

## Production of Ordinary Superphosphate for Immediate Use in Ammoniation and Granulation Processes

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Small-scale tests of the reaction of phosphate rock with sulfuric acid resulted in the identification of conditions that yielded superphosphate of high phosphorous pentoxide availability and of such physical condition that it could be ammoniated about 1 hour after mixing. These results were verified in a pilot plant that consisted of a TVA funnel-type mixer and a continuous den. A conversion of 95% was achieved in 1 hour by slightly overacidulating finely ground rock with acid of about 60% concentration. Fresh superphosphate from the den was used immediately in the production of several grades of granular fertilizers by the TVA continuous ammoniation process.

ORDINARY SUPERPHOSPHATE, made by conventional methods, requires curing for 2 to 6 weeks to obtain satisfactorily high conversion of phosphorus pentoxide to an available form. In studies directed toward decreasing the time required for curing, small-scale tests were made of the effects of several process variables on the rate of conversion and on the physical properties of superphosphate. The variables included particle size of phosphate rock, sulfuric acid-to-rock ratio, acid concentration, and mixing and curing temperatures. As the work progressed, conditions were established that gave conversions of 95% or more of the phosphorus pentoxide to an available form only 1 hour after mixing. The superphosphate appeared to have very satisfactory physical properties for immediate ammoniation. This suggested the possibility of an integrated process in which ordinary superphosphate could be produced continuously and used, immediately after denning, in the continuous ammoniator process for the production of granular high-analysis fertilizers. Studies of the variables mentioned were also reported by Nunn and Dee (6). However, their investigation did not extend to the determination of conditions for producing superphosphate having a high degree of phosphorus pentoxide conversion and physical properties suitable for ammoniation immediately after denning. Bridger and associates (7-3) reported on related studies in which phosphate rock was acidulated with 55% sulfuric acid and the mixture was quick-cured by drying.

The feasibility of an integrated process was demonstrated in the present work by pilot-plant tests. The acidulation step was carried out in a pilot plant that consisted of a TVA-type funnel mixer (8) and a continuous den of the Broadfield type. After a denning time of 1 hour, the fresh superphosphate was used

in the production of granular fertilizers in the TVA ammoniation-granulation pilot plant (5).

### Small-Scale Tests

The procedure developed for the small-scale tests was as follows: Sulfuric acid and phosphate rock (Florida land pebble) were preheated to a temperature of about 240° F. and mixed for 2 minutes in a kitchen mixer. This preheating resulted in a maximum temperature, during mixing, of 250° to 260° F., which was the approximate temperature range expected in large-scale operation. About 500 grams of superphosphate were prepared in each batch. After mixing, the superphosphate was cured in closed jars in an oven maintained at a temperature of 200° F. The loss of moisture during curing and handling was about the same as experienced in storage piles of commercial plants. After curing periods of 1, 5, and 24 hours, a sample of about 1 gram was removed, pulverized, weighed accurately, and washed immediately on a pulped suction filter as prescribed by the first step of the Association of Official Agricultural Chemists (AOAC) procedure for the determination of citrate-insoluble phosphorus pentoxide; the analytical procedure was resumed within 1 hour after washing. Duplicate samples were analyzed for total phosphorus pentoxide and moisture contents. Moisture was determined by the AOAC vacuum desiccator method. A typical chemical analysis of the phosphate rock used in the small-scale tests is shown below:

Chemical Analysis, %								
P <sub>2</sub> O <sub>5</sub>	CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	F	CO <sub>2</sub>	H <sub>2</sub> O	Ignition loss
32.1	45.8	7.1	2.1	1.7	3.6	2.8	0.8	6.6

The results of small-scale studies of effects of the process variables, given in the following discussions, are from tests in which the conditions were near optimum for rapid conversion.

**Particle Size of Rock.** The effect of finer grinding of rock was determined in tests in which the acidulation mole ratio  $[(P_2O_5 + SO_3)/CaO]$  was maintained at 1.10 or 0.66 pound of sulfuric acid per pound of rock, and sulfuric acid of 60% concentration was used. Tests were made with rock pulverized to the approximate fineness used at present in the industry and with more finely pulverized rock. Screen analyses used in these tests are shown in the following tabulation.

