

Pilot Plant Studies of a Nitric Phosphate Process

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Pilot plant studies on the production of a wide range of nitric phosphates, using a rotary ammoniator-granulator, are discussed. An important feature of the process is that the ratio of water-soluble to citrate-soluble P_2O_5 can be varied—water-soluble P_2O_5 being produced either as monocalcium phosphate or as monoammonium phosphate, depending on the formulation. The process was considered to be very flexible, and as a result of these studies, a commercial plant was constructed.

MOST NITRIC PHOSPHATE PROCESSES in use at present are of the slurry type—i.e., ammoniation is carried out in stirred reactors in the slurry phase. To ensure complete absorption of the ammonia, the slurry must be kept sufficiently fluid, which means that evaporation must be kept to a minimum by cooling. Moreover, ammoniation has to be carried out in very carefully regulated steps to prevent sudden changes in the viscosity of the slurry, and the danger of local over-ammoniation, as a result of unequal distribution of ammonia, causing reversion of P_2O_5 into insoluble compounds, is great unless the reactors are well stirred. In some cases, certain additives are required (7).

As a result, the ammoniated slurry, having a relatively high water content, must be granulated using a high recycle ratio. This is usually carried out in a series of highly powered blungers or pug mills.

The authors believed that most of the disadvantages of these processes did not occur when using a rotary ammoniator-granulator as described in various TVA reports and studies (4, 5).

In the course of many experiments carried out in the Central Laboratory with this type of equipment, its versatility and flexibility had been proved on many raw materials and products, all based on the reaction of ammonia with single acids or acid mixtures.

It was therefore decided to construct a complete pilot plant, with a view of studying the entire process of production of granular fertilizers based on phosphate rock, nitric acid, phosphoric acid and/or sulfuric acid, a potassium salt, and ammonia.

Description and Operation of the Pilot Plant

Figure 1 is a flow sheet showing how the process was carried out in the pilot plant. The pilot plant consisted of

an extraction unit, an ammoniator-granulator, a rotary dryer, a rotary cooler, a double-deck vibrating screen, a roll-crusher, two identical elevators, a belt conveyor, and two table feeders.

Extraction Unit. Extraction of phosphate rock with acid was carried out in three stainless steel tanks, 63.5 cm. in diameter and 90 cm. high. To remove any possible fumes, the tops of the tanks were covered and connected through a plastic duct to a plastic fan and stack. The tanks were equipped with air-powered agitators of the propeller type, with continuously variable speed from 0 to 500 r.p.m. Foam breakers were mounted on the agitator shafts. Extraction was carried out batchwise. Nitric acid was fed from a stainless steel measuring tank into the first extraction tank. The weighed amount of phosphate rock was added and then the required amount of phosphoric acid from a plastic measuring tank. Phosphoric acid was added afterward as this reduced foaming.

After about 10 minutes, the required amount of sulfuric acid was added from another plastic measuring tank. This time lag of about 10 minutes prevented the formation and agglomeration of large gypsum crystals. At a later stage, however, sulfuric acid was fed into the ammoniator. Within half an hour, the extraction was completed.

Only two reaction tanks were required to provide for sufficient reaction time. From these, the slurry was pumped alternatively into a third tank and from this tank to the ammoniator. Pumping of all acids and of the extraction slurry was effected by a tube pump with a suitable, highly accurate, variable speed drive (Croft's variable speed unit; 0 to 1420 r.p.m.).

Ammoniator-Granulator. The ammoniating drum (90 cm. in diameter, length 90 cm., slope 4.5%) was equipped with a 1.5-hp. motor and P.I.V. unit (rotation rate, 0 to 30 r.p.m.; average, 17 r.p.m.).

Recycle and dry raw materials were fed into this ammoniator by one of the elevators. The extraction slurry was distributed on the surface of the bed of material from a stainless steel slotted pipe (30-cm. length, 2-mm. slot), alongside of which a perforated pipe was welded, through which auxiliary air was blown at 6 atm. to produce a fine spray.

Ammonia gas was measured by a rotameter and fed under the rolling bed, under reduced pressure of 0.5 atm., through a slotted stainless steel pipe of 30-cm. length, the slot pointing upstream. Steam could be introduced through this ammonia distributor, so as to be able to regulate the temperature of the bed and the granulation of the material. The distributor was placed in the first half of the drum, about 10 cm. from the inlet side. Sulfuric acid was also distributed in the first half of the ammoniator by a perforated stainless steel pipe (1-mm. holes over 30 cm. of length). First, the sulfuric acid was added under the bed; later, it was sprayed on top of the bed. It was measured by a rotameter and pumped with the previously mentioned tube pump. Cooling air could be blown on the bed through a perforated pipe.

The ammoniator was provided with a hood at the inlet side to remove exhaust gases. Gases were removed through a mild steel duct by a blower having a capacity of 550 cubic meters per hour. Gas samples for determining ammonia losses were taken from this duct. Retention time in the ammoniator was approximately 9 minutes, which proved sufficient for the different reactions to reach completion.

Rotary Dryer. This unit was 63 cm. in diameter and 3 meters long, and was equipped with directional flights over about 80 cm. at the inlet side and with 24 lifting flights (Figure 2) over the next 2 meters. To enlarge the holdup, a cone-shaped ring was attached to the inlet side and a 13-cm. retaining ring

