

## Pilot Plant Production of Nitric Phosphate Fertilizers Using the TVA Continuous Ammoniator

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Nitric phosphate fertilizers were produced by reaction of phosphate rock with nitric acid or a mixture of nitric and sulfuric or phosphoric acids, followed by simultaneous ammoniation and granulation in a TVA continuous ammoniator. Product fines, consisting of undersize and crushed oversize from the product screens (-6, +12 mesh), were recycled to aid granulation. The production of granular products of 12-12-12, 14-14-14, 10-20-15, and 10-15-20 grades was demonstrated in pilot plant tests. The process requires considerably less investment and is more versatile than nitric phosphate processes in which the ammoniation step is carried out in a fluid state and granulation in a separate step. It may be carried out in conventional fertilizer granulation plants by the addition of a relatively inexpensive extraction unit and other minor changes. Estimates indicate that the production of nitric phosphates should be more economical than the production of other high-nitrogen fertilizers in some locations.

IN PROCESSES previously developed by the Tennessee Valley Authority for the production of nitric phosphate fertilizers (3, 5-9), phosphate rock was extracted with nitric acid or with mixtures of nitric and phosphoric or sulfuric acids. The extraction slurry was ammoniated in a series of tanks, and the ammoniated slurry was dried in one or two stages. Similar processes have been developed and are in use in Europe.

The main advantage of the nitric phosphate processes is the low cost of raw materials (8), as compared with conventional processes. Another advantage is that the products are well granulated and homogeneous. The processes have not yet gained wide acceptance in this country, because of the following disadvantages: The equipment required is more expensive than that used in the usual fertilizer manufacturing plant, entirely new plants would be required, because little use could be made of existing plants, and the nitric phosphate processes are not adaptable to the manufacture of as large a variety of grades as most manufacturers deem necessary. The equipment is not adaptable to make use of other processes.

This paper describes a newly developed method that overcomes most of the disadvantages of the previous processes.

### Description and Operation of Pilot Plant

The experimental work was carried out in the TVA continuous ammoniator pilot plant, described in detail in an earlier publication (7). The original facilities consisted of a rotary ammoniator, a rotary granulator, a direct gas-

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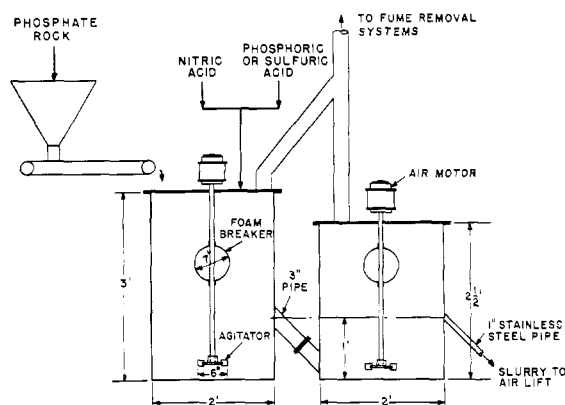


Figure 1. Pilot plant extraction unit

fired rotary dryer, equipment for metering and feeding liquids and solids to the ammoniator, and equipment for screening the product, crushing oversize, and recycling fines. The only additions required to permit the production of nitric phosphates were an extraction unit and equipment for feeding the extraction slurry to the ammoniator. A flowsheet of the modified process has been published (2). Figure 1 is a drawing of the extraction unit. Typical chemical and screen analyses of the solid raw materials used in the pilot plant tests are given in Table I.

In the earlier work on the production of nitric phosphates (6), it was found that a retention time of 30 minutes was adequate for essentially complete extraction of the phosphate from the phosphate rock. Therefore, for the present work, the extraction unit was designed to provide a minimum retention of 30 minutes. The unit consisted of two stainless steel tanks in series with facilities for metering rock and acids to the first tank. Both

tanks were 2 feet in diameter. The first tank was 3 feet high and the second was 2.5 feet high. The additional height of the first tank allowed space for foam control. The extraction tanks were equipped with turbine-type agitators that were powered with air motors. Egg beater-type foam breakers were mounted on each agitator shaft above the level of the overflow, which was about 1 foot from the bottom of the tank. Both extractors were covered, except for small openings for the feeds, and a duct connected the tanks to a fume-removal system.

The slurry overflowing from the second extractor was fed onto the surface of the bed of material in the ammoniator from an open-end pipe which was moved back and forth across the length of the bed by a mechanical device at a rate of about 30 passes per minute. In preliminary tests, the slurry was pumped to the distributor (4) in the ammoniator. However, because of the corrosive and erosive nature of the slurry, it was difficult to maintain

