SUPERPHOSPHATE MANUFACTURE

Partial Replacement of Sulfuric Acid with Nitric Acid

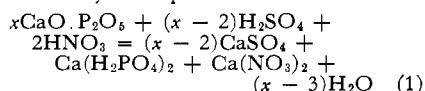DAVID McKNIGHT, J. F. ANDERSON, Jr., M. M. STRIPLIN, Jr., and T. P. HIGNETT

Tennessee Valley Authority, Wilson Dam, Ala.

The object of this work was to develop a process in which nitric acid would replace some of the sulfuric acid used in making superphosphate without substantial alteration of the manufacturing equipment. Expected advantages of the process were lower cost of fertilizer manufacture and saving of scarce sulfuric acid. Promising results were obtained in a pilot plant using either a batch, pan-type mixer or a continuous, funnel-type mixer discharging into a box den. When phosphate rock was acidulated with mixtures of nitric and sulfuric acid containing about 30% water, the product solidified, and after 10 to 30 minutes it was a solid resembling fresh superphosphate. About half the sulfuric acid required to make ordinary superphosphate was replaced with nitric acid. Two days' curing time was required to develop the maximal phosphorus pentoxide availability of about 98%. After curing, the product was ammoniated in a drum mixer with gaseous, anhydrous ammonia; a typical product, after ammoniation, contained about 6% nitrogen and 18% available phosphorus pentoxide. The results are considered to be technically and economically promising. Development on a pilot plant scale is being continued.
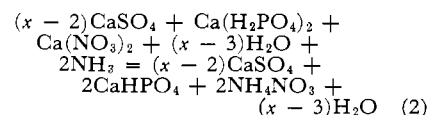
FORECASTS OF GREATLY INCREASED NEED for fertilizers coupled with depletion of our sulfur reserves have resulted in an active interest by the fertilizer industry in new processes that require less sulfuric acid. In the United States, the most promising of such processes are those in which nitric acid replaces some or all of the sulfuric acid that is used to acidulate phosphate rock. In processes developed commercially in Europe (2, 5, 6) and in several processes developed through the pilot plant stage by the Tennessee Valley Authority (3, 4, 7), a slurry is formed by the acidulation of phosphate rock with nitric acid or a mixture of nitric acid with sulfuric or phosphoric acid and the slurry is ammoniated, dried, and granulated.

While these processes produce homogeneous, granular fertilizers at favorable costs, they involve methods of operation which are radically different from usual fertilizer practice, and their commercial development requires the construction of new plants involving the use of scarce materials of construction. Therefore, an investigation was begun to determine whether a modified process could be carried out in the type of equipment commonly used for acidulation and ammoniation in the superphosphate industry. It was believed that, if phosphate rock were treated with a mixture of nitric and sulfuric acids in proportions to convert the phosphorus pentoxide in the rock to monocalcium phosphate rather than to phosphoric acid, the acidulate would set to a friable solid similar to superphosphate and suitable for solid-state ammoniation. The postulated acidulation reaction can be represented by the equation

$$x\mathrm{CaO \cdot P_2O_5} + (x-2)\mathrm{H_2SO_4} +$$
$$2\mathrm{HNO_3} = (x-2)\mathrm{CaSO_4} +$$
$$\mathrm{Ca(H_2PO_4)_2} + \mathrm{Ca(NO_3)_2} +$$
$$(x-3)\mathrm{H_2O} \quad (1)$$

where x = the $\mathrm{CaO:P_2O_5}$ mole ratio in the phosphate rock and the ammoniation reaction can be represented by the equation

$$(x-2)\mathrm{CaSO_4} + \mathrm{Ca(H_2PO_4)_2} +$$
$$\mathrm{Ca(NO_3)_2} + (x-3)\mathrm{H_2O} +$$
$$2\mathrm{NH_3} = (x-2)\mathrm{CaSO_4} +$$
$$2\mathrm{CaHPO_4} + 2\mathrm{NH_4NO_3} +$$
$$(x-3)\mathrm{H_2O} \quad (2)$$