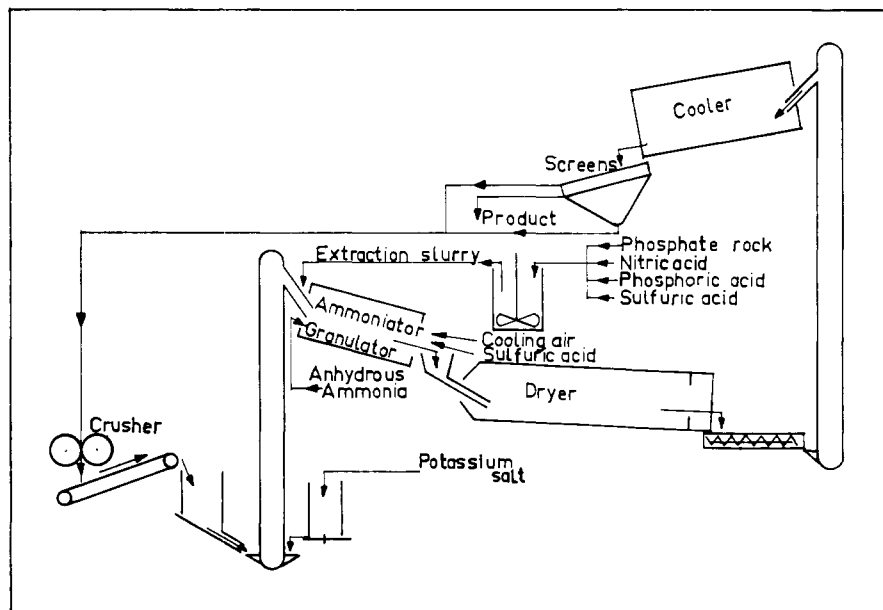


Figure 1. Flow sheet

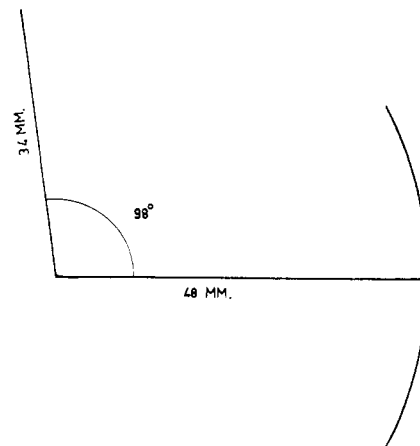


Figure 2. Lifting flight

placed 20 cm. before the outlet side. The flow of the gases and solids was concurrent, and the retention time under normal conditions about 15 minutes. Heat for drying was supplied by the combustion of a propane-butane mixture in a brick-lined chamber, adjacent to the dryer. Inlet temperature of the dryer gases varied between 150° and 200° C. in the different experiments, outlet temperature between 70° and 100° C. For the exhaust gases, a 1000-cubic meter per hour blower was used. The speed of the dryer was variable, usually 17 r.p.m. The slope of the dryer was 0.5%.

Rotary Cooler. This cylindrical unit was 65 cm. in diameter and 3 meters long. Air flow was also concurrent with the flow of solids. The unit was equipped over its entire length with 24 lifting flights of the same type as those of the dryer. The slope was 2.5%, and the rotation rate was usually 40 r.p.m. The exhaust fan also had a capacity of 1000 cubic meters per hour.

Double-Deck Vibrating Screen. The cooled material passed over a double-deck vibrating screen of 45 × 68 cm. For the undersize, a screen of 2 × 2 mm. was used; for the oversize, a 3 × 3 mm. or a 4 × 4 mm. screen was used. Oversize and undersize both went to the roll-crusher, while part of the onsize product also could be fed to the crusher. Because of lack of space, the undersize material had to pass through the crusher too.

Roll-Crusher. This unit consisted of two rolls of 35-cm. diameter and 50-cm. length, at equal speed. The identical speed of the rolls gave a rather poor result as much of the coarse material came out as flakes, which had to be screened out once more and separately crushed when cool.

Conveying of Solids. The material

passed by gravity through an air-cooled chute from the ammoniator into the dryer. From the dryer, it was transported via a small screw-conveyor and a 4-meter elevator into the cooler. From the cooler, the material went by gravity over the screens and through the roll-crusher, then by means of a belt conveyor into a table feeder. The latter apparatus smoothed out the circulation stream. From this table feeder, material passed by gravity into the second elevator, into which was also fed the required amount of pre-crushed potassium salts, sometimes pre-mixed with magnesium salts. This second elevator discharged into the ammoniator.

Raw Materials

The materials generally were normal products, as used in our commercial plants. Typical chemical analyses are given in Table I. Some chemical and screen analyses of the phosphate rock (usually mixtures of different types) are given in Table II.

Chemical and Physical Considerations

Chemically, the desired product was assumed to consist of a mixture of ammonium nitrate, monocalcium phosphate monohydrate or monoammonium phosphate, anhydrous dicalcium phosphate, calcium sulfate dihydrate, and potassium chloride or potassium sulfate (7). The required amounts of raw materials were calculated on this basis. Whether water-soluble P_2O_5 in the product was present as monocalcium phosphate monohydrate or as monoammonium phosphate depended on this calculation. For this purpose, the mole ratio CaO/P_2O_5 in the phosphate rock used in the experimental run had

Table I. Raw Materials

Sulfuric acid	76% H_2SO_4
Nitric acid	52.5% HNO_3
Phosphoric acid	53-54% P_2O_5 (wet-process)
KCl	59-60% K_2O
K_2SO_4	48-49% K_2O

Table II. Chemical and Screen Analyses of Phosphate Rock

(Values given as percentages)

	Phosphate Mixture		
	Kola	Morocco	Florida
	25	25	35
	25	25	..
	50	50	65
CHEMICAL ANALYSIS			
P_2O_5	35.55	35.5	36.25
CaO	50.8	50.75	50.75
CO_2	1.7	1.5	1.48
Fe_2O_3	0.5	0.44	..
Al_2O_3	1.0	0.99	..
SiO_2	1.95
F	3.4
H_2O	0.6
SCREEN ANALYSIS			
<50 μ	63.3	57.1	57.5
50-75 μ	16.5	19.2	22.4
75-105 μ	12.3	15.6	12.1
105-150 μ	6.1	6.8	6.1
150-210 μ	0.7	1.2	11.2
>210 μ	0.1	0.1	0.25

to be adjusted to the mole ratio in the desired mixture of water-soluble and citrate-soluble P_2O_5 in the end product by the addition of either sulfuric acid or phosphoric acid or mixtures thereof. The amount of nitric acid, usually to the extent of 50% of the total N content of the product, in most cases was more than sufficient to dissolve the phosphate rock. In accordance with literature (8), it was found that, taking into account the amount of