**Table I. Typical Chemical and Screen Analyses of Raw Materials Used in Pilot Plant Tests**

| Raw Material                             | Chemical Analysis, % |                                     |                                    |                                    |      |                  |          | Screen Analysis, %<br>Standard Tyler Screens |         |          |           |      |
|--|----------------------|-------------------------------------|------------------------------------|------------------------------------|------|------------------|----------|--|---------|----------|-----------|------|
|  | N                    | Total P <sub>2</sub> O <sub>5</sub> | C.I. P <sub>2</sub> O <sub>5</sub> | W.S. P <sub>2</sub> O <sub>5</sub> | CaO  | K <sub>2</sub> O | Moisture | +20  | -20 +28 | -28 +100 | -100 +200 | -200 |
| Phosphate rock <sup>a</sup>              | ...                  | 34.7                                | ...                                | ...                                | 49.2 | ...              | 0.6      | 6.2  | 9.4     | 73.6     | 10.1      | 0.7  |
| Potassium chloride                       |                      |                                     |                                    |                                    |      |                  |          |  |         |          |           |      |
| Fine size                                | ...                  | ...                                 | ...                                | ...                                | ...  | 60.7             | ...      | 0.5  | 0.8     | 46.7     | 44.6      | 7.4  |
| Medium size                              | ...                  | ...                                 | ...                                | ...                                | ...  | 60.2             | ...      | ...  | 22.7    | 58.6     | 13.5      | 5.2  |
| Concentrated superphosphate <sup>b</sup> | ...                  | 49.5                                | 0.7                                | 45.9                               | 21.5 | ...              | 0.6      | 1.4  | 2.2     | 44.5     | 42.3      | 9.6  |
| Ammonium nitrate (crystalline)           | 34.7                 | ...                                 | ...                                | ...                                | ...  | ...              | ...      | 33.3   | 32.7    | 34.0     | ...       | ...  |
| Calcium metaphosphate                    | ...                  | 64.6                                | 1.1                                | ...                                | 28.6 | ...              | 0.1      | ...  | ...     | ...      | ...       | ...  |

<sup>a</sup> Florida flotation concentrates.

<sup>b</sup> Made with electric furnace phosphoric acid.

<sup>c</sup> Calcium metaphosphate ground so that substantially all passed 100-mesh screen.

continuous operation of the pumps that were available, and a gravity flow system was installed. Because it was not possible to mount the extractors in the pilot plant building, at a sufficient elevation above the ammoniator to assure gravity flow, an air lift was installed to raise the slurry to a small tank about 10 feet above the level of the ammoniator, from which the slurry flowed by gravity to the ammoniator.

**Ammoniation and Granulation.** The 3 × 3 foot ammoniator was operated at a speed of 15 r.p.m. and with a bed depth of 9 inches. The distributor for ammonia or ammoniating solution used in most of the tests was of the slotted type (10). It was 30 inches long and was positioned 6 inches below the surface of the bed. The slots were so graduated in size that the feed was concentrated in the center of the ammoniator. Equally satisfactory results were obtained with anhydrous liquid and gaseous ammonia and with ammonia-ammonium nitrate solution. A few tests with liquid ammonia were made with a distributor designed to give uniform distribution. With this distributor, which consisted of a 1/2-inch stainless steel pipe with 19 equally spaced holes 0.040 inch in diameter, there was some indication that the product could be ammoniated to a slightly higher degree without loss of ammonia.

Granulation was controlled mainly by recycling product fines. Cooling air directed onto the bed of material was used to help control granulation in some runs.

The granular material was discharged from the ammoniator at a temperature of about 150° to 190° F. and passed through the granulator. Although no tests were made in which it was not used, it is believed that the granulator could have been left out of the system without harmful effect.

**Drying.** The material from the granulator was dried in a cocurrent rotary dryer. The inlet gas temperature was 300° to 350° F. and the temperature of the product from the dryer was 200° to 225° F. The product became plastic and agglomerated at higher temperatures. A cooler was not available for use in the pilot plant. However, one

would be required in a commercial plant for cooling the product to a reasonable temperature for bagging and for crushing oversize.

The dried material usually was screened to separate the -6- +12-mesh fraction as product. The oversize was crushed in a roll crusher. The undersize and crushed oversize were recycled to the ammoniator.

**Chemical Requirements.** When phosphate rock is extracted with nitric acid and the extract is ammoniated, the resulting mixture is excessively hygroscopic, because it contains calcium nitrate. Availability of the phosphate in the product is low if the product is fully ammoniated (6). In the nitric phosphate processes, various means are employed to obtain high availability and to avoid the presence of calcium nitrate. In earlier work at TVA, this was accomplished by adding sulfuric or phosphoric acid so that the mole ratio (CaO-CaSO<sub>4</sub>) to P<sub>2</sub>O<sub>5</sub> would be 2.3 or less. In the present work, satisfactory results were obtained when the mole ratio was adjusted with concentrated superphosphate or calcium metaphosphate as well as with phosphoric or sulfuric acid.

### Operating Results

Fertilizers of the following grades were produced in pilot plant tests of the modified nitric phosphate process: 14-14-14, 12-12-12, 10-15-20, and 10-20-15. These tests were made at production rates of 500 to 1500 pounds per hour. Operation at a production rate of 2000 pounds was not possible, because the drying, crushing, and conveying systems were overloaded. Operating data for the tests are given in Table II. The formulations represent actual weights used and are slightly different from the calculated formulations, because of inaccuracies in feeding. Analyses for nitrogen, phosphorus, and potassium were made by AOAC procedures. The moisture contents of in-process materials were determined by oven-drying at 175° F. The moisture contents of the final products were determined by the AOAC vacuum desiccation method.

