular Concentrated Superphosphate

Test	Wet-Process Phosphoric Acid		Electric-Furnace Phosphoric Acid
	A	B	C
Production rate, tons/hr.	0.49	1.09	0.87
Formulation, lb./ton product			
Phosphate rock	814	821	865
Phosphoric acid	1237	1278	1188
Steam	285	183	287
Recycled fines	2208	2354	873
Recycle ratio, lb./lb. product	1.1	1.2	0.4
Temperature, ° F.			
Acid preheat	196	265	...
Acidulator product	216	212	208
Granulator product	178	195	174
Cooler product	87	...	81
Screen analysis of granulator product (Tyler), %			
+6 mesh	47.9	38.1	35
-6 +20 mesh	45.0	44.6	54
-20 mesh	7.1	17.3	11
Chemical analysis of product after curing, %			
	2 weeks		1 week
P_2O_5			
Total	46.8	47.9	49.4
Available	46.0	46.9	48.9
Water soluble	44.0	44.4	46.7
Free acid	3.2	2.1	0.9
CaO	19.6	20.3	21.0
H ₂ O	5.1	4.1	3.6
F	...	1.6	...
$P_2O_5:CaO$ mole ratio	0.94	0.93	0.93
P_2O_5 availability, %			
Cured 1 day	95.8	96.6	97.0
Cured 1 week	97.7	97.4	99.0
Cured 2 weeks	98.5	97.9	98.8
Cured 4 weeks	99.0
Net conversion of P_2O_5 from rock, %			
Cured 1 day	87	89	90
Cured 1 week	93	91	96
Cured 2 weeks	94	93	96
Cured 4 weeks	97

In test A, the production rate was about 0.5 ton per hour. The recycle rate was 1.1 pounds per pound of product, and the steam rate was 250 to 300 pounds

good throughout the test. About 45% of the product from the granulator was - 6 + 20 mesh in size. The particle size distribution in the product from the acidulating drum and from the cooler generally was about the same as that from the granulator. The acidulation ratio (moles of phosphorus pentoxide to moles of calcium oxide) determined by chemical analysis of the product was 0.94. Conversion of the phosphate in the rock to a citrate-soluble form was 93% complete after 1 week, 94% after 2 weeks, and 97% after 4 weeks of curing in a pile at room temperature. The product contained 46.0% available and only 0.8% citrate-insoluble phosphorus pentoxide giving an availability of 98% after 2 weeks of curing.

In test B, the production rate was about 1 ton per hour. A phosphorus pentoxide to calcium oxide mole ratio of 0.93 was used. The recycle ratio was 1.2 pounds and the steam rate was 183 pounds per ton of product. The acid was preheated to 265° F. and the temperature of the material as discharged from the acidulating drum averaged 212° F. About 45% of the product from the granulator was of the desired size. The conversion of phosphate in the rock to a citrate-soluble form was 93% complete after 2 weeks of curing at room temperature. The product contained 46.9% available and only 1% of citrate-insoluble phosphorus pentoxide.

Effects of Process Variables. Increasing the production rate from 0.5 to 1.0 ton per hour increased the tendency toward overagglomeration in the acidulating drum. This was due presumably to the decrease in retention time (3 vs. 6 minutes) which resulted in an increase in the proportion of material still in the fluid or plastic state. To control granulation at the higher production rate, the acid temperature was increased from 200° to 265° F. Increasing the recycle rate also was helpful in controlling granulation but was not as effective as increasing the acid temperature. Conversion was not affected by the decrease in retention time, which indicated that there was sufficient time for good mixing at the higher rate.

In order to obtain good mixing and

through the upper arc of rotation. The acid flowed by gravity from the collecting funnel to a positive suction pump which delivered the acid to the distributor in the acidulating drum. The metering rate was varied by varying the speed of the wheel with a speed reducer. The pilot-plant unit with four rectangular dippers $2 \times 3 \times 3.5$ inches in size gave dependable rates in the range of 0.5 to 3 gallons per minute with a speed range of 2 to 12 revolutions per minute.

Distributor Design. Some modifications in design and arrangement of the distributors were tested in the pilot plant. The most satisfactory operation was obtained when the acid was distributed in the first half of the drum through a $1/4$ -inch pipe drilled with 20 holes spaced 1 inch apart. The steam was added through a full-length distributor of the slotted type used previously for the distribution of ammonia (6). The distributors, constructed of A.I.S.I. Type 316 stainless steel, were located about 2.5 to 3 inches above the shell.

There was a tendency toward lump formation on the distributors, and occasional manual rodding was required to prevent excessive build-up, which would interfere with the rolling action of the bed. A scraper bar fabricated from 3-inch angle iron was mounted inside the drum above the bed to prevent build-up of material on the walls.