The equations indicate that the process would require the same amount of sulfuric acid and half the amount of nitric acid required for the acidulation of phosphate rock by the slurry-type process (7), in which sufficient nitric and sulfuric acids were used to convert the phosphorus pentoxide of the rock into phosphoric acid. This amount of sulfuric acid is about 60% of that required for the production of an equivalent amount of available phosphorus pentoxide in ordinary superphosphate.
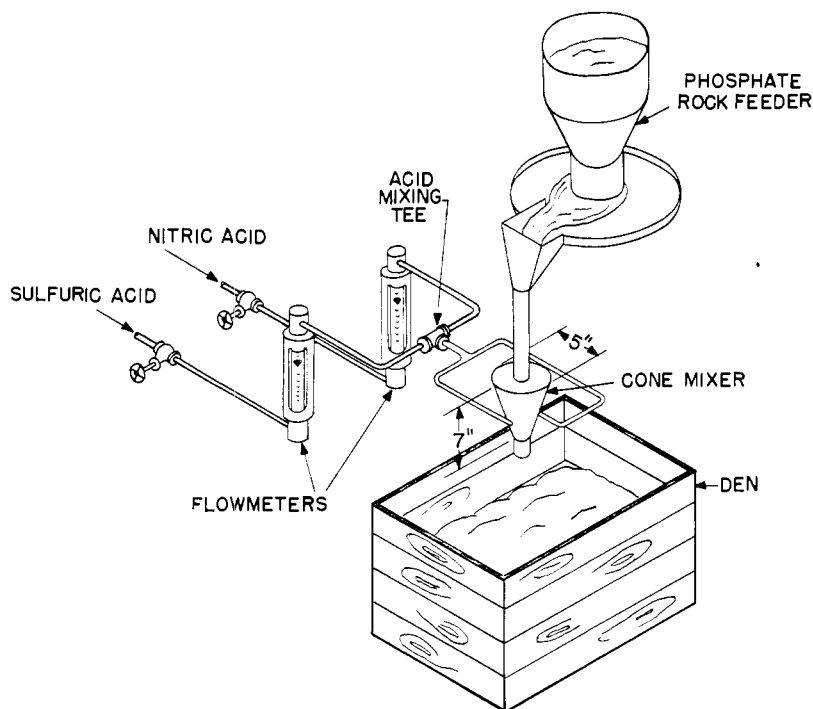
Figure 1. Pilot plant cone mixer

Exploratory tests in small scale equipment showed that friable acidulates, in which substantially all the phosphorus pentoxide was available, could be prepared from ground phosphate rock and a mixture of nitric and sulfuric acids in the proportions indicated by Equation 1. Just as in the acidulation of ordinary superphosphate, products of the best physical properties were prepared when the rock and acid were mixed quickly and allowed to remain quiescent for such a period as required for the acidulate to set into a friable solid. The exploratory tests also showed that friable solids produced by acidulation could be ammoniated without appreciable loss of phosphorus pentoxide availability.

The exploratory tests were so promising that a more complete study in small scale and pilot plant scale equipment was initiated. The present paper is a progress report on that study.

Equipment and Procedure

The apparatus used for small scale acidulation tests consisted of a stainless steel cylindrical mixing vessel 4 inches in diameter and 6 inches high with means for rapid, simultaneous delivery of measured amounts of rock and mixed acid, a paddle-type stirrer mounted on a shaft driven at 1000 r.p.m. for vigorous agitation of the mixture, and a hinged bottom closure for rapid dumping of the contents of the mixer.

Ammoniation of acidulates was tested in a horizontal cylinder 10 inches in diameter and 10 inches long that rotated

at 10 to 15 r.p.m. It had a tight-fitting cover and was supplied with a metered amount of gaseous ammonia through a $3/_8$-inch pipe inserted through a stuffing box in the center of the cover.

Two types of pilot plant scale equipment were used for acidulation tests. A 1-ton Stedman pan mixer was used in several tests, but most of the tests were made with a cone mixer (8) discharging into a wooden box. The pan mixer was provided with means for quick charging with a weighed quantity of rock and a measured quantity of mixed acid. It was mounted so that on the completion of mixing the pan charge could be dropped into a wood-lined den that held 1 ton of acidulate.