**Tests of 14-14-14.** Five different formulations were used in the production of 14-14-14 grade products to demonstrate the versatility of the process with respect to raw materials. The mole ratio of calcium oxide to phosphorus pentoxide was adjusted to about 2.3 by the addition of phosphoric acid, concentrated superphosphate, or calcium metaphosphate.

In test A, phosphate rock was extracted with nitric acid (57.9% HNO<sub>3</sub>) and wet-process phosphoric acid (76% H<sub>3</sub>PO<sub>4</sub>). At the feed rates used in this test, the total retention time in the extractors was about 80 minutes. Analysis of the slurry indicated that extraction of the phosphate from the rock was 99.8% complete. The temperature averaged 140° F. in the first extractor and 128° F. in the second extractor. The slurry contained 28% water; it flowed readily through the air lift and the slurry distributor. Potassium chloride, recycle fines, and liquid ammonia were added in the ammoniator. When cooling air at a rate of 5500 cubic feet per ton of product was used, good granulation was obtained when the moisture in the feed to the ammoniator (input moisture) was 6.6% and the recycle rate was 3.5 pounds per pound of product. Without cooling air, a slightly higher recycle rate was required. Ammonia was absorbed without significant losses until the ratio of ammonia to nitrate nitrogen in the product was about 1.1. If additional ammonia was supplied, it was not absorbed. Availability of the phosphate in the products was 96% or higher. From 20 to 24% of the phosphate was water-soluble.

In tests B and C, nitric acid (57% HNO<sub>3</sub>) alone was used for extraction of the phosphate rock, and the mole ratio of calcium oxide to phosphorus pentoxide was adjusted to about 2.3 by the addition of concentrated superphosphate or calcium metaphosphate. Ammoniation was carried out with gaseous ammonia. In test B, concentrated superphosphate was added to the ammoniator with the other dry ingredients. Granulation was good with 5.0% input moisture and a recycle ratio of 3.7. The physical properties of the product were fully as good as