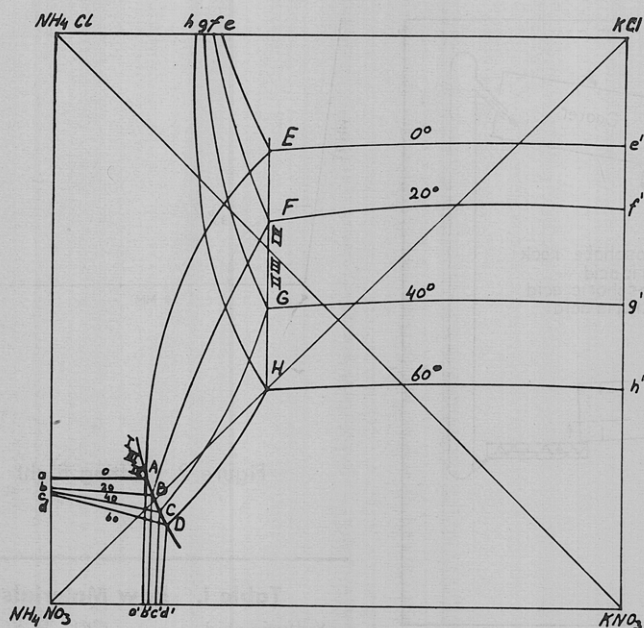


Figure 3. System $\text{NH}_4^+ - \text{K}^+ - \text{NO}_3^- - \text{Cl}^-$

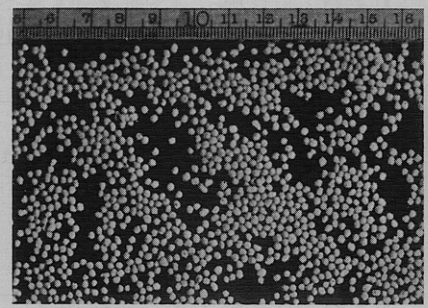


Figure 4. Product

H_2SO_4 or H_3PO_4 used in the formula, a mole ratio of HNO_3/CaO of 1.9 was desired to reach a sufficient degree of extraction of the P_2O_5 within the required time.

Double decomposition takes place between a number of salts, such as $\text{NH}_4\text{NO}_3 - \text{KCl}$ and $\text{K}_2\text{SO}_4 - \text{Ca}$ phosphates. This influences the mechanism of the process and has its effect on the final product. In fact, these reactions are highly desirable as they tend to stabilize the product. Any reactions taking place during storage, either on the heap or in the bags, may cause unpleasant consequences, such as evolution of heat, decomposition of nitrates, and caking (5-7).

However, since these reactions in no way influenced the required amounts of raw materials, they were not considered for the calculation as a rule. Neither was the presence of fluorine in the phosphate rock taken into account. During nitric acidulation, fluorine is evolved only to a very limited amount (8) with the result that any acidulation based on total CaO content necessarily means slight overacidulation. The net result, however, means only that slightly more water-soluble P_2O_5 will be present in the final product than was calculated, which served as a safety margin against any possible reversion. As the latter never has been encountered, it would be perfectly safe to subtract a certain percentage of CaO from the total amount for the calculation in the future.

The mole ratio $\text{KCl}/\text{NH}_4\text{NO}_3$ plays an important part in this process insofar as it influences the amount of liquid phase in the ammoniator-granulator and, in doing so, has its bearing on the recycle ratio and hence on the ca-

capacity of the plant. A study of Jänecke's work (6) shows that in the system $\text{NH}_4^+ - \text{K}^+ - \text{NO}_3^- - \text{Cl}^-$ at a mole ratio $\text{KCl}/\text{NH}_4\text{NO}_3 < 1$, a saturated solution results (point D, Figure 3), having about twice the weight (and, specific gravity being in the same order, having about twice the volume) as saturated solutions resulting from mixtures in which the mole ratio is > 1 (point H, Figure 3) (at the same temperature and moisture content). This can clearly be understood from the data in Table III, calculated for points D and H in Figure 3 at 60°C . (6).

In some formulations, K_2SO_4 had to be used instead of KCl for agricultural reasons. This too had a marked effect on the final composition of the product. The SO_4 ions contained in the sulfate, as might be expected, react with Ca ions in the nitric acid solution under the formation of calcium sulfate (8), thus having a positive influence on the amount of water-soluble P_2O_5 . In fact, the use of K_2SO_4 offers the possibility of a substantial saving in sulfuric acid consumption.

Description of Process

The process basically consists of recycling a certain amount of undersize product through the plant, injecting raw materials into this circuit in the ammoniator-granulator, and removing an amount of onsize product, equivalent to the raw materials feed, from the circuit after the screens.

The required amount of recycle is dependent on the amount of water introduced into the system with the raw materials and the recycle, and, as has been explained previously, on the amount of liquid phase to be ex-

pected from the composition of the product. As an average, approximately 18% of liquid phase in the ammoniator-granulator produced a well-granulating rolling bed in this part of the plant, which could be satisfactorily handled in the following phases of the process (drying, screening, crushing). With some formulations, mainly those having a very high N content, the amount of liquid phase could be controlled to a certain extent by introducing part of the N in the form of either solid NH_4NO_3 or a hot concentrated solution. Table IV gives an example of the influence of this technique.

In experiment I, the amount of water to be evaporated was decreased to 25 kg. per 100 kg. of product by introducing part of the ammonium nitrate in the solid form. This resulted in a recycle ratio of 1:10.5.