	Wet-screen Analysis, % through Indicated Tyler Screen		
	100	200	325
Standard grind	90.5	78.8	61.8
Sample 1	99.1	89.6	74.7
Sample 2	99.5	96.3	89.9

Figure 1 shows the effect of the particle size of rock on the conversion after 1 hour. The conversion was 89% when rock equivalent to standard grind was used, but increased to 95% with rock pulverized to 90% -200 mesh (sample 1). A further reduction in particle size to 96% -200 mesh (sample 2) gave 96%. In addition, the more finely pulverized rock resulted in a more porous and friable product at the end of 1 hour.

**Acidulation Ratio.** The acidulation mole ratio  $[(P_2O_5 + SO_3)/CaO]$  was

varied from 0.95 to 1.14 (0.54 to 0.69 pound of sulfuric acid per pound of rock) in a series of tests using sulfuric acid of 60% concentration and rock of the finest particle size (96% -200 mesh). The conversion data after 1 hour, which show a steady increase from 85% with acidulation of 0.95 to 97% with acidulation of 1.14, are plotted in Figure 2. Over the entire range, the superphosphate was porous and friable and appeared to be suitable for immediate ammoniation.

**Acid Concentrations.** Acid concentrations of 55, 60, 65, and 70% were used in a series of tests with the most finely pulverized rock and with 1.10 acidulation. Data plotted in Figure 3 show that the conversion increased steadily from 92% with acid of 70% concentration to 97% as the concentration was decreased to 55%. The moisture content of the products after 1 hour ranged from 17.1% when 55% acid was used to 9.8% when 70% acid was used. The physical properties of the superphosphate from all tests were good.

**Temperature of Mixing.** The temperature (maximum) of mixing was varied from 156° to 260° F. by preheating or cooling the acid and rock. Rock of the finest size was used with 1.10 acidulation and acid of 70% concentration. The effects of temperature of mixing on the conversion and on the moisture content after 1 hour are shown in the following tabulation.

Temp. of Mixing, °F.	Conversion after 1 Hour, %	Moisture Content, %
156	92.5	14.0
172	92.6	13.9
182	92.5	13.7
209	92.2	12.7
226	92.3	13.3
250	91.7	13.3
260	83.5	10.9

Over the range of 156° to 250° F., variation in the temperature of mixing

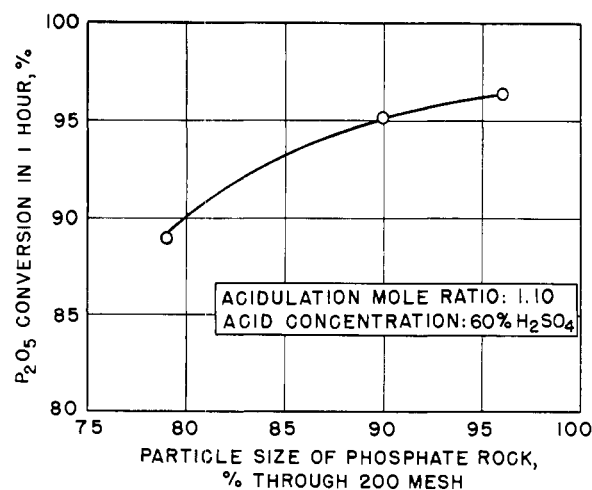


Figure 1. Effect of particle size of rock on P<sub>2</sub>O<sub>5</sub> conversion in 1 hour

had no appreciable effect on conversion. The significantly lower percentage obtained at 260° F. was attributed to a higher rate of moisture removal. This was assumed to be equivalent to the use of more concentrated acid. Similar effects were noted in later pilot-plant work when the moisture content after 1 hour was below about 12%.

Curing Time, Hr.	P <sub>2</sub> O <sub>5</sub> , %		H <sub>2</sub> O, %	P <sub>2</sub> O <sub>5</sub> Conversion, %
	Total	Citrate-insoluble		
Best small-scale conditions (96% -200-mesh rock, 1.10 acidulation ratio, 55% H <sub>2</sub> SO <sub>4</sub> )				
1	15.6	0.5	17.1	97
5	16.6	0.4	12.0	98
24	17.8	0.2	6.9	99
Conventional conditions (79% -200-mesh rock, 0.98 acidulation ratio, 70% H <sub>2</sub> SO <sub>4</sub> )				
1	18.6	4.0	12.7	78
5	18.7	3.6	12.5	81
24	18.5	3.5	10.5	81
3 weeks	20.3	1.1	2.4	95

**Temperature of Denning.** The effect of denning temperature was studied in tests in which freshly made superphosphate was held for 1 hour at various temperatures. Other conditions were the same as for the tests in which the temperature of mixing was varied. The results, shown in the following tabulation, indicate a significant increase (from 88 to 92%) in conversion when the denning temperature was increased from 100° to 150° F. At 200° F., a slight further increase to 93% was indicated, while higher temperatures did not give further increase. In a continuous acidulation process, the average temperature of the superphosphate in the den is expected to be about 225° F.