**Table II. Production of Nitric Phosphates in TVA Continuous Ammoniator Pilot Plant**

|  | 14-14-14        |         |         |        |        | 12-12-12 | 10-15-20 | 10-20-15 |
|--|-----------------|---------|---------|--------|--------|----------|----------|----------|
|  | A               | B       | C       | D      | E      | F        | G        | H        |
| Production rate, ton/hr.   | 0.25            | 0.25    | 0.25    | 0.51   | 0.52   | 0.41     | 0.75     | 0.50     |
| Formulation, lb./ton   |                 |         |         |        |        |          |          |          |
| Phosphate rock   | 512             | 420     | 432     | 406    | 405    | 707      | 456      | 362      |
| Nitric acid <sup>a</sup>   | 1120(B)         | 1100(A) | 1163(A) | 750(C) | 745(C) | 973(B)   | 798(C)   | 738(A)   |
| Phosphoric acid (76% H <sub>3</sub> PO <sub>4</sub> )  | 200             | ...     | ...     | ...    | ...    | ...      | ...      | ...      |
| Sulfuric acid (93% H <sub>2</sub> SO <sub>4</sub> )  | ...             | ...     | ...     | ...    | ...    | 241      | ...      | ...      |
| Anhydrous ammonia <sup>b</sup>   | 180(L)          | 196(G)  | 180(G)  | 120(L) | ...    | 151(L)   | 129(G)   | 156(G)   |
| Nitrogen solution <sup>c</sup>   | ...             | ...     | ...     | ...    | 435    | ...      | ...      | ...      |
| Ammonium nitrate   | ...             | ...     | ...     | 304    | ...    | ...      | ...      | ...      |
| Concentrated superphosphate  | ...             | 316     | ...     | 281    | 310    | ...      | 341      | 566      |
| Calcium metaphosphate  | ...             | ...     | 248     | ...    | ...    | ...      | ...      | ...      |
| Potassium chloride   | 500             | 480     | 480     | 436    | 437    | 371      | 676      | 418      |
| Total  | 2512            | 2508    | 2503    | 2297   | 2332   | 2443     | 2400     | 2240     |
| Recycle ratio, lb. recycle/lb. product   | 3.5             | 3.7     | 3.4     | 2.6    | 2.8    | 3.2      | 2.4      | 2.5      |
| Temperature, ° F.  |                 |         |         |        |        |          |          |          |
| Extractor 1  | 140             | ...     | ...     | 142    | 146    | 200      | 157      | 150      |
| Extractor 2  | 128             | ...     | ...     | 136    | 136    | 174      | ...      | 130      |
| Ammoniator product   | 154             | 159     | 171     | 165    | 156    | 155      | 184      | 189      |
| Dryer product  | 206             | 202     | 199     | 210    | 191    | 190      | 214      | 213      |
| Moisture content, %  |                 |         |         |        |        |          |          |          |
| Input to ammoniator <sup>d</sup>   | 6.6             | 5.0     | 5.2     | 5.9    | 4.7    | 6.4      | 5.1      | 5.6      |
| Ammoniator product <sup>e</sup>  | 4.9             | 3.4     | 3.9     | 3.8    | 4.4    | 5.4      | 4.1      | 3.9      |
| Dryer product <sup>e</sup>   | 1.5             | 1.1     | 2.3     | 1.3    | 1.3    | 2.3      | 0.9      | 0.9      |
| Screen analysis of product, % (Tyler)  |                 |         |         |        |        |          |          |          |
| Granulator   |                 |         |         |        |        |          |          |          |
| Oversize (+6)  | 19              | 32      | 47      | 44     | 45     | 18       | 8        | 21       |
| On-size (-6 +12)   | 41 <sup>f</sup> | 64      | 46      | 40     | 39     | 50       | 42       | 35       |
| Undersize (-12)  | 40              | 4       | 7       | 16     | 16     | 32       | 50       | 44       |
| Screened unconditioned product   |                 |         |         |        |        |          |          |          |
| Chemical composition, %  |                 |         |         |        |        |          |          |          |
| Total N  | 14.1            | 14.2    | 13.0    | 14.1   | 14.4   | 12.3     | 10.0     | 10.7     |
| NH <sub>3</sub> -N   | 7.4             | 7.2     | 6.7     | 7.1    | 7.3    | 6.1      | 5.4      | 6.1      |
| Total P <sub>2</sub> O <sub>5</sub>  | 14.8            | 16.0    | 15.0    | 14.5   | 14.6   | 12.4     | 15.4     | 22.2     |
| Available P <sub>2</sub> O <sub>5</sub>  | 14.3            | 15.1    | 14.1    | 13.6   | 13.8   | 12.1     | 14.7     | 21.3     |
| W.S. P <sub>2</sub> O <sub>5</sub>   | 3.1             | 3.1     | 2.3     | 2.6    | 3.4    | 2.8      | 3.8      | 6.2      |
| K <sub>2</sub> O   | 14.2            | 14.1    | 14.3    | 14.3   | 13.9   | 11.7     | 20.8     | 14.3     |
| CaO  | 12.6            | 13.4    | 13.7    | 13.3   | 12.5   | 15.8     | 12.8     | 15.1     |
| SO <sub>4</sub>  | ...             | ...     | ...     | ...    | ...    | 9.8      | ...      | ...      |
| H <sub>2</sub> O <sup>g</sup>  | 1.9             | 0.9     | 1.6     | 1.0    | 0.9    | 2.2      | 0.6      | 0.9      |
| Available P <sub>2</sub> O <sub>5</sub> , % of total P <sub>2</sub> O <sub>5</sub>                                       | 97              | 94      | 94      | 94     | 96     | 99       | 97       | 96       |
| W.S. P <sub>2</sub> O <sub>5</sub> , % of available P <sub>2</sub> O <sub>5</sub>  | 21              | 21      | 16      | 19     | 25     | 23       | 26       | 29       |
| Acidulation mole ratio<br>(HNO <sub>3</sub> + H <sub>3</sub> PO <sub>4</sub> + 2H <sub>2</sub> SO <sub>4</sub> )/<br>CaO | 2.6             | 2.7     | 2.8     | 2.0    | 2.0    | 2.2      | 1.9      | 2.1      |
| NH <sub>3</sub> -N:NO <sub>3</sub> -N ratio in product   | 1.10            | 1.03    | 1.06    | 1.01   | 1.04   | 1.00     | 1.13     | 1.36     |
| CaO:P <sub>2</sub> O <sub>5</sub> mole ratio<br>(exclusive of CaSO <sub>4</sub> )  | 2.2             | 2.1     | 2.3     | 2.3    | 2.2    | 2.2      | 2.1      | 1.8      |
| Loss, % (by gas analysis)  |                 |         |         |        |        |          |          |          |
| NO <sub>3</sub> -N from extractors   | 0.3             | ...     | ...     | 0.2    | 0.2    | ...      | ...      | 0.5      |
| Free NH <sub>3</sub> from ammoniator   | 0.3             | 4.9     | 2.5     | 3.6    | 3.4    | ...      | 5.5      | 2.8      |

<sup>a</sup> Concentration of acid, % HNO<sub>3</sub>: A = 57, B = 58, and C = 60.

<sup>b</sup> G, gaseous; L, liquid.

<sup>c</sup> 69% ammonium nitrate, 25% ammonia, and 6% water.

<sup>d</sup> Calculated (includes moisture in recycle).

<sup>e</sup> By oven drying.

<sup>f</sup> On-size, -6 +10 (Tyler); undersize, -10.

<sup>g</sup> AOAC vacuum desiccation method.

those produced in tests in which the ratio was adjusted in the extraction slurry with sulfuric or phosphoric acid. In test C, calcium metaphosphate was added with the phosphate rock and nitric acid to the first extractor, because it was believed that more hydrolysis would occur if the metaphosphate was mixed with the acid. The slurry contained 27% water and was sufficiently fluid to flow readily. Granulation was good under about the same conditions of moisture content and recycle rates as in test B. Because the water solubility of the phosphate in the product from test C was slightly lower than in the other products (16% *vs.* 20% and higher), it appeared that hydrolysis of the calcium metaphosphate was not complete. The availability of the phos-

phate in the products from test B and C was 94%, which was slightly lower than in the products from tests in which phosphoric or sulfuric acid was used with nitric acid for extraction.