Screening and Crushing. The product screens were cleaned fairly frequently to maintain efficient separation when the wet-process acid was used. This was especially true for the undersize screen. Screens constructed of parallel wires with longitudinal slots gave better service and were more easily cleaned than woven-wire screens.

There was a tendency for the oversize material to cake on the crushing equipment when being crushed for use as recycle. A hammer mill could not be used for this reason. However, satisfactory results were obtained with a roll mill and cage mill in series. The roll mill formed the oversize lumps into loose flakes that were disintegrated easily in a single pass through the cage mill.

In most of the tests with wet-process acid, the particle size of the cooled product was such that screening at 6 to 16 or 6 to 20 mesh would yield sufficient oversize and fines for control of granulation. The screened product was comprised of well-rounded granules that had a somewhat porous structure. The strength of the particles increased with age. After 1 to 2 weeks of curing, the particles appeared to be about as strong as those of most of the high-analysis granular mixed fertilizers produced in the continuous ammoniator.

Several runs were made to test the

effect of drying rather than merely cooling the product. Drying was expected to reduce the amount of recycle required, as dried recycle would be more efficient in control of granulation. However, when the material from the granulator was dried to about 2% moisture in a rotary dryer at a product temperature of 170° to 190° F., a decrease of 7 to 10% in conversion occurred. Drying at 140° F. to a moisture content of about 3% resulted in a 4 to 6% decrease in conversion. Control of a drying operation to avoid reversion appeared to be difficult. Drying therefore is not recommended in this process.

Operation Using Electric-Furnace Phosphoric Acid

The use of electric-furnace phosphoric acid allowed much more latitude in control of granulation. Lower rates of recycle were required, preheating of the acid was not necessary, and the steam rate could be varied quite widely without adverse effects on granulation. Conversion was good with somewhat lower acidulation than was required with wet-process acid, and the free acid content of the cured product was lower.

Data from a typical test in which electric-furnace acid was used are given in Table I (test C). The production rate was 0.9 ton per hour. The acid contained 56% phosphorus pentoxide; the rock contained 32.7% phosphorus pentoxide and 45.7% calcium oxide. Rock and acid were fed in proportions such that the acidulation mole ratio was 0.93 and the ratio of phosphorus pentoxide from acid to that from rock was 2.38. Good granulation was obtained with 0.4 pound of recycle and 290 pounds of steam per ton of product.

The material was discharged from the acidulating drum at a temperature of 208° F., from the granulator at 174° F., and from the cooler at 81° F. The material contained about 5% moisture after cooling. The product of the granulator contained 54% of product-size granules ($-6 +20$ mesh) with 35% oversize and 11% undersize. No appreciable difficulties in screening and crushing were experienced. The net conversion of phosphorus pentoxide from rock was 90% complete after 1 day of curing and 96% after 1 week. This degree of conversion is about the same as that obtained in fully cured material in large-scale production of nongranular triple superphosphate from electric-furnace acid. The available phosphorus pentoxide content of the product was 48.9%, the citrate-insoluble was only 0.5%—the moisture was 3.6—and the free acid was 0.9% after 1 week of curing. The granules were well rounded and hard, although porous in structure.

Fluorine Evolution

The products made with either wet-process or electric-furnace acid contained 1.5 to 1.7% fluorine, which indicated that 15% or less of the input fluorine was evolved. This is about the same proportion as is evolved in conventional triple superphosphate processes. It was necessary to provide exhaust hoods on the acidulating drum, granulator, and cooler in the pilot plant to prevent excessive atmospheric pollution in the operating area. Provisions for fume removal at the screens and crushing equipment also might be necessary in a large-scale plant.

Corrosion

There was no apparent corrosion of the processing equipment and exhaust system, which were constructed of mild steel. The acid distributor, which was constructed of A.I.S.I. Type 316 stainless steel, was corroded and had to be replaced occasionally as corrosion enlarged the holes.

Use in the Production of Granular Mixed Fertilizers

Pilot-plant tests were made to determine whether granular triple superphosphate produced by the present process would be ammoniated when used as an ingredient in the production of granular mixed fertilizers. A 5-20-20 grade was made in which about 16 units of phosphorus pentoxide were supplied as granular triple superphosphate and the balance as nongranular ordinary superphosphate. Nongranular potassium chloride was used. Nitrogen was supplied as anhydrous ammonia. The formulation was similar to one containing nongranular superphosphate tested in previous work (2). The overall input degree of ammoniation in this formulation was 3.9 pounds of ammonia per unit of available phosphorus pentoxide. Assuming that the ordinary superphosphate in the formulation was ammoniated to the extent of 5.8 pounds per unit, the input degree of ammoniation of the triple superphosphate was 3.5. The loss of ammonia was about 5%. These results are within the range of those obtained when nongranular triple superphosphate is used in formulating 5-20-20. The ability of the granular triple superphosphate to absorb ammonia was attributed to the porous structure of the granules. Granulation efficiency was such that 90% of the product, including crushed oversize, was $-6 +28$ mesh in size.