Denning Temp., °F.	Conversion after 1 Hour, %	Moisture Content, %
100	87.6	13.0
150	92.2	12.7
200	93.2	11.9
230	93.0	11.2
280	92.8	10.2

**Comparison with Conventional Conditions.** The following tabulation shows the conversions obtained with the best conditions found in the small-scale tests and those obtained in the manufacture of ordinary superphosphate. The physical condition of the superphosphate produced was as good as or better than that produced under conventional conditions.

### Pilot-Plant Studies of Continuous Acidulation

The superphosphate pilot plant consisted of a funnel mixer and a continuous den of the Broadfield type. The capacity was about 1 ton of superphosphate per hour. The funnel mixer was similar in design to that previously developed by TVA for use in the manufacture of ordinary and concentrated superphosphates (4, 8). Details of the mixer are shown in Figure 4. A lead-coated agitator operated by a 1/8-hp., high-speed air motor was installed in the cylinder to ensure adequate mixing of the rock and acid. This may not be required in commercial installations, as it has been reported that complete mixing is achieved in commercial funnel mixers without mechanical agitation.

The slat conveyor that formed the floor of the den was 30 inches wide and 9 feet 3 inches long, made up of 50 slats of 10-gage American Iron and Steel Institute Type 430 stainless steel. The end and side walls that retained the bed of acidulate on the conveyor were 24 inches high. A squirrel-cage type rotary cutter was mounted at the discharge end to break up the acidulate as it was discharged from the den. The arrangement of the funnel mixer and den is shown in Figure 5.

Phosphate rock was fed into the funnel by means of a disk feeder at rates of 800 to 900 pounds per hour. Sulfuric acid (66° Baumé) and water for dilution were metered with rotameters and fed into a lead mixing tee. The diluted acid entered the mixer through the acid nozzles at a velocity of about 10 feet per second. The rock and acid were partially mixed by the swirling action in the funnel. The propeller agitator served to complete the mixing. The mixture discharged at temperatures of 260° to

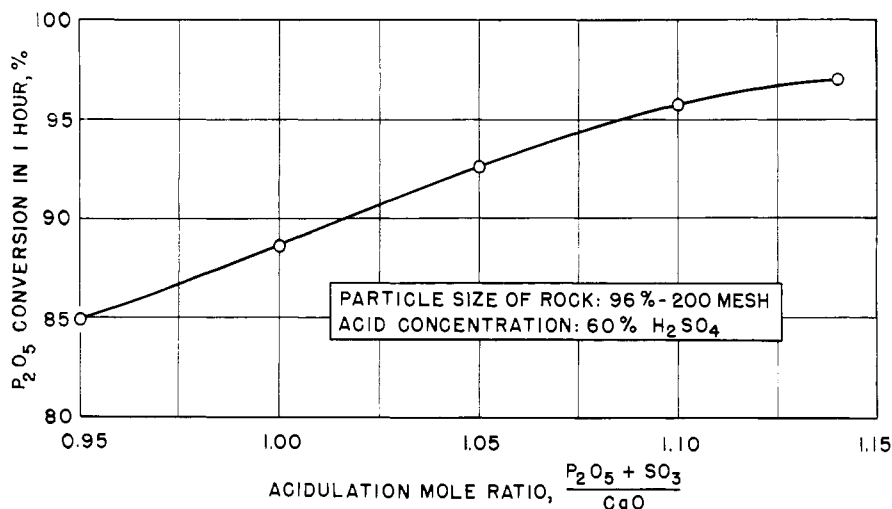


Figure 2. Effect of acidulation ratio on  $P_2O_5$  conversion in 1 hour

280° F. onto the continuous den, which was operated to provide a retention time of about 1 hour. The depth of the bed of superphosphate on the den was usually about 2 feet. Immediately before the cutter, the temperature of the bed was about 220° F. In acidulation tests in which the superphosphate was not ammoniated, it was allowed to form a pile in an enclosed bin below the den. After 1 day of curing, the temperature in the center of a 2-ton pile was usually about 150° F.