In tests D and E, concentrated superphosphate again was used to adjust the mole ratio of calcium oxide to phosphorus pentoxide. However, the amount of nitric acid used was reduced to about the minimum previously found necessary for complete extraction of the phosphate (7), so that the amount of water introduced and, hence, the recycle ratio would be lower. At the net production rate of about 0.5 ton per hour used in these tests, the retention time in the extraction unit was 55 minutes. Slurry analyses indicated 98.8% extraction of the phosphate

from the rock. The slurry contained 26% water and flowed readily. In test D, the slurry was ammoniated with liquid anhydrous ammonia. Solid ammonium nitrate was added in the ammoniator to supply the additional nitrogen required. The amount of recycle required for granulation was 2.6 pounds per pound of product, which was the lowest in this series of tests. In test E, a nitrogen solution containing 69% ammonium nitrate, 25% free ammonia, and 6% water was used instead of solid ammonium nitrate and liquid anhydrous ammonia. The recycle requirement (2.8 pounds per pound of product) was about the same as in test D.

**Production of 12-12-12.** A 12-12-12 fertilizer was made (test F) by extracting

phosphate rock with a mixture of nitric and sulfuric acids. Sufficient sulfuric acid was used to form calcium sulfate with the calcium in excess of that required for a mole ratio of about 2.3. The retention time in the extraction unit was about 70 minutes, and 98.3% of the phosphate was extracted. The temperature in the extractors was somewhat higher than in tests in which sulfuric acid was not used. The slurry contained 23% water.

Liquid anhydrous ammonia was used in this test. Granulation was very good with a recycle ratio of 3.2 pounds per pound of product. The use of cooling air in the ammoniator did not appear to affect granulation. The phosphate in the product was 99% available and was 23% water soluble.

**Tests of 10-15-20 and 10-20-15.** Two other products that were produced to demonstrate further the versatility of the process were 10-15-20 and 10-20-15 fertilizers. These were made by extracting phosphate rock with nitric acid only and adding concentrated superphosphate, ammonia, and potassium chloride in the ammoniator. In the 10-15-20 grade (test G), the calcium oxide to phosphorus pentoxide mole ratio was 2.3 when the required amount of concentrated superphosphate to give the desired grade was added. In producing the 10-20-15 fertilizer (test H), more concentrated superphosphate was required to make the grade. This resulted in a mole ratio of calcium oxide to phosphorus pentoxide of 1.8 and permitted a higher ratio of ammonia to nitrate nitrogen (1.36 vs. 1.13). Because of the low water-to-solids ratios in these two tests, the recycle requirement for good granulation was only about 2.5 pounds per pound of product.

About 96% of the phosphate was in an available form in both products. The water solubility of the phosphate was 26% in the 10-15-20 and 29% in the 10-20-15 product.

**Granulation.** Granulation occurred readily in the ammoniator. The material leaving the granulator contained about 3 to 5% moisture, and 40 to 50% of it was -6- +12-mesh in size. Very little change in particle size occurred in drying. In most tests the amount of undersize and oversize was less than that required for recycle, and it was necessary to crush a portion of the on-size product to obtain enough recycle. In general, higher input moisture could be tolerated and less recycle was required, when the recycle material was fine (-12-mesh) and cool. Lower recycle rates should be possible in plants equipped with an effective cooler.

**Losses.** To determine loss of nitrogen during extraction, the rate of flow of the gas exhausted from the extractor was measured with an orifice meter, and samples of the gas were analyzed periodi-

**Table III. Bag Storage Tests of Nitric Phosphates Produced in Pilot Plant Ammoniator Granulator**

| Product Grade | Moisture Content as Bagged, % | Results of 3-Month Storage Tests <sup>a</sup> |                          |               |                          |
|---------------|-------------------------------|---|--------------------------|---------------|--------------------------|
|               |                               | Uncured                                       |                          | Cured 7 Days  |                          |
|               |                               | Unconditioned                                 | Conditioned <sup>b</sup> | Unconditioned | Conditioned <sup>b</sup> |
| 14-14-14      | 0.6                           | H-0   | L-0                      | M-0           | L-0                      |
|               | 0.9                           | ...   | ...                      | M-0           | L-0                      |
|               | 1.6                           | ...   | ...                      | M-0           | L-0                      |
| 12-12-12      | 2.3                           | H-13  | H-0                      | H-1           | H-0                      |
|               | 1.5                           | H-5   | L-0                      | M-0           | L-0                      |
|               | 1.2                           | H-0   | L-0                      | M-0           | L-0                      |
|               | 0.3                           | L-0   | O-0                      | ...           | ...                      |
| 10-15-20      | 0.4                           | M-0   | L-0                      | M-0           | L-0                      |

<sup>a</sup> Letters represent bag set before dropping: O, none; L, light; M, medium; and H, hard. Numbers represent per cent +2-mesh lumps remaining after dropping four times from 3-foot height, once on each side and face. All bags were six-ply, two asphalt-laminated.