The cone mixer found to function best for mixing phosphate rock with nitric-sulfuric acid mixtures had a 75° angle between the cone walls and the horizontal; the mixer and accessories are shown in Figure 1. Ground phosphate rock was fed by means of a disk feeder that discharged through a spout above the center of the cone; mixed acid was fed through two tangential inlets located about midway in the height of the cone. Acid was premixed in a tank and metered through a rotameter to the line that fed the two acid inlets, or the two acids were metered separately and mixed continuously in a tee in the acid feed line; the latter method was used most of the time. The cone mixer was operated at a rate of about 1 ton of acidulate per hour. The acidulates discharged into boxes, each of which held about 500 pounds, where they were al-

lowed to remain until they had set sufficiently to be handled; in most cases 30 minutes was sufficient for this purpose. After removal from the boxes the acidulates were stored in piles for from 2 days to 1 week. They were reduced to a particle size suitable for ammoniation by being passed through a 4-mesh screen; the few lumps on the screen were broken up with a shovel. In plant operation this could be accomplished by the usual procedure for preparing normal superphosphate for ammoniation.

Acidulate prepared in pilot plant scale equipment was ammoniated batchwise in a mild steel drum mixer (Figure 2) 5 feet in diameter by 5 feet long, that rotated at 13.5 r.p.m. It had 21 short flights 10 inches deep, and the flights were inclined so as to direct the material toward the discharge end during rotation. A 1.25-inch pipe, located in the lower part of the drum about 2 inches above the top of the flights, was used for introduction of gaseous, anhydrous ammonia, which was metered through an orifice meter. Several types of perforations were tried in the ammonia inlet, but the best results were obtained with a pipe that was open only at the end and extended to near the discharge end of the drum. A feed chute extended through the cover at one end of the drum. The cover at the other end of the drum was movable inward to permit the introduction of a discharge chute. The ammoniator normally was charged with about 1 ton of acidulate.

After ammoniation was completed, the product was stored in piles for curing before being bagged. After curing, it was necessary to pass the product again through a 4-mesh screen and to break up a few soft lumps that formed during curing.

All products were analyzed by official methods of the Association of Official Agricultural Chemists (7).

Acidulation Tests

In preliminary small scale tests in which finely ground phosphate rock was
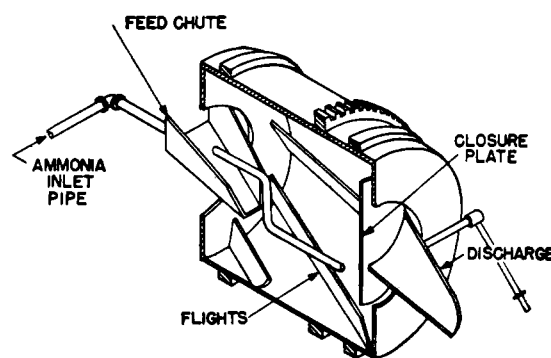
Figure 2. Drum ammoniator

Table I. Effect of Water Content of Mixed Acid on Loss of Nitrogen in Pilot Plant Acidulation Tests

Mixed Acid Used[a]		Chemical Analysis of Acidulate,[b] %				
Lb./100 lb. rock	H₂O in mixed acid, %	N	P₂O₅	Available P₂P₅	Free H₂O[c]	Nitrogen loss, %
122	41	3.3	17.2	17.1	11.2	1
108	34	3.4	17.4	17.1	7.0	2
100	28	3.5	17.3	17.1	9.2	2
98	27	3.3	18.1	18.0	5.0	7

[a] Acid proportions in all tests were stoichiometric in accordance with Equation 1. Florida phosphate rock used contained 34.8% P_2O_5, 50.6% CaO, and about 40% −200-mesh particles.
[b] Acidulates analyzed 4 to 7 days after mixing.
[c] Determined by vacuum desiccation method (1).

acidulated with mixed nitric and sulfuric acids, high losses of nitrogen occurred, and several means for reducing the losses were investigated. Cooling of the reaction mixture so that the temperature did not exceed 150° F. during acidulation reduced nitrogen losses appreciably, but the acidulates were not so friable as those prepared without cooling. As cooling did not appear to be readily applicable to large scale operation, this method was not investigated further.

Loss of nitrogen was high when the temperature of the mixed acid, as measured in the stream beyond the mixing tee, was above 130° F. In two tests with mixed acid at 118° F., the nitrogen loss was 5%. In four tests with the mixed acid at 142° F., the nitrogen loss was 20%. In these tests the mixed acid contained 31% water and the rock was of such size that about 40% passed a 200-mesh screen.