The particle size of the phosphate rock (Florida land pebble) used in the pilot plant was 90 to 95% -200 and 75 to 80% -325 mesh. This was some-

what coarser than the finest rock used in the small-scale tests. Chemical and screen analyses of rock typical of that used in the pilot plant follow:

Chemical Analysis, %								
$P_2O_5$	CaO	$SiO_2$	$Fe_2O_3$	$Al_2O_3$	F	$CO_2$	$H_2O$	Ignition loss
33.0	49.9	5.5	0.8	0.9	3.9	3.3	0.6	6.6

Wet-screen Analysis, % through Indicated Tyler screen				
100	150	200	270	325
99.6	97.9	93.2	87.6	79.5

Figure 3. Effect of sulfuric acid concentration on  $P_2O_5$  conversion in 1 hour

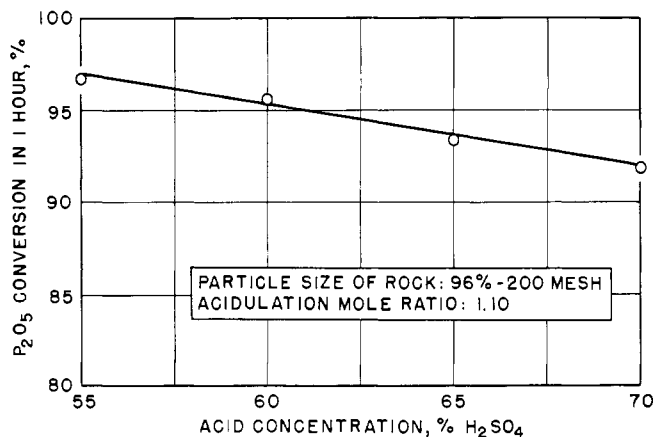
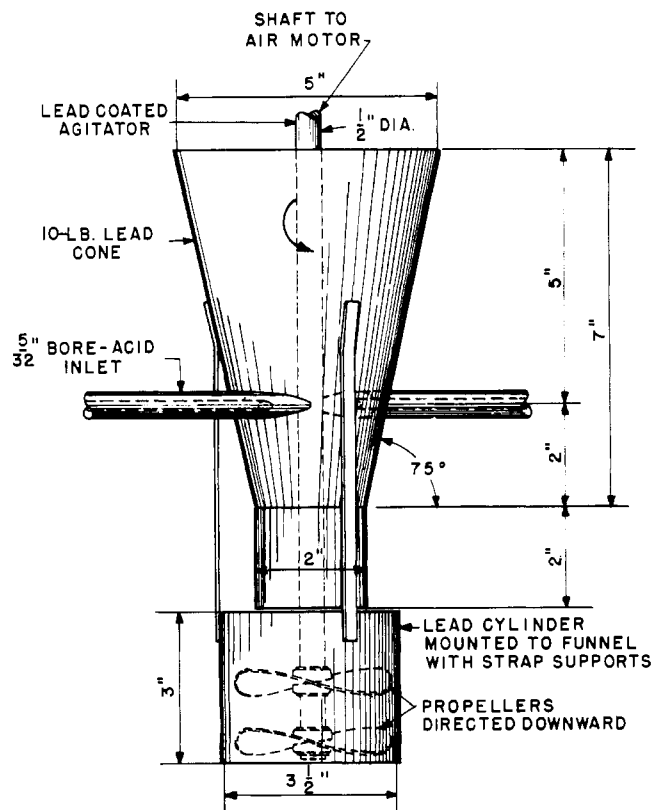


Figure 4. Detail of funnel mixer used in pilot-plant tests



The operating conditions and results of the pilot-plant tests are presented in Table I. Tests were made with acidulation mole ratios of 1.06 to 1.19 and with acid concentrations from 56 to 71%. Although a systematic study of these variables was not made in the pilot plant, the data of Table I show that conversion increased with increased acidulation ratio and with decreased acid concentration. The highest conversion obtained 1 hour after mixing was 96% using an acidulation ratio of 1.18 and 60% acid. The product from the den was friable and porous at acidulations of 1.06 to 1.19 when acid concentrations of 60% or higher were used. When lower concentrations were used, the product from the den was damp and, although it was not tested, it appeared to be too wet for satisfactory handling and ammoniation.