<sup>b</sup> Conditioning was with 2.5% of kaolin or kieselguhr; similar results were obtained with each.

cally for total oxides of nitrogen. The analysis was made by drawing a metered gas sample through two absorbers in series. The first absorber contained acidified potassium permanganate solution to oxidize nitric oxide to nitrogen dioxide, and the second contained sodium hydroxide solution to absorb the nitrogen dioxide. After the sample had been drawn through the absorbers, the contents of both absorbers were analyzed for total nitrogen. These analyses indicated that less than 0.5% of the nitrate nitrogen was lost during extraction. It is possible that small amounts of nitrogen oxides were reduced to elemental nitrogen and escaped detection by this method. However, material balance data based on feed rates and product analyses usually showed over-all nitrogen losses of less than 3%. There were no visible fumes from any parts of the system during operation at production rates as high as 1000 pounds per hour; at production rates of 1500 pounds per hour and higher, some brown fumes were visible in the gases exhausted from the extractors.

Loss of ammonia during ammoniation was determined from the rate of flow of the gas exhausted from the ammoniator and the concentration of ammonia in the gas. A metered gas sample was passed through scrubbers containing dilute sulfuric acid and the scrubber solution was titrated to determine the amount of ammonia absorbed. The amount of ammonia supplied to the ammoniator was controlled so as to maintain the ammonia loss in the range of 1 to 3%. This was done to obtain the maximum degree of ammoniation without excessive ammonia loss.

#### Physical Properties of Products

The pilot plant products were hard, well-rounded granules. Bag and bulk storage tests of several of the products were made. These tests included study of effects of a 7-day curing period prior to

bagging and effects of conditioning the granules with 2.5% by weight of kaolin or kieselguhr prior to bagging or bulk storage. Six-ply paper bags with two asphalt-laminated plies were used. The filled bags were stacked on a wooden platform on a concrete floor in a large unheated, well-ventilated building, which simulated open warehouse storage. The bags of product being tested were placed in the lower four positions of 12-bag stacks with dummy bags of sand stacked on top of them.

When the bags were inspected, observation was made before each bag was moved to determine the degree of bag set that had occurred. Each bag was then dropped four times from a height of 3 feet, once on each face and side, to simulate handling between warehouse and field. It was cut open and screened to determine the percentage of +2-mesh lumps.

Results of inspections of bagged products after 3 months of storage are shown in Table III. The products tested included 14-14-14, 12-12-12, and 10-15-20 grades. Conditioned products containing 1.6% or less moisture developed only light bag set during 3 months of storage. There were no lumps after the bags of these products were dropped. Unconditioned products that had been cured for 7 days prior to bagging had medium bag sets, but there were no lumps after dropping. Unconditioned, uncured products containing up to 1.2% moisture showed no lumps after the drop test, but bag sets were hard when the moisture content was above about 0.4%. The 12-12-12 product that contained 2.3% moisture had a hard bag set, but there were no lumps after the drop test when the product was cured or conditioned prior to bagging. A combination curing-conditioning treatment was no more effective with any of these products than conditioning alone.

Open-pile storage tests were made on 500-pound portions of most of the prod-

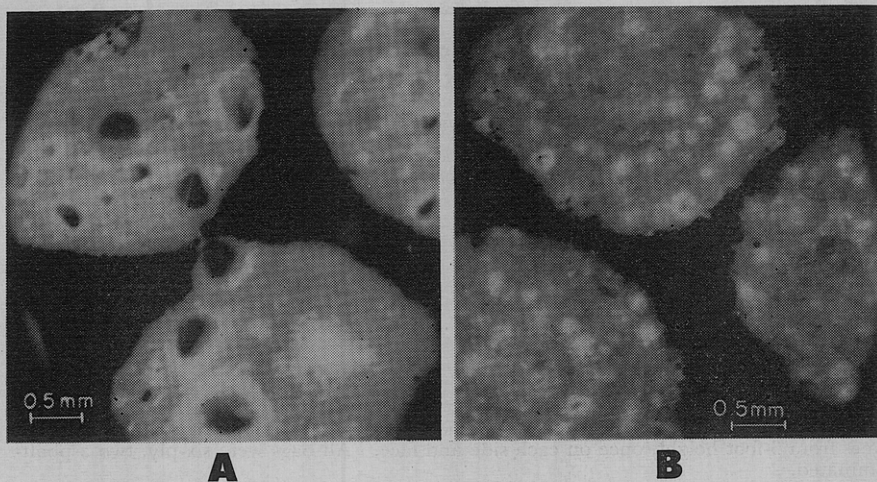


Figure 2. Photomicrographs of granules of 14-14-14 product

- A. Made with medium-sized potassium chloride  
 B. Fine potassium chloride used

ucts included in Table III. When the piles were inspected after 3 months of storage in an unheated building, crusts of up to 1/2 inch in thickness were found on the surfaces of the piles; however, the material underneath the crust was in good condition when the original moisture content was 1.6% or less. Products that had been conditioned prior to storage were free flowing beneath the surface crusts. Unconditioned products were lightly packed, but were easily broken up. The product that contained 2.3% moisture stored well when conditioned, but was caked in the pile when not conditioned.