Tests also indicated that the proportion of water in the mixed acid had a significant effect on the loss of nitrogen during acidulation. A series of pilot plant tests, the results of which are shown in Table I, indicated that when the mixed acid contained 28 to 41% water not more than 2% nitrogen was lost. In one test with acid containing 27% water the loss of nitrogen was 7%. In several small scale tests with mixed acid containing 26 and 23% water, loss of nitrogen was considerably higher than when the acid contained 28% water or more. In most subsequent pilot plant tests, using phosphate rock of 40% −200-mesh size, nitrogen losses were less than 5% when the mixed acid contained at least 29% water and was used at a temperature below 120° F. A mixed acid of suitable concentration was obtained by mixing 92% sulfuric acid and 53% nitric acid in proportions corresponding to Equation 1.

The results of small scale tests to determine the effects of degree of acidulation and of duration of curing the acidulate on phosphorus pentoxide availability are plotted in Figure 3. The curves show that maximum phosphorus pentoxide availability was obtained in 48 hours and that stoichiometric acidulation was required for substantially complete availability. The latter conclusion was confirmed in pilot plant tests. In one test in which 80% of the stoichiometric acidulation was used, the maximum phosphorus pentoxide availability in the product was 88.5%; in three tests with 90% of the stoichiometric acidulation the availability averaged 90.7%; and in 14 tests with stoichiometric acidulation the availability averaged 98.8%.

Several tests were made to study the use of a pan mixer for the acidulation operation, this being the most common type of acidulation equipment in existing fertilizer plants. Data from these tests are given in Table II. In each test a charge of 900 pounds of phosphate rock and the measured amount of mixed acid was dumped into the rotating pan. Approximately stoichiometric proportions of nitric and sulfuric acids were used. The flow of rock was started first and the flow of acid was started when about half of the rock had been added. The combined charge was mixed and then dumped into the den below.

With raw Florida phosphate rock, satisfactory mixing was obtained in 1 minute, but the calcined rock required 1.75 minutes for adequate mixing. Acidulates from both types of rock set up into friable solids within 30 minutes after mixing. The acidulates were more porous and friable than fresh ordinary superphosphate; the acidulate obtained with calcined rock was softer and more granular than that from raw rock. When the raw rock was acidulated, brown fumes were evolved from the time the materials were charged to the pan until after the acidulate had been cut from the den. When the calcined rock was acidulated, there was very little fuming until several minutes after the charge had been dumped into the den. At that time a copious evolution of brown fumes began and continued for a brief period, after which there was very little fuming. Tests of the atmosphere above the acidulate stored in a closed bin indicated evolution of nitrogen oxides in quantity sufficient to constitute a hazard

to personnel working in an enclosed area for several days after preparation, but the amount evolved was not sufficient to be detected by analyses of the material before and after storage.

Availability of phosphorus pentoxide was satisfactory in all the acidulates, which were cured for periods varying from 6 days to 3 weeks before being ammoniated.

It was concluded that products of good physical properties can be made in the conventional pan mixer and mechanical den without excessive losses of nitrogen. It would be necessary to provide an acid-resistant lining to a pan mixer and to equip a plant for effective fume removal in the area occupied by the den cutter and storage pile.

Ammoniation Tests

Results of ammoniation tests in the pilot plant drum ammoniator with gaseous anhydrous ammonia are given in Table III. The end of the pipe through which the ammonia was discharged was in the deepest part of the bed of acidulate, as best absorption was obtained in this way. The data from the first three tests show that the products readily absorbed an amount of ammonia equivalent to their nitrate content, as indicated by Equation 2. When the product was ammoniated very slowly, there was no appreciable reversion of available phosphorus pentoxide (test 1). More rapid ammoniation resulted in decreasing phosphorus pentoxide availability from 99 to 93% in the fully ammoniated products (tests 2 and 3). In the last three tests only 88% of the stoichiometric amount of ammonia was added, and ammoniation at the highest rate decreased the phosphorus pentoxide availability only to 97% (test 6). No reversion of phosphorus pentoxide to citrate-insoluble forms was noted in any ammoniated products in storage. Recovery of ammonia was satisfactory in all these tests.

The maximum rate of ammoniation in the pilot plant was limited to about 18 pounds of ammonia per minute by the facilities for supplying ammonia, but higher rates of ammoniation may be possible. In the ammoniation of ordinary superphosphate, rates of 40 pounds of ammonia per minute per ton of acidulate are attained.