In experiment II, so much ammonium nitrate was added as a 90% solution that the amount of nitric acid required to complete the formulation was just sufficient to dissolve the phosphate rock. In this way, only 21.1 kg. of water had to be evaporated per 100 kg. of product, which resulted in a recycle ratio of 1:7.8.

In the last experiment, all nitrogen was supplied as nitric acid and ammonia. Thirty-nine kilograms of water had to be evaporated per 100 kg. of product; a recycle ratio of 1:20.9 was the result.

The following materials were introduced into the ammoniator-granulator.

Recycle. This consisted of the fines plus the oversize after crushing. Usually part of the onsize product had to be crushed and recycled too, since the amount of onsize material generally far exceeded the amount of raw materials feed. As an example, 70 to 80% of

Table III. Composition of Liquid Phase in the System $\text{NH}_4^+ - \text{K}^+ - \text{NO}_3^- - \text{Cl}^-$

Point	Moles, %				H_2O , Moles per 100 Moles Salts	Composition of Solution in Grams					Composition of Solution		Kg. of Liquid Phase per 1 Kg. of Water
	K	NH_4	Cl	NO_3		K	NH_4	Cl	NO_3	H_2O	% Salts	% Water	
D	20	80	14.5	85.5	80	780	1440	515	5301	1444	84.7	15.3	6.53
H	37	63	37	63	190	1443	1134	1314	3906	3420	69.4	30.6	3.86

Table IV. Formulation for 18-12-6 + 4MgO Grade

Raw Materials, Kg.	Expt. I	Expt. II	Expt. III
Phosphate rock, 35.5% P_2O_5	14.8	14.8	14.8
Phosphoric acid, 53% P_2O_5	12.7	12.7	12.7
Nitric acid, 52.5% HNO_3	47.7	32.5	77.2
Ammonium nitrate	19.8	33.4	..
Muriate of potash, 60% K_2O	10.0	10.0	10.0
Kieserite, 28% MgO	14.3	14.3	14.3
Ammonia gas	6.75	4.6	10.9
Water, kg., to be evaporated per 100 kg. of product	25	21.1	39
Recycle ratio	1:10.5	1:7.8	1:20.9

onsize product in the material stream, at a recycle ratio of 1:8 to 1:10, was normal. Since from this stream only 12.5 to 10% had to be removed as product (equivalent to the raw materials input), 60 to 70% of onsize material was recycled after crushing; consequently, it is possible to screen out a product within a very narrow size range (Figure 4).

Crushing was done by a roller crusher. Unfortunately, because of bad cooling of the material, this crusher gave a poor performance. As many of the larger granules were still rather warm and consequently plastic, they tended to form flakes which disturbed the rolling bed. This was finally overcome by screening out these flakes and recrushing them after proper cooling.

It was found that very much depends on the crushing equipment. Any dry material, whether it be recycle, potash, or other, must be ground well below product size. Any particles equal to or larger than product size entering the ammoniator-granulator will have to be crushed and recycled. Furthermore, the specific surface area has a distinct influence on ammonia absorption and physical condition of the rolling bed.

Feeding into the ammoniator-granulator was effected by a table feeder via an elevator into which the potash and any other dry materials were fed too.

Extraction Slurry. This slurry was produced batchwise. This form of operation was preferred above a continuous method to avoid difficulties inherent in small-scale continuous feeders. Acidulation was carried out in stainless steel stirred reactors. Phosphate rock was fed slowly into the calculated acid mixture and dissolved without any

excessive foaming. A retention time of approximately 20 minutes was found to be quite sufficient to effect complete extraction of the rock. Table V shows the result of a comparative experiment with a ground phosphate mixture and with an unground Morocco sample.

Nitrogen losses during this extraction stage were negligible, and, although they were never determined, analyses of the end products never gave reason to suspect any appreciable loss from this part of the operation.

Temperature always remained well below any troublesome level.

Sulfuric Acid. After some initial trouble with gypsum crystallizing in the feed line and clogging the acid distributors, this acid was distributed into the ammoniator-granulator. The result of this procedure was very beneficial, as the amount of heat of reaction definitely improved evaporation of moisture and granulation. As a result, the recycle ratio dropped sharply.

Initially, the sulfuric acid was fed under the bed. However, as frequent build-up on the distributor was encountered, the acid was finally sprayed onto the bed. Although some fuming was noticed, losses were negligible and operation was much easier.

Potassium Salts and Other Dry Raw Materials. These were fed into the plant, after crushing and screening, by means of a table feeder into the same elevator where the recycle was introduced.

Some grades were prepared with muriate of potash; in others, which for agricultural reasons should have a low chlorine content (less than 3%), potassium sulfate (50% K_2O) was used. These latter mixtures gave rise to interesting phenomena as a result of

Table V. Influence of Grinding on Extraction

(Values given as percentages)

	Phosphate Mixture	Marocco Rock
CHEMICAL ANALYSIS		
CaO	50.8	51.4
P_2O_5	35.55	33.7
CO_2	1.7	2.85
Fe_2O_3	0.5	0.13
Al_2O_3	1.0	0.55
SiO_2	1.95	1.6
F	3.4	3.4
Moisture	0.6	0.6

SCREEN ANALYSIS

	Phosphate Mixture	Marocco Rock
>500 μ	...	10.0
210-500 μ	0.1	28.4
150-210 μ	0.7	29.1
105-150 μ	6.1	20.7
75-105 μ	12.3	7.2
50-75 μ	16.5	3.25
<50 μ	63.3	1.4

EXTRACTION TIME

	Phosphate Mixture	Marocco Rock	
15 min.	98.4	99.3	100.0
20 min.	...	98.5	100.0
25 min.	100.0	99.3	99.7
35 min.	100.0

double decomposition between the sulfate and Ca salts (8). Among other things, the ratio of water-soluble P_2O_5 rose sharply and reached 90 to 95%. Even in experiments where this reaction was used to effect a saving in sulfuric acid, water-soluble P_2O_5 reached very high values.