Microscopic examination of the 12-12-12 that contained 2.3% moisture and caked during storage showed that caking was a result of intergrowth of crystalline hulls that formed on the granules during storage. The hulls were about 50 microns thick and consisted of

fine-grained, intergrown crystallites. Ammonium nitrate was the principal phase in these hulls; lesser amounts of potassium nitrate and ammonium chloride were also present.

Examination of the 14-14-14, 12-12-12, and 10-15-20 products showed that the water-soluble phosphate was predominantly monoammonium phosphate. The water-insoluble phosphatic content appeared in the form of anhydrous dicalcium phosphate and a precipitated colloidal phosphate, more basic than dicalcium phosphate, in approximately equal proportions. Reaction between potassium chloride and ammonium nitrate was observed to have occurred at the interfaces between the potassium chloride grains and the granules in which they were imbedded; with small particles of potassium chloride, reaction was complete. Figure 2 shows photomicrographs of cross sections of granules of two

products of 14-14-14 grade in which this reaction may be observed. In the product (Figure 2A) made from medium-sized potassium chloride containing about 23% +28-mesh particles, unreacted cores of potassium chloride may be seen as dark grains surrounded by hulls of white reaction product. In the product (Figure 2B) made from the finer (essentially all -28-mesh) potassium chloride, only a few very small cores of unreacted potassium chloride were found.

The nitric phosphates produced in the pilot plant work were reanalyzed after storage for 3 months or more. There was no loss of availability of phosphate during storage, nor was there any other significant change in composition.

## Discussion

Expected advantages of the present process over the original process, which were confirmed by pilot plant work, include lower investment cost, ease of adaptation to existing plants, and flexibility with respect to products. Other advantages were:

A larger variety of raw materials can be used. In the modified process, concentrated superphosphate and calcium metaphosphate replaced an equivalent amount of phosphoric acid and phosphate rock. When this was tried in the original process, the slurry gelled during ammoniation. In many locations the market price of concentrated superphosphate or calcium metaphosphate is less than that of an equivalent amount of phosphoric acid and phosphate rock.

The process can be operated with less water in the system. In the earlier work, 40% water in the slurry was required to prevent thickening during ammoniation. In the present work, the extraction slurry, which contained 23 to 28% water, was fed to the continuous ammoniator together with recycle material and ammoniated without difficulty. As a result, a much smaller amount of water had to be removed by drying.

Careful control of ammoniation was not required. In the original process, careful control was required because overammoniation was likely to cause loss of availability of the phosphate (5). In the modified process, overammoniation did not occur. When an excess of ammonia was supplied, it was not absorbed and losses of ammonia were high, but there was no loss in availability of phosphate.

Another advantage, of lesser importance, was the higher water solubility of the phosphate in the products. In several tests of the 12-12-12 grade made by the modified process, an average of 27% of the phosphate in the product was water-soluble, whereas an average of only 17% was obtained in similar tests with the original process.

Cost estimates indicated that nitric

Table IV. Comparison of Costs of Nitric Phosphates and a Conventional Mixed Fertilizer

| Raw Material  | Price, \$/ton | Nitric Phosphate |       |          |       | Conventional Fertilizer, 12-12-12 |        |
|---|---------------|------------------|-------|----------|-------|-----------------------------------|--------|
|   |               | 12-12-12         |       | 14-14-14 |       | Lb./ton                           | \$/ton |
| Phosphate rock (35% P <sub>2</sub> O <sub>5</sub> ) | 15.50         | 707              | 5.48  | 402      | 3.12  | ...                               | ...    |
| Superphosphate                                      |               |                  |       |          |       |                                   |        |
| Concentrated (46% P <sub>2</sub> O <sub>5</sub> )   | 60.00         | ...              | ...   | 329      | 9.87  | 300                               | 9.00   |
| Ordinary (20% P <sub>2</sub> O <sub>5</sub> )       | 22.00         | ...              | ...   | ...      | ...   | 537                               | 5.91   |
| Nitric acid (57% HNO <sub>3</sub> )                 | 26.70         | 960              | 12.82 | 743      | 9.92  | ...                               | ...    |
| Sulfuric acid (93% H <sub>2</sub> SO <sub>4</sub> ) | 23.00         | 232              | 2.67  | ...      | ...   | 162                               | 1.86   |
| Ammonia (anhydrous liquid)                          | 93.37         | 154              | 7.19  | ...      | ...   | ...                               | ...    |
| Solution X-6 (44.8% N)                              | 61.20         | ...              | ...   | 441      | 13.49 | ...                               | ...    |
| Solution X (41% N)                                  | 56.26         | ...              | ...   | ...      | ...   | 494                               | 13.90  |
| Ammonium sulfate (20.5% N)                          | 38.00         | ...              | ...   | ...      | ...   | 195                               | 3.70   |
| Potassium chloride (60% K <sub>2</sub> O)           | 35.00         | 400              | 7.00  | 467      | 8.17  | 400                               | 7.00   |
| Raw materials cost/ton product                      |               |                  | 35.16 |          | 44.57 |                                   | 41.37  |
| Raw materials cost/unit plant food                  |               |                  | 0.98  |          | 1.06  |                                   | 1.15   |
| Other costs/ton product                             |               |                  |       |          |       |                                   |        |
| Operating   |               |                  | 7.10  |          | 7.10  |                                   | 6.00   |
| Bags  |               |                  | 2.80  |          | 2.80  |                                   | 2.80   |
| Freight (100 miles)                                 |               |                  | 3.00  |          | 3.00  |                                   | 3.00   |
| Sales   |               |                  | 3.00  |          | 3.00  |                                   | 3.00   |
| Delivered cost/ton product.                         |               |                  | 51.06 |          | 60.47 |                                   | 56.17  |
| Delivered cost/unit plant food.                     |               |                  | 1.42  |          | 1.44  |                                   | 1.56   |