Some agglomeration of fines occurred during ammoniation, so that the ammoniated product consisted of rounded particles of good particle size range (90% −4 +50 mesh) for fertilizer use. The addition of potassium chloride before ammoniation resulted in a product of homogeneous appearance. Chemical and screen analyses of several products of different potash contents are given in Table IV.

The "free moisture" contents of the

Table II. Acidulation Tests in 1-Ton Pan Mixer

Type of Phosphate Rock	Mixed Acid Used Lb./100 lb. rock	Composition, % H₂SO₄	HNO₃	H₂O	Temp., °F. Mixed acid	Den[a]	Chemical Analysis of Acidulate[b], % Total P₂O₅	Available P₂O₅	N	Free H₂O[c]	Nitrogen Loss, % of N Charged
Raw[d]	101.6	43	29	28	73	202	17.0	16.9	2.9	13.3	8
Raw[d]	101.6	43	29	28	82	232	18.5	18.4	3.2	15.0	7
Raw[d]	101.6	41	29	30	88	242	17.8	17.7	3.2	12.7	4
Calcined	98.0	40	30	30	85	254	17.5	17.4	3.3	9.7	2
Calcined[e]	98.0	45	24	31	85	258	17.4	17.0	3.3	9.7	2

[a] Maximum.
[b] Acidulates analyzed about 1 week after preparation.
[c] Determined by vacuum desiccation method (7).
[d] Raw Florida phosphate rock containing 35.1% P₂O₅ and 50.4% CaO (5.5% ignition loss). Size. 35% +100-mesh, 39% −230-mesh.
[e] Calcined Florida phosphate rock containing 33.6% P₂O₅ and 48.8% CaO (1.0% ignition loss). Size. 22% +100-mesh, 46% −230-mesh.

Table III. Ammoniation Tests in 1-Ton Drum Ammoniator

Test No.	Chemical Analysis of Acidulate[a], % P₂O₅ Total	Avail-ability	N	Free H₂O[d]	Acidu-late Charged, Lb.	Ammonia Rate[b] Lb./hr.	Time, min./ton	Lb./(min.) (ton of acidulate)	Chemical Analysis of Product[c], % P₂O₅ Total	Avail-ability	Total N[e]	Am-monia N[f]	Free H₂O[d]	Ratio Ammonia N / Nitrate N	NH₃ Loss, %
1	18.1	99	3.3	10.4	2000	160	30.0	2.7	18.8	97	6.5	3.4	9.2	1.10	0
2	18.0	99	2.9	9.5	1691	255	17.8	5.9	18.1	93	6.3	3.1	9.8	0.97	2
3	18.0	99	3.3	10.3	1588	660	7.6	12.8	18.0	93	6.8	3.4	10.2	1.0	3
4	17.0	99	2.9	13.3	1401[g]	470	9.0	9.8	16.0	99	6.2	2.9	7.7	0.88	0
5	18.5	99	3.2	15.0	1495	470	7.7	10.4	18.1	99	6.2	2.9	7.9	0.88	0
6	19.6	99	3.1	7.8	2000	1100	3.6	18.3	18.8	97	5.8	2.7	8.6	0.87	0

[a] Acidulates analyzed about 3 days after preparation.
[b] In first three tests amount of ammonia added was essentially equivalent to nitrate content of acidulate; in last three tests equivalent to about 88% of nitrate content.
[c] Products analyzed 3 to 7 days after ammoniation.
[d] Determined by vacuum desiccation method (7).
[e] Total nitrate and ammonia nitrogen determined by Devarda method (7).
[f] Ammonia nitrogen determined by magnesium oxide method (7).
[g] 200 pounds of KCl added with acidulate; analyses showed 7.4% K₂O in product.

Table IV. Chemical and Screen Analyses of Typical Products

Total N[b]	Ammonia N[c]	Chemical Analysis[a], % P₂O₅ Total	Available	Water-soluble	K₂O	Free H₂O[d]	Screen Analysis, % of Size Fraction Indicated (U. S. Series No.) −4 +6	−6 +12	−12 +50	−50
6.2	2.9	18.1	17.9	7.4	0	7.9	8.6	24.2	56.5	10.7
6.2	2.9	16.0	15.8	5.3	7.4	7.7	4.2	26.7	66.6	2.5
5.0	2.6	15.3	14.5	5.6	10.7	9.4	4.1	19.8	61.0	15.1

[a] Products analyzed 3 days or 3 weeks after ammoniation gave essentially same results.
[b] Total nitrate and ammonia nitrogen determined by Devarda method (7).
[c] Ammonia nitrogen determined by magnesium oxide method (7).
[d] Determined by vacuum desiccation method (7).