Table VI shows average figures of a series of experiments on the production of a 12-5-20 grade. In experiment A, sulfuric acid was added in the extractors; in experiment B, no sulfuric acid was used resulting in a maximum acid saving; in experiment C, sulfuric acid was injected under the bed; in experiment D, it was sprayed onto the bed.

The influence of the various techniques on reaction temperature and recycle rate is obvious. Also, the value for water-soluble P_2O_5 approaches 100% even in experiment B, showing that the reaction between Ca ions and sulfate ions reached completion, and in this product potassium nitrate was produced.

Ammonia. This was introduced into the bed under reduced pressure (0.5 atm.) through a stainless steel slotted pipe, the slot pointing upstream. Am-

Table VI. Effect of Sulfate on Water-Solubility of P₂O₅

	12-5-20			12-5-24,
	A	B	C	D
RAW MATERIALS, KG./100 KG.				
Phosphate rock	14.1	14.1	14.1	14.1
Sulfuric acid	9.75	...	9.75	9.75
Nitric acid	51.5	60.3	51.5	51.5
Potassium sulfate	40.8	40.8	40.8	...
Potassium chloride	40.8
Ammonia	7.3	6.0	7.3	7.3
PRODUCT ANALYSIS, %				
N, total	12.3	12.6	12.0	12.8
N, ammoniacal	6.1	4.9	5.9	6.4
P ₂ O ₅ , total	5.7	5.25	5.1	5.25
P ₂ O ₅ , available	5.5	5.1	5.0	5.15
P ₂ O ₅ , water-soluble	5.3	5.15	4.7	3.8
K ₂ O	17.9	21.15	20.1	24.2
Moisture	2.2	1.2	1.0	0.7
Recycle, %	950	700	600	730
Production rate, kg./hr.	100	100	100	150
Temp. in ammoniator, ° C.	55	50	55	65
Ammonia losses, %	<0.6	0.3	0.3	0.1

Table VII. Storage Test

	Grade		
	12-10-15	12-10-20	13-12-8
Storage time in bulk	1 month	2 weeks	1 month
Product temperature, ° C. ^a	7.6	7.0	12.8
Air temperature, ° C. ^a	2.2	2.4	2.3
Relative humidity, % ^a	87	83	87
Storage time in bags	4 months	4 months	4 months
BAG No.			
No lumps	1-14	1-8	1-6
Less than 1% lumps	15-21	9-16	7,8
1 to 3% lumps	...	17-19	9-14
3 to 6% lumps	...	20,21	15,16
6 to 20% lumps	17-20
More than 20% lumps	21

^a During bagging.

Table VIII. Hardness Test

	A	B	C
	12-10-20	12-10-18	15-15-15
Mean granular diameter, mm.	2.5	1.8	2.6
Mean maximum load, kg.	2.6	2.2	1.4
Mean maximum pressure, kg./sq. mm.	0.54	0.87	0.25

monia losses, regularly determined in gas samples taken from the exhaust duct, apart from exceptional cases, never exceeded 0.5% and generally stayed well below this figure. This, although seemingly in contradiction with many figures in the literature, no doubt is a result of the fact that the process is carried out at a rather low pH (4 to 5).

Steam. The ammoniator-granulator was provided with steam, which could be introduced through the ammonia inlet, and with cooling air, which was blown onto the bed. Both facilities helped greatly in keeping the process under control whenever quick intervention was called for. The effect of changes in raw materials feed or recycle ratio is rather slow. Introduction of steam or cooling air usually provided for the time necessary to change operating conditions more gradually without having the process unbalanced.

In the ammoniator-granulator, a bed temperature of 55° to 65° C. was normal. An average evaporation of approximately 45% of the total water, introduced with the raw materials, was reached. In some cases, 60% evaporation occurred. The introduction of

Table IX. Example of Complete Calculation for 12-10-18

(P₂O₅ w.s./c.s. = 35/100; NH₃/NO₃ = 1/1)

Raw Materials		COMPOSITION PER 100 KG. OF PRODUCT					
		Moles	Total Wt.	H ₂ O	N	P ₂ O ₅	K ₂ O
Phosphate rock	P ₂ O ₅ 34% CaO 50%						
H ₃ PO ₄	50% P ₂ O ₅						
H ₂ SO ₄	78% = 60° Bé						
HNO ₃	52%						
Remarks:	The 12-10-18 may contain chlorine.						
Mole ratio CaO/P ₂ O ₅ = 3.7							
NH ₃ 100% KCl 60% K ₂ O							
14.5 grams of impurities per mole CaO							
RAW MATERIALS REQUIRED PER 100 KG. OF PRODUCT							
Phosphate		52.2	21.79	7.41	...
H ₃ PO ₄		18.2	5.18	2.59	...	2.59	...
H ₂ SO ₄		77.1	9.69	3.52
HNO ₃		428.5	51.91	24.92	6.00
NH ₃		428.5	7.28	...	6.00
KCl		...	30.00	18.00
Total			125.85	31.03	12.00	10.00	18.00
H ₂ O in product				5.93			
To evaporate				25.10			
Net				100.75			

cooling air stimulates evaporation by the removal of vapor from the drum. This serves in hardening the outer shells of the granules too, thus preventing or stopping any tendency of overgranulation. This, however, should not be overdone as, by lowering the temperature too much, evaporation is slowed down.

From the ammoniator-granulator, the material passed into the drying drum. At a gas inlet temperature of 150° to 200° C. and a moisture content of 4 to

4.5%, no troubles from mudding up or agglomeration were experienced. Some troubles were encountered initially through radiant heat, which tended to melt down the material at the inlet side of the dryer and in some cases even started decomposition and fires. These were overcome finally by installing an air-cooled chute with forced draught and directional flights at the inlet side of the dryer.