In one pilot-plant test, rock of a fineness typical of that now used in the industry (79% -200 mesh) was used with an acidulation ratio of 1.06 and 70% sulfuric acid. In addition to a low

conversion (79%), the superphosphate was wet and sticky and was not considered suitable for immediate ammoniation. Even after 1 day of curing in a pile, the conversion was only 86% and the physical condition was not greatly improved.

### Ammoniation and Granulation

A limited number of tests were made in which fresh superphosphate, produced in the cone mixer and Broadfield-type den, was processed in the TVA ammoniation-granulation pilot plant to produce granular, high-analysis fertilizers. This pilot plant, described in a recent publication (5), was operated at a production rate of about 1 ton per hour. The superphosphate, as it was discharged from the den, was collected in buckets and charged to a volumetric feeder, which was used to regulate the rate of feed to the ammoniator. The handling and feeding characteristics of this material were similar to those of conventional superphosphate. The total time of denning and transfer to the ammoniator was about 1.3 hours.

The grades of granular fertilizers produced were 6-12-12, 10-10-10, and 4-16-16. The formulations and data for typical tests are given in Table II. The fresh superphosphates used in these tests were made with acidulation ratios of 1.10 to 1.14 and with acid of from 64 to 67% sulfuric acid concentration. The conversion of phosphorus pentoxide to an available form ranged from 91 to 94%. Conditions required for higher conversion were not achieved consistently because of the lack of precise control of feed rates.

The granular fertilizers were not dried because it was desired to determine the moisture content obtainable, with cooling only, when fresh superphosphate was used, for comparison with similar data when cured superphosphate was used. The products made with fresh superphosphate contained about 1% more moisture than those made with cured superphosphate.

The moisture contents of the pilot-plant products were somewhat higher than would be expected in commercial operation. This was due largely to the relatively high proportion of heat losses from the pilot-plant size ammoniator and from the superphosphate as it was transferred from the cutter to the ammoniator. During transfer to the ammoniator, the superphosphate cooled from about 220° F. at the cutter to about 110° F. at the ammoniator inlet. In commercial operation, it is expected that the superphosphate would be transferred continuously with only a small loss of sensible heat.

The 6-12-12 grade was made by using fresh superphosphate, nitrogen solution Y (26.0% of free ammonia, 55.5% of ammonium nitrate, and 18.5% of water),

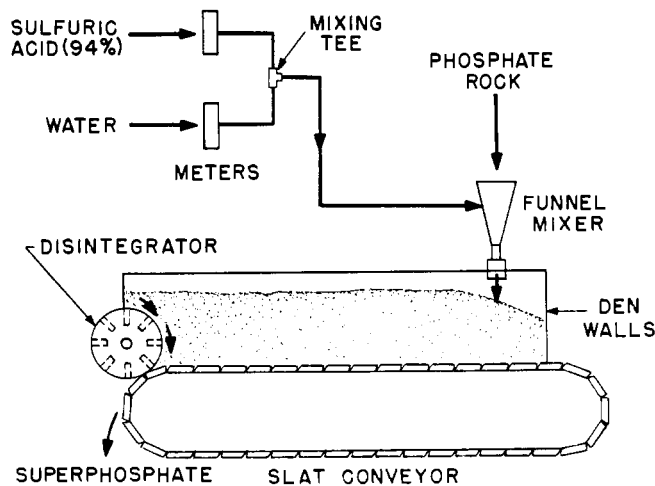


Figure 5. Arrangement of pilot-plant funnel mixer and den

and potassium chloride. Steam was used in the ammoniator to promote granulation. The recycle rate was 17% of the total feed to the ammoniator. After the oversize (+6 mesh) was crushed, 80% of the granular product was in the product-size range (-6 +28 mesh). The net input degree of ammoniation, after the ammonia required to neutralize the excess acid in the superphosphate was deducted, was 4.5 pounds of ammonia per unit of available phosphorus pentoxide. The loss of free ammonia was 2%. The loss of phosphorus pentoxide availability during ammoniation was 0.8%. These results are substantially the same as has been experienced in the use of conventional cured superphosphate to produce 6-12-12 fertilizer. About

61% of the available phosphorus pentoxide in the product was water-soluble. This compares with water solubility of about 42% obtained when conventional superphosphate is ammoniated to the same degree (7). The higher water solubility in the present test resulted from the greater amount of phosphoric acid present in the overacidulated superphosphate. The moisture content of the product was 5.5%—drying to about 2% would be required to ensure the desired grade.