Table V. Effect of Variation in Acid Proportions on Analysis of Products
(100% acidulation)

Mixed Acid Used Grams/100 grams rock	Composition, % H₂SO₄	HNO₃	H₂O	H₂SO₄ Used, % of Stoichiometric	Chemical Analysis of Acidulate[a], % Total P₂O₅	Available P₂O₅	Total N[c]	Free H₂O	Chemical Analysis of Ammoniated Product[b], % Total P₂O₅	Available P₂O₅	Total N[c]	Ammonia N[d]	Free H₂O
98	40	31	29	100	18.9	18.7	3.1	6.8	19.3	18.1	6.2	3.0	7.9
100	33	38	29	85	18.3	18.0	3.8	6.7	18.5	17.2	7.1	3.3	9.7
102	29	42	29	75	17.7	17.1	4.4	4.9	18.9	17.2	8.4	3.9	5.7
103	24	47	29	65	18.4	18.0	4.9	5.0	18.3	17.6	8.6	3.8	9.2
105	20	51	29	55	18.6	18.2	5.4	4.7	17.9	17.2	9.4	4.1	9.2

[a] Acidulates analyzed after curing 3 weeks.
[b] Ammoniated products analyzed after curing 3 days; hygroscopicity tests made on products cured about 30 days.
[c] Total nitrate and ammonia nitrogen determined by Devarda method (7).
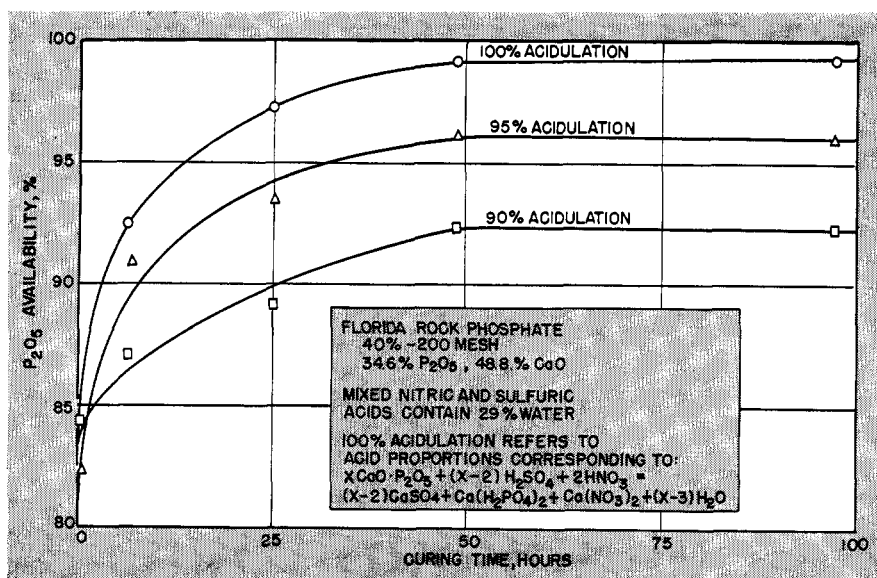[d] Ammonia nitrogen determined by magnesium oxide method (7).

Figure 3. Effects of acidulation and curing time on phosphorus pentoxide availability. Small scale tests

products, as determined by the A.O.A.C. vacuum desiccation method which includes some water of hydration, varied erratically, probably because of the variations in the hydration reactions that occurred with different curing times and conditions. The total moisture contents of the products were calculated from the weights of materials charged and from the phosphorus pentoxide contents of the products. In the three tests in which raw phosphate rock was acidulated in the pan mixer (Table II), it was calculated that 8% of the water in the mixed acid was evaporated during acidulation and that the moisture contents of the acidulates averaged 15% as compared with 13.7% free moisture by the vacuum desiccation method. These acidulates were ammoniated after curing for 1 week in piles, and the ammoniated products were cured in piles for 3 days before being sampled. From the analyses, it was calculated that 21% of the water content of the mixed acid was evaporated in ammoniation and that the ammoniated products contained 10% moisture as compared with 7.9% free moisture by the vacuum desiccation method. When the products were allowed to cure in piles for 3 weeks, the calculated moisture content was 9.3% as compared with 7.1% free moisture by the vacuum desiccation method. The products in this condition were bagged in six-ply paper bags having two asphalt-laminated plies and were found to be free-flowing after 3 months in storage. Studies of physical properties as affected by curing time and moisture content are continuing.