Screening the material before cooling

was not tried for fear of clogging the screens. It is uncertain that this could not be done after all. The final product screened out within a narrow range (1 to 3 mm.) was in the form of very uniform, well-rounded granules. Although at present not many figures are available, there are strong indications that the product, after normal conditions, stores very well, both on the heap and in bags.

In one test, 50-kg., 4-ply paper bags with one bituminous ply were stacked on wooden pallets, which stood on a concrete slabbed floor. Each stack contained 21 bags. The warehouse was unheated.

After 4 months, the bags were inspected for bag set. For this purpose, each bag was dropped from 1.50 meters onto its flat side by a specially designed Drop-Test machine (2), after which the remaining lumps were screened out on a 4 × 4 cm. screen and weighed. The products had been conditioned with 0.5% of a steared limestone and stored in bulk for some time prior to bagging. The bags were numbered from top to bottom, 1 to 21. The results are shown in Table VII.

Table VIII shows the mean results of a hardness test carried out on three different grades. A and B were nitric phosphates; C was a conventional

granular product containing ammonium nitrate. Representative selections of 20 granules of each grade were taken, measured, and crushed.

Tests showed that the granules produced by the nitric phosphate process had a higher density than those produced by a conventional process (1.92 against 1.64).

Calculations

A special method and a form were developed for the calculation of any

Table X. Experimental Data

	Water-Soluble P ₂ O ₅ , %	Potassium Salt	Ratio KCl/NH ₄ NO ₃	Kg. Water to Evaporate per 100 Kg.	Moisture Content in Ammoniator-Granulator, %			Temperature in Ammoniator-Granulator, ° C.	Liquid Phase, Weight %	Evaporation Ratio in Ammoniator-Granulator	Recycle Ratio
					Recycle	Bed	Product				
16-10-10 + 3MgO	50	K ₂ SO ₄	..	32.8	1.5	5.0	3.5	61	..	43	1: 7.8
18-12- 6 + 4MgO ^a	40	KCl	<1	25.0	2.0	4.0	3.35	45	20.5	32	1:10.5
18-12- 6 + 4MgO ^b	40	KCl	<1	21.1	2.9	4.87	3.5	38	22.1	64.5	1: 7.8
18-12- 6 + 4MgO	40	KCl	<1	39	2.4	4.04	3.55	42	19.2	28.5	1:20.9
12- 5-20	50	K ₂ SO ₄	..	23.2	1.8	3.89	3.0	55	..	40.9	1: 9.4
	50	K ₂ SO ₄	..	23.0	1.3	3.93	3.0	50	..	35.6	1: 7.3
	50	K ₂ SO ₄	..	23.2	1.1	4.26	2.8	56	..	47.0	1: 6.0
12- 5-24	50	KCl	>1	23.2	1.3	4.18	2.8	62	14.4	48.3	1: 6.6
12-10-24	100	KCl	>1	25.3	1.7	4.82	3.0	49	13.0	57.6	1: 6.5
	100	KCl	>1	22.9	1.3	4.57	2.5	64	15.8	63.3	1: 5.6
12-10-18	50	KCl	<1	23.8	1.5	3.62	2.8	62	16.2	38.2	1: 9.65

^a NH₄NO₃ added as solid. ^b NH₄NO₃ added as 90% solution.

Table XI. Detailed Figures on Raw Materials and Process Conditions

16-10-10 + 3MgO	18-12-6 + 4MgO				12-5-20			12-5-24	12-10-24			12-10-18
	1	2	3	4	5	6	7	8	9	10	11	12
Water-soluble P ₂ O ₅ (% rel.)	50	50	50	50	50	50	50	50	100	100	100	50
Mole ratio NH ₃ /NO ₃	1.13	1.0	1.0	1.0	1.0	0.7	1.0	1.0	1.0	1.0	1.39	1.0
Production rate, kg./hr.	100	100	100	100	100	100	100	200	75	75	100	100
KG. OF RAW MATERIALS PER 100 KG.												
Phosphate rock	11.7 ^a	14.8 ^a	14.8 ^a	14.8 ^a	14.1 ^b	14.1 ^b	14.1 ^b	14.1 ^b	11.3 ^b	11.3 ^b	8.4 ^b	21.7 ^c
Phosphoric acid	11.0 ^d	12.7 ^d	12.7 ^d	12.7 ^d	11.2 ^e	11.2 ^e	13.1 ^e	3.88 ^e
Sulfuric acid	4.8 ^f	9.75 ^f	..	9.75 ^f	..	4.3 ^g	4.3 ^g	10.2 ^g	10.0 ^g
Nitric acid	64.3	47.7	32.5	77.2	51.5	60.3	51.5	51.5	51.4	51.4	43.0	51.5
Ammonia	10.32	6.75	4.6	10.9	7.3	6.0	7.3	7.3	7.3	7.3	8.5	7.3
Potassium sulfate	20.0 ^h	40.8 ⁱ	40.8 ⁱ	40.8 ⁱ
Potassium chloride	..	10.0 ^j	10.0 ^j	10.0 ^j	40.8 ^k	40.0 ^k	40.0 ^k	40.0 ^k	30.0 ^k
Kieserite	10.7	14.3	14.3	14.3
Ammonium nitrate	..	19.8
Ammonium nitrate solution, 90%	33.4
Water to be evaporated	32.8	25.0	21.1	39.0	23.2	23.0	23.2	23.2	25.3	25.3	22.9	23.8
Recycle ratio	7.8	10.5	7.8	20.9	9.4	7.3	6.0	6.6	12.9	6.4	5.6	9.0
TEMPERATURES, ° C.												
Recycle	34	40	36	36	41	42	43	43	44	36	39	52
Reaction	61	53	38	42	..	50	56	54	45	50	63	60
Ammoniator product	51	44	36	40	43	43	47	46	48	49	53	54
Dryer product	71	69	56	57	64	71	80	78	62	64	81	88
Cooler product	46	48	41	41	46	51	53	57	49	48	55	64

(Table XI continued on page 440)