In another run on 6-12-12, for which data are not given in Table II, granular instead of regular (nongranular) potassium chloride was used. In this run, steam was not required to aid granulation and the moisture content of the product

Table I. Pilot-Plant Production of Ordinary Superphosphate

Acidulation Mole Ratio <sup>a</sup>	Acid Concn., % H <sub>2</sub> SO <sub>4</sub>	Chemical Analysis of Product, %			P <sub>2</sub> O <sub>5</sub> Conversion, %		Physical Appearance of Product after Denning
		Total P <sub>2</sub> O <sub>5</sub>	C.I. P <sub>2</sub> O <sub>5</sub> <sup>b</sup>	H <sub>2</sub> O	After denning	Cured 1 day	
Tests with Finely Ground Phosphate Rock <sup>d</sup>							
1.06	56	17.4	1.1	14.7	94	..	Damp
1.06	58	18.2	1.2	14.7	93	99	Slightly damp
1.06	64	18.4	1.6	9.4	91	..	Dry, friable
1.10	60	18.6	1.8	9.9	90	..	Slightly damp
1.10	65	18.3	1.4	12.5	92	..	Dry, friable
1.10	69	18.8	2.7	10.6	86	98	Dry, friable
1.12	71	18.8	2.5	9.5	87	92	Dry, friable
1.14	60	17.3	1.3	14.5	93	96	Slightly damp
1.14	65	17.8	1.0	12.4	94	..	Dry, friable
1.16	64	18.3	1.2	12.1	93	..	Dry, friable
1.17	62	17.4	0.8	13.0	95	..	Dry, friable
1.18	60	16.4	0.6	16.0	96	99	Slightly damp
1.19	64	17.2	1.1	13.2	94	99	Dry, friable
Test with Phosphate Rock Ground to Standard Size <sup>e</sup>							
1.06	70	18.8	3.9	10.7	79	86	Wet

<sup>a</sup> [(P<sub>2</sub>O<sub>5</sub> + SO<sub>3</sub>)/CaO]. Calculated from chemical analysis of product.

<sup>b</sup> Samples washed immediately after 1-hour denning time.

<sup>c</sup> Conversion of P<sub>2</sub>O<sub>5</sub> to citrate-soluble form.

<sup>d</sup> Florida land pebble ground so that 90 to 95% passed 200-mesh sieve and 75 to 81% passed 325-mesh sieve.

<sup>e</sup> 79% - 200 mesh and 62% - 325 mesh.

**Table II. Production of Granular Fertilizers from Fresh Superphosphate in TVA Ammoniation-granulation Pilot Plant**

Grade	Actual Formulation		
	6-12-12	10-10-10	4-16-16
Feed rates, lb./ton product			
Nitrogen solution (X, Y) <sup>a</sup>	330(Y)	490(X)	...
Anhydrous liquid ammonia	...	...	108
Fresh ordinary superphosphate	1361	1314	982
Available P <sub>2</sub> O <sub>5</sub> content, %	16.8	15.7	16.9
Concentrated superphosphate (49% available P <sub>2</sub> O <sub>5</sub> )	...	...	343
Potassium chloride, 60% K <sub>2</sub> O (S, G) <sup>b</sup>	436(S)	311(S)	533(G)
Sulfuric acid (94%)	...	60	...
Steam	135	...	...
Water	...	...	258
Input moisture content, %	13.9	9.7	16.4
Recycle, % of total feed	17	16	14
Availability of P <sub>2</sub> O <sub>5</sub> in ordinary superphosphate, %	94	91	93
Degree of ammoniation of ordinary superphosphate, lb. free NH <sub>3</sub> /unit available P <sub>2</sub> O <sub>5</sub>			
Gross	7.5	10.3	9.2
Net <sup>c</sup>	4.5	6.0	6.1 <sup>d</sup>
Losses, %			
Free NH <sub>3</sub>	2.0	5.3	0.8
P <sub>2</sub> O <sub>5</sub> availability in ordinary superphosphate	0.8	1.3	0
Temperature, °F.			
Ammoniator product	182	157	173
Granulator product	159	146	145
Product size (-6 +28 mesh) after crushing oversize, %	80	84	79
Moisture content, %			
Ammoniator product	7.6	4.5	10.9
Screened product	5.5	3.2	8.4
After 1 week of curing	4.1	2.8	5.5
Chemical analysis of screened product, %			
Total N	6.3	9.7	4.0
Ammoniacal N	4.8	6.9	4.0
Total P <sub>2</sub> O <sub>5</sub>	12.3	11.3	17.2
Available P <sub>2</sub> O <sub>5</sub>	11.5	10.1	16.4
W.S. P <sub>2</sub> O <sub>5</sub>	7.0	5.3	8.2
K <sub>2</sub> O	11.0	10.0	15.9
SO <sub>3</sub>	22.1	19.7	...
CaO	17.7	15.6	...
H <sub>2</sub> O	5.5	3.2	8.4