phosphate fertilizers made by the modified process should be attractive economically, when nitric acid is available at a reasonable price. Table IV shows the comparison of costs of 12-12-12 and 14-14-14 nitric phosphates and of a 12-12-12 conventional granular fertilizer. The prices of raw materials used in the estimates, except that for nitric acid, are believed to be typical of September 1957 delivered prices to a midwestern plant located about 75 miles from a producer of nitrogen materials. The delivered price for nitric acid was calculated to allow the producer the same return on investment as obtained when the nitric acid was converted to and sold as ammoniating solutions for fertilizer use. The costs of bags, freight, and sales were assumed to be the same for the nitric phosphates as for the conventional fertilizer. The plant operating cost was assumed to be somewhat greater for the production of nitric phosphates than for the production of conventional fertilizer, primarily because of the higher recycle rate required.

The data in Table IV show that the costs of raw materials per unit of plant food in the nitric phosphates are considerably lower than in the conventional fertilizer. The delivered costs per unit of plant food in the 12-12-12 and 14-14-14 nitric phosphates are from \$0.12 to \$0.14 lower than the delivered cost per unit of plant food in the 12-12-12 conventional product.

Other estimates indicated that the cost advantage for the nitric phosphates would not be so great for products in which the nitrogen to phosphate ratios are less than 1 to 1. For example, in comparison of a 9-18-18 nitric phosphate with a 9-18-18 conventional mixed fertilizer, it was calculated that the cost advantage for the former over the latter was \$0.07 per unit of plant food.

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## FERTILIZER TECHNOLOGY

# Ammoniation of Nitric Acid Extracts of Rock Phosphate

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The phosphorus in a nitric phosphate fertilizer usually is assumed to be present largely as dicalcium phosphate, but much of it often is present as an apatite. In a small-scale study of the neutralization step of a nitric phosphate process, fluorine had a marked adverse effect, promoting the precipitation of apatitelike phosphates instead of dicalcium phosphate—an effect prevented only by removal of 90% of the fluorine from the system by precipitation and filtration. The low fluorine filtrate was ammoniated rapidly without formation of significant amounts of apatite, and the slurry was dried to form a highly citrate-soluble nitric phosphate. The fluorine was recovered by heating the high fluorine precipitate with sulfuric acid. The phosphatic residues could be returned to the system.

NITRIC PHOSPHATE FERTILIZER has been made commercially in Europe for more than 20 years. Although the processes are described in a general way (4, 5, 13, 14), and patents cover many variations, details are lacking about the equipment, the operating procedure, and the chemistry of the processes, particularly the chemistry of the ammoniation step. Plusjè (12) studied the chemistry of the process, but restricted his work to fluorine-free systems. The phosphorus in the product usually is assumed to be present as dicalcium phosphate, but in many nitric phosphates whose phosphorus is nearly all citrate soluble, much of the phosphorus is present as apatite.

In slurry-type nitric phosphate processes (7, 10, 11, 16), nearly all the phosphorus is in solution at the end of the

extraction step, and the extract is neutralized with ammonia in a continuous operation comprising three or more stages. This paper relates to these slurry-type processes, and the results may not be directly applicable to the solids-type processes (6) in which more concentrated acids are used and the phosphorus is never all in solution at once.

The rate of ammoniation (amount of ammonia added to a given stage in a continuous slurry-type process) is critical in at least part of the neutralization step. Several factors apparently influence the citrate solubility of the phosphate in the final product. Although a satisfactory ammoniation procedure on a pilot plant scale was found through trial and error, a more rational basis is desirable for the design of large-scale ammoniation equipment.

#### Background

In most domestic rock phosphates the lime ratio (mole ratio CaO to P<sub>2</sub>O<sub>5</sub>) is 3.3 to 4.0. Dissolution of the phosphatic constituent in nitric acid is virtually congruent. The extract contains more calcium than is required to form dicalcium phosphate with all the phosphorus and is said to be unadjusted.

An unadjusted extract yields a nitric phosphate that contains calcium nitrate and is markedly hygroscopic. In some processes (7, 16), the composition of the extract is adjusted by addition of phosphoric acid or sulfuric acid in the extraction step in such proportion that no soluble calcium salts remain when the extract is ammoniated to neutrality.

The ammonia requirement for neutralization of an extract of known com-