Table XI. Continued

	16-70- 70 + 3MgO											
	18-15-6 + 4MgO				12-5-20			12-5-24	12-10-24			12-10-13
	1	2	3	4	5	6	7	8	9	10	11	12
GAS FROM AMMONIATOR												
Flow rate, cu. meter/hr.	485	450	435	480	445	430	450	450
Temperature, ° C.	50	50	60	44	47	53	53	49
Ammonia loss, %	0.3	0.4	0.6	0.4	0.6	0.4	0.3	0.1	0.2	0.5
DRYER GAS												
Flow rate, cu. meter/hr.	760	720	700	890	850	830	840	860
Inlet temperature, ° C.	112	100	135	133	160	165	130	170	170	177
Outlet temperature, ° C.	76	60	57	55	64	69	70	72	67	70	81	92
CHEMICAL ANALYSIS, %												
N, total	16.0	17.8	17.9	17.4	12.3	13.2	13.5	12.55	12.7	12.6	12.6	12.3
N, NH ₃	8.4	8.7	8.6	8.5	6.3	5.3	6.8	6.2	6.4	6.6	7.4	6.0
N, NO ₃	7.6	9.1	9.3	8.9	6.0	7.9	6.7	6.35	6.3	6.0	5.2	6.3
P ₂ O ₅ , total	10.2	11.8	12.0	12.6	5.8	5.1	5.35	5.3	10.6	9.6	10.1	10.4
P ₂ O ₅ , available	10.0	11.8	11.8	12.5	5.8	5.1	5.4	4.95	10.6	9.5	10.1	10.4
P ₂ O ₅ , water-soluble	8.1	6.5	6.75	7.25	5.45	4.1	5.0	4.0	8.9	8.7	9.7	5.3
K ₂ O	9.1	5.6	5.7	5.35	18.1	21.9	18.0	24.5	23.0	23.2	23.7	17.9
MgO	3.1	3.7	3.7	3.6
Moisture	2.3	2.5	1.3	1.5	1.2	1.4	1.3	1.9	0.9	1.2
pH, 10% solution	5.4	3.3	4.95	3.8	4.0	3.1	3.9	3.3	...
NH ₃ /NO ₃	1.11	0.96	0.92	0.96	1.05	0.67	1.01	0.98	1.02	1.10	1.42	0.95
Av. P ₂ O ₅ , % of total	98.1	100	98.3	99.3	100	100	100	93.4	100	99.1	100	100
W.s. P ₂ O ₅ , % of total	81.0	55.1	57.1	58.0	93.2	80.5	92.7	80.8	83.9	91.6	96.1	50.9
MOISTURE CONTENT, %												
Recycle	...	1.8	2.1	1.9	2.1	0.6	0.6	1.0	1.1	1.15	0.7	0.8
3 hr. at 60° C.	...	1.8	2.1	1.9	2.1	0.6	0.6	1.0	1.1	1.15	0.7	0.8
60 v., 15 min. ^m	1.5	2.0	2.9	2.4	1.8	1.3	1.1	1.3	2.0	1.7	1.3	1.6
Ammoniator product	...	2.9	3.4	2.7	2.2	2.3	2.2	2.6	2.1	2.1	2.1	1.6
3 hr. at 60° C.	...	2.9	3.4	2.7	2.2	2.3	2.2	2.6	2.1	2.1	2.1	1.6
60 v., 15 min. ^m	3.5	3.35	3.5	3.55	3.0	3.0	2.8	2.8	2.8	2.9	2.5	3.0
Dryer product	...	2.1	2.8	2.0	1.4	0.7	0.7	1.2	1.3	1.2	0.8	1.0
3 hr. at 60° C.	...	2.1	2.8	2.0	1.4	0.7	0.7	1.2	1.3	1.2	0.8	1.0
60 v., 15 min. ^m	...	2.6	3.0	2.6	1.9	1.5	1.3	2.0	1.9	1.7	1.1	1.8
Cooler product	...	1.9	2.3	2.1	1.3	0.7	0.7	1.1	1.1	1.2	0.7	0.9
3 hr. at 60° C.	...	1.9	2.3	2.1	1.3	0.7	0.7	1.1	1.1	1.2	0.7	0.9
Ammoniator bed ⁿ	5.0	4.0	5.0	4.0	3.9	3.9	4.0	4.2	3.7	4.9	4.6	3.8
Evaporation in ammoniator	42.7	32.0	62.2	29.7	41.6	31.3	42.1	48.3	50.2	72.9	63.4	37.0
SCREEN ANALYSIS, %												
Recycle
>6 mm.
5-6 mm.
4-5 mm.	0.5	0.6	1.1	0.3	...	1.0	0.2	1.0
3-4 mm.	3.5	0.5	5.7	3.1	7.7	1.9	0.2	3.6	0.9	1.2	0.2	...
2-3 mm.	13.1	1.3	25.4	15.2	30.7	5.8	3.1	20.5	25.2	3.9	1.4	...
1-2 mm.	53.6	41.2	50.7	58.7	48.0	56.6	70.0	55.6	59.3	60.9	52.5	...
<1 mm.	29.8	57.0	17.7	22.4	12.5	36.3	26.7	19.3	14.4	33.0	45.9	...
Ammoniator product	4.9	5.4	4.9	9.0
>6 mm.	4.9	5.4	4.9	9.0
5-6 mm.	34.6	2.8	7.6	2.8	13.8	0.4	0.6	...	1.6	2.0
4-5 mm.	14.4	1.1	2.4	0.8	7.4	0.7	1.4	21.1	1.6	3.6	0.1	...
3-4 mm.	14.2	1.2	8.7	2.9	10.5	1.0	2.1	13.9	3.3	2.5	0.2	...
2-3 mm.	16.3	5.0	23.9	17.2	30.4	8.3	12.3	32.0	38.1	14.3	2.1	...
1-2 mm.	16.6	49.7	47.8	58.3	32.0	62.1	68.3	22.2	53.1	65.4	69.2	...
<1 mm.	3.9	40.2	9.6	18.0	1.0	22.1	10.4	1.8	2.3	12.2	28.4	...
Product
>6 mm.
5-6 mm.
4-5 mm.	2.5	0.8	1.3	2.3	3.6
3-4 mm.	20.3	3.7	13.1	6.1	16.2
2-3 mm.	36.6	26.9	35.9	31.7	45.7	76.0	21.2	61.3	41.7	67.4	36.2	...
1-2 mm.	40.0	67.1	48.3	58.2	34.0	22.9	76.5	37.1	56.0	31.8	57.4	...
<1 mm.	0.6	1.5	1.4	1.7	0.5	1.1	2.3	0.7	1.9	0.8	6.6	...