<sup>a</sup> Nitrogen solution X. 21.7% free NH<sub>3</sub>, 65.0% NH<sub>4</sub>NO<sub>3</sub>, 13.3% H<sub>2</sub>O. Nitrogen solution Y. 26.0% free NH<sub>3</sub>, 55.5% NH<sub>4</sub>NO<sub>3</sub>, 18.5% H<sub>2</sub>O.

<sup>b</sup> S standard potassium chloride; G granular (90% -6 +28 mesh) potassium chloride.

<sup>c</sup> Degree of ammoniation of ordinary superphosphate after deducting ammonia required to neutralize excess acid and any acid included in formulation.

<sup>d</sup> Calculated assuming degree of ammoniation of concentrated superphosphate to be 3.8.

was lower (4.4%). Efficiency was improved to the extent that 91% was on-size after crushing the oversize.

The amount of acid present in the fresh superphosphate in excess of that present in conventional cured superphosphate was equivalent to 98 pounds of sulfuric acid per ton of 6-12-12. Although this grade can be made with nitrogen solution without the addition of acid, some producers prefer to add acid (about 75 pounds per ton of product) to supply heat for improving granulation.

The formulation for the 10-10-10 grade consisted of ordinary superphosphate, nitrogen solution X (21.7% of free ammonia, 65.0% of ammonium nitrate and 13.3% of water), and potassium chloride. A small amount of sulfuric acid was added, and air was blown onto the bed of solids in the ammoniator for control of granulation.

Recycle was added to the ammoniator at the rate of 16% of the total feed. About 84% of the product was -6 +28 mesh after crushing the oversize. The net input degree of ammoniation, after deducting the ammonia required to neutralize the excess acid in the superphosphate and the sulfuric acid added in the formulation, was 6.0 pounds of ammonia per unit of available phosphorus pentoxide. The loss of free ammonia was 5%. The loss of phosphorus pentoxide availability during ammoniation was 1.3%. These results are similar to those obtained with the use of conventional superphosphate. About 53% of the phosphorus pentoxide in the product was water-soluble, compared with about 28% usually obtained.

The excess acid present in the fresh superphosphate was equivalent to 68 pounds per ton of product. Thus, the total acid, including 60 pounds added

during ammoniation, was 128 pounds of sulfuric acid per ton, which is about equal to the amount used in the formulation of 10-10-10 with conventional superphosphate.

The 4-16-16 grade was formulated with ordinary superphosphate, concentrated superphosphate produced from electric-furnace phosphoric acid, anhydrous liquid ammonia, and granular (about 90% -6 +28 mesh) potassium chloride. Water was fed to the ammoniator together with the liquid ammonia to prevent freezing of the moist material on the ammonia distributor and to promote granulation. The recycle rate was 14% of the total feed to the ammoniator. After crushing oversize, 79% of the product was in the product-size range. The net input degree of ammoniation for the ordinary superphosphate, assuming that the concentrated superphosphate absorbed 3.8 pounds of ammonia per unit of available phosphorus pentoxide, was 6.1. The loss of free ammonia was 1%. No loss of phosphorus pentoxide availability occurred during ammoniation. Similar results are generally obtained when conventional ordinary superphosphate is used. The water-soluble phosphorus pentoxide in the product was 50% of the total, compared with about 27% using conventional ordinary superphosphate.

The excess acid present in the fresh superphosphate was equivalent to 73 pounds of sulfuric acid per ton of 4-16-16 product. When conventional ordinary superphosphate is used in this formulation, 100 to 150 pounds of acid are generally used to obtain satisfactory granulation.