Variation in Proportions of Acid

Variations in proportions of the two acids, particularly increase in nitric acid with corresponding decrease in sulfuric acid, are of interest because through such variations the sulfuric acid requirement can be reduced and the amount of nitrogen in the product can be increased. As the proportion of nitric acid is increased, and that of the sulfuric acid is decreased in the proportion of 2 moles of nitric acid to 1 mole of sulfuric acid, there occurs an increase in the amount of calcium nitrate in the acidulate, and any calcium in excess of that forming calcium sulfate, calcium fluoride, or dicalcium phosphate remains as calcium nitrate in the ammoniated product. The limitation on this variation probably would be the extent to which the proportion of calcium nitrate can be increased without imparting excessive hygroscopicity to the ammoniated product.

To investigate this limitation, a series of small scale tests was made in which phosphate rock was acidulated with mixed acids, in which the proportions of nitric and sulfuric acids were varied, and the acidulates were ammoniated. The analyses of the acidulates and of the ammoniated products are given in Table V. Tests indicated that the products made with 100, 85, and 75% of the stoichiometric proportion of sulfuric acid, as indicated by Equation 1, had satisfactory physical properties, but those made with less than 75% of the stoichiometric proportion of sulfuric acid were excessively hygroscopic. Although pilot plant production and bag-storage tests of the products will be needed for confirmation, it appears that a product having good physical properties can be made with nitric acid and 75% of the stoichiometric proportion of sulfuric acid, which corresponds to only about 45% of the sulfuric acid required for ordinary superphosphate. The product would have a

nitrogen–phosphorus pentoxide ratio of about 1 to 2.

Conclusions

The investigation has shown that superphosphate can be made by a process using mixed nitric and phosphoric acids in equipment of the type used in the present commercial process. However, the equipment must be made resistant to the corrosive action of nitric acid. Because of the evolution of oxides of nitrogen, which are toxic and can be fatal if inhaled, the system for removing fumes from the mixer, den, and storage pile should be more effective than the type provided in most fertilizer plants. The plant probably would have to include facilities for producing nitric acid, because few plants are so located that purchased nitric acid can be delivered at a reasonable cost.

Production costs have been estimated, for the production of 50,000 tons per year of 5–15–10 fertilizer, using ammonia purchased at the market price ($80 per ton) and nitric acid produced at the fertilizer plant. It was assumed that acidulation and ammoniation would be carried out in equipment like that used for making and ammoniating superphosphate, except for changes mentioned. Under these conditions the estimated cost per ton of plant food was about 15% lower than that of commercial mixed fertilizer of 5–15–10 grade.

The process appears technically and economically promising, and the products appear to have good physical and agronomic properties. The experimental study will be continued to obtain more complete data, particularly as to suitable equipment and operating procedures.

Literature Cited

(1) Assoc. Offic. Agr. Chem., "Official Methods of Analysis," 7th ed., Chap. 2, 1950.
(2) Chaudron, *Proc. 11th Intern. Congr. Pure Applied Chem., London, 1947*, **3**, 45–9 (1951).
(3) Hignett, T. P., *Chem. Eng.*, **58**, No. 5 166–9 (1951).
(4) Houston, E. C., Hignett, T. P., and Dunn, R. E., *Ind. Eng. Chem.*, **43**, 2413–18 (1951).
(5) Plusje, M. H. R. J., *Chem. Eng.*, **58**, No. 5, 169 (1951).
(6) Quanquin, M., *Ind. Chem.*, **34**, 165–7 (1947).
(7) Striplin, M. M., Jr., McKnight, David, and Hignett, T. P., *Ind. Eng. Chem.*, **44**, 236–42 (1952).
(8) Yates, L. D., and Williams, W. B., *Farm Chemicals*, **115** No. 9, 29 (1952).