Tests also were made to compare the use of granular triple superphosphate with granular potassium chloride to promote granulation in the production of a 4-16-16 grade. Granulation of

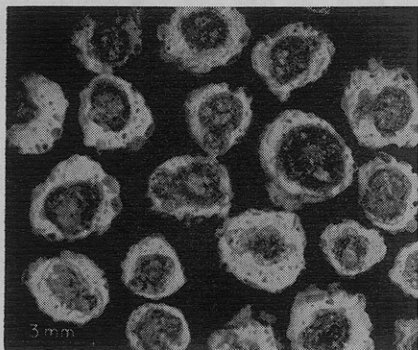


Figure 1. Sectional photograph of granules of mixed fertilizer made with granular triple superphosphate

this grade is very difficult unless some granular material is used in the formulation. It was believed that the granular superphosphate would be helpful in promoting granulation of low-nitrogen grades by providing nuclei around which granules would form (5).

In one test the triple superphosphate was granular and the other ingredients were nongranular; in another test, only the potassium chloride was in granular form. Sulfuric acid, in the amount of 135 pounds per ton of product, was added as a further aid to granulation. The results showed that the granular triple superphosphate was as effective as granular potassium chloride in promoting granulation; the on-size (-6 +28 mesh) recoveries were

82 and 88%, respectively. The difference was attributed to the fact that there was more potassium chloride than triple superphosphate in the formulation.

Of the products made with granular triple superphosphate, the triple superphosphate granules formed the nucleus of almost every particle. Figure 1 is a photograph of cross sections of particles of a 5-20-20 grade made with dark-colored granular triple superphosphate.

Storage Properties

Granular triple superphosphates made from electric-furnace and wet-process phosphoric acids were inspected after 6 months of storage. The bag set was judged to be medium to hard after storage, but none of the products showed lumps after the standard drop test designed to simulate normal handling of the bags. There was no evidence of bag rot. All of the materials tested had been allowed to cure in open-pile storage for 1 or 2 weeks prior to bagging. Product bagged directly from the pilot plant without curing rotted the bags, presumably, because of the higher free acid content of the fresh material. The granular triple superphosphate remained entirely free from caking and was free flowing in open-pile storage for several weeks.

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NITROGEN SOLUTIONS ANALYSIS

Rapid Method for Determination of Urea in Nitrogen Solutions

Application of an enzyme, urease, makes possible a direct method for analyzing urea in water solutions of urea, ammonium nitrate, and ammonia. This method has given fast, accurate, and reliable results.

CURRENT METHODS for determining urea in nitrogen solutions are time-consuming, require constant attention, and are subject to inaccuracies. The procedure outlined here provides a rapid method, which requires no special equipment and can be performed by plant operating personnel. Analyses can be completed within 30 minutes after sampling, with a maximum error of 1%.

In setting up a sequence of analyses for aqueous solutions of ammonia, ammonium nitrate, and urea, a wide choice of methods for the individual components is available.

A volumetric method for ammonia and the AOAC formaldehyde procedure for ammonium nitrate (7) were selected as the standard methods of analysis for these components. These methods are simple to perform, rapid, require no

special equipment, and give reliable results.

Considerable thought was given to the selection of a method for urea. The precipitation with xanthydrol is specific, and accurate for urea (13), but is time-consuming. The gasometric methods—release of nitrogen by use of sodium nitrite or sodium hypobromite—while rapid, need special equipment and are reported to be inaccurate (3). The Kjeldahl procedures are widely used, but they have several disadvantages. To obtain the nitrogen in an analyzable form, a digestion period is needed to break down the urea, the addition of a reducing agent is necessary because of the presence of nitrate, and a distillation step is required to collect the ammonia. The introduction of the reducing agent causes considerable foaming in both the

digestion and distillation steps, necessitating attention to prevent carry-over.

In the enzymatic method, an enzyme, urease, is used to decompose urea into ammonia and carbon dioxide. The ammonia can then be determined by titration and converted into a urea value.

The employment of urease in urea analyses is not novel, but apparently has not been reported previously in connection with nitrogen solutions. Urease has been used for over 40 years in clinical analyses pertaining to urea (8, 9, 14). The urea content of blood (7), urine (5), body organs (4), and milk (12) has been determined by the use of urease. Other applications of urease to determine urea have been in mixed animal feeds (2, 11), mixtures of cyanamide compounds (6), and ammoniated dentifrices (10).

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