The 6-12-12, 10-10-10, and 4-16-16 granular products were cured for 1 week and then stored in multiwall paper bags containing one or two asphalt-laminated plies. Inspections were made after 6 months of storage in stacks 12 bags high. Even though the moisture contents were somewhat higher than would be expected in products made in large-scale operation, the bagged products contained practically no lumps after the standard drop test—four drops from waist height, once on each face and side. Before the bags were moved from the storage racks, they had medium to hard bag sets, which would be somewhat less with products of lower moisture content.

### Discussion

The process described for the production of superphosphate suitable for immediate ammoniation should be adaptable for use in granulation plants that have acidulation units without appreciable modification of equipment. The increased amount of acid over that used in the production of conventional superphosphate serves two functions: It aids in rapid conversion of phosphorus

pentoxide and serves to fix ammonia and aid granulation when the superphosphate is used in the production of high-analysis granular fertilizers. The amount of excess acid is no greater than the acid used in the formulation of most grades of fertilizers. Therefore, in most cases, it does not increase the over-all materials cost.

Suppliers of phosphate rock estimate that fine grinding of rock to the size desired for this process would increase the cost of the rock by about 40 cents per ton or about 13 cents per ton of fertilizer containing 10 units of phosphorus pentoxide from the superphosphate. This should be offset by savings in reduced inventories, lower cost of handling materials, and other inherent advantages of a continuous, integrated process. More precise control of acidulation probably would be required; however, this would have the advantage of ensuring uniformity of the physical and chemical properties of the superphosphate.

The continuous den was used in the pilot-plant tests because it was available and because it would permit integration

of acidulation and ammoniation into a single continuous process. There is no obvious reason why batch mixing and denning techniques would not be suitable for producing superphosphate for immediate ammoniation. Retention times in batch dens are usually in the range of 5 to 24 hours. Under these conditions, a higher conversion could be obtained with the same acidulation ratio, or the same conversion could be obtained with somewhat less acid.

Studies are in progress in which similar techniques are being applied to processes for the manufacture of concentrated and enriched superphosphates.

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## SWINE NUTRITION

### Digestive Enzymes of the Baby Pig. Pepsin and Trypsin

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The relative proteolytic activities of the gastric mucosa and pancreas of the baby pig were estimated from birth through 6 weeks of age. Although there was a rapid initial rate of development of pepsin during the first week, which lessened as age increased, the total levels of pepsin per unit of tissue were low until the third to fourth week of age. An apparent increase, with age, in the quantity of trypsin per pig was due to increased size of the pancreas, but no definite increase was noted per unit of pancreatic tissue. The relationship of these results to recent research in swine nutrition is discussed.

QUANTITATIVE and qualitative changes in digestive enzyme secretions occur in the early life of the pig. Sewall (1) was unable to demonstrate peptic activity in the gastric mucosa of fetal pigs nearly at term. Langendorff (2) found that, in general, pepsin was present just before birth but in very low concentrations. He pointed out that pepsin appeared prior to birth in herbivora, after birth in carnivora, and that the pig was intermediate in this respect. Mendel (3) found no pepsin or sucrase activity in pig embryos nearly at term but maltase was plentiful. Lactase was secreted in the young pig but not in the

older pig. Plimmer (4) concluded that the secretion of lactase in the young but not in the old was characteristic of all animals. Recently, Heilskov (5) demonstrated that lactase secretion in rabbits and cows decreased with age. Bailey, Kitts, and Wood, (6) working with the baby pig, found lactase activity in intestinal extracts high at birth, followed by subsequent decrease of activity with age, while the reverse was found for maltase and sucrase. Kitts, Bailey, and Wood (7) found that amylase activity of pancreatic extracts increased with the age of the young pigs, while lipase activity was high at birth and remained high as growth proceeded.

Recent investigations on the nutrition of the baby pig, by Lewis and others (8),

have shown that soybean proteins are very poor substitutes for milk proteins in the formulation of rations for early weaning. Noller, Ward, and Huffman (9) have observed similar results with young calves. However, the gain and feed efficiency of young pigs fed soybean protein basal diets were improved by either the addition of proteolytic enzymes to the diet (10) or by partial prehydrolysis of soybean protein with enzymes (11).

As the ability of the baby pig to utilize various rations might be reflected in the enzyme content of the digestive glands, studies have been made on the enzyme activities of extracts of certain digestive enzyme secretory tissues taken from pigs at various ages. The studies reported

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