^a 35.5% P₂O₅, 50.75% CaO, 1.5% CO₂.
^b 35.55% P₂O₅, 50.8% CaO, 1.7% CO₂, 3.4% F.
^c 36.5% P₂O₅, 50.85% CaO, 1.35% CO₂, 3.85% F.
^d 53.1% P₂O₅. ^e 53.6% P₂O₅. ^f 76.0% H₂SO₄. ^g 73.94% H₂SO₄.
^h 50.0% K₂O. ⁱ 48.5% K₂O. ^j 60.0% K₂O. ^k 59.9% K₂O.
^m Determined with infrared moisture tester.
ⁿ Calculated moisture content in ammoniator bed before evaporation.

grade of nitric phosphate fertilizer. The form consists of three main parts:

Data of the grade to be calculated and of the available raw materials, necessary for the ensuing calculations.

Calculated composition per 100 kg. of product. At this stage double decompositions were not taken into account.

Amounts of raw materials to be used.

An example of this form, made up for a 12-10-18, is given in Table IX.

The first part is self-explanatory. From the composition of the raw phosphate, it follows that the mole ratio $\text{CaO}/\text{P}_2\text{O}_5$ is 3.7, and the amount of impurities in the phosphate, such as SiO_2 , Fe_2O_3 , Al_2O_3 , CO_2 , F, is 16%, of which 3% will escape in the gaseous form. Loss of fluorine is not considered because of the low temperature and the low concentration during acidulation. This means that approximately 13% of the impurities will remain in the reaction mass or 14.5 grams per mole of CaO . For this reason, the molecular weight of CaO in these calculations is taken as $56 + 14.5 = 70.5$.

Composition per 100 Kg. of Product. The 35% of P_2O_5 required to be water-soluble is calculated as monocalcium phosphate monohydrate, whereas the remaining 65% of P_2O_5 required to be citrate-soluble is calculated as anhydrous dicalcium phosphate (3).

By using the molecular weights of 266.5 and 150.5, respectively, the amounts of these two compounds are calculated from the number of moles of P_2O_5 .

In this product, all the nitrogen being present as ammonium nitrate, the amount of this compound in kilograms is easily calculated from the number of moles of nitrogen. The amount of KCl to be used follows from its grade. The sum total of water (including chemically bound water) in the different compounds plus 1% of moisture (assumed) is determined.

The total of the different compounds being 85.62 kg., 14.38 kg. of a filler can be used. In this process, gypsum, formed by the reaction of sulfuric acid with CaO , is commercially the most attractive filler. By using the molecular weight, $172 + 14.5 = 186.5$, the number of moles of gypsum and, hence, the amount of sulfuric acid to be used can be calculated.

From the data calculated so far, the total number of moles of CaO is found, from which, by using the mole ratio $\text{CaO}/\text{P}_2\text{O}_5$ in phosphate rock, the amount of P_2O_5 from this source is calculated.

Raw Materials per 100 Kg. of Product. From the figures calculated so far, the amounts of raw materials can easily be determined as well as the total water input with the raw materials. The difference between total water and water in product gives the amount of water to be evaporated in the process. This figure serves as a check on the calculations, small errors being due to incomplete analyses and approximations.

Conclusion

Pilot plant experiments on a nitric phosphate process using a rotary ammoniator-granulator have proved that any predetermined ratio of water-soluble/citrate-soluble P_2O_5 could be prepared. Reversion was not encountered during production nor after storage for as long as 6 months. The ammoniator-granulator serves as reactor, granulator, and dryer or evaporator.

Reactor. By simple calculation, the required amounts of raw materials can be determined to give a fertilizer grade of the desired composition. The amount of nitric acid should be at least such that 1.9 moles are present for each mole of CaO from rock. Part of the nitric acid may be replaced by sulfuric or phosphoric acid. The possibility of the formation of $\text{Ca}(\text{NO}_3)_2$ should be prevented. Double decomposition between a number of salts takes place. This has a beneficial influence on the conditions in the ammoniator and on the properties of the final product.

Granulator. Recycle and dry raw materials should be pretreated (crushed and screened). Any particles equal to or larger than product size entering the granulator will reappear as oversize and have to be crushed and recycled again. Granulation in its simplest form takes place by layering, although agglomeration occurs too. Because of the temperature's developing in the granulator, the reaction mixture consists of a very large percentage of liquid phase. A percentage of liquid phase in the order of 18% produces good results. Recycle ratio is influenced by its moisture content,

by the water input with the raw materials, and by the ratio $\text{KCl}/\text{NH}_4\text{NO}_3$, and generally varied between 600 and 1000% of production rate. As the granulation rate generally is very high, close screening is possible, and a very high quality product, consisting of hard, round granules, is obtained.

Dryer or Evaporator. The heat of reaction is quite sufficient to cause a considerable degree of evaporation. In the authors' experiments, an average of 45% of water input was evaporated; in some cases, evaporation reached 60%. Nitrogen losses can be kept very low and generally do not exceed 0.5%.

Table X gives some average figures of some of the experiments. Table XI gives more detailed figures on raw materials and process conditions.

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