

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 P₂O₅) 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-

position is calculated on the basis of the composition of an ideal precipitate. Complete ammoniation of an unadjusted extract is assumed to yield a precipitate comprising dicalcium phosphate, the normal phosphates of iron and aluminum, and calcium fluoride, and a solution containing calcium nitrate and ammonium nitrate. The ammonia requirement is calculated by the equation:

$$\begin{aligned} (\text{NH}_3\text{-N}) \text{ reqd.} = & (\text{NO}_3\text{-N}) + \\ & 0.395(\text{P}_2\text{O}_5) + 0.737(\text{F}) - \\ & 0.500(\text{CaO}) - 0.550(\text{Al}_2\text{O}_3) - \\ & 0.351(\text{Fe}_2\text{O}_3) \quad (1) \end{aligned}$$

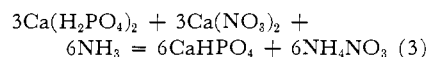
where the chemical formulas represent grams of the components. Complete ammoniation of an adjusted extract is assumed to yield a precipitate comprising the same solid phases and a solution containing monoammonium phosphate and ammonium nitrate. The ammonia requirement then is calculated by the equation:

$$\begin{aligned} (\text{NH}_3\text{-N}) \text{ reqd.} = & (\text{NO}_3\text{-N}) + \\ & 0.197(\text{P}_2\text{O}_5) + 0.368(\text{F}) - \\ & 0.250(\text{CaO}) - 0.275(\text{Al}_2\text{O}_3) - \\ & 0.175(\text{Fe}_2\text{O}_3) \quad (2) \end{aligned}$$

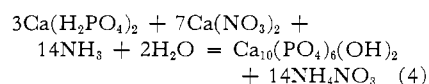
Equations 1 and 2 are practical tools and are not intended to indicate the chemistry of the reactions.

The degree of ammoniation (neutralization) of a partially ammoniated extract is the ammonia addition divided by the ammonia requirement—a quotient conveniently expressed in per cent. The ammonia requirement of an extract depends upon the ratio of acid to rock used in the preparation of the extract—a value conveniently expressed as the acid ratio (mole ratio N_2O_5 to CaO) in the initial extract.

The precipitation of calcium phosphate is assumed in Equations 1 and 2 to occur according to the equation:



where precipitation of 3 moles of phosphoric oxide requires 6 moles of ammonia. Under certain conditions of ammoniation, however, the precipitated calcium phosphate is an apatite, as in the equation:



where precipitation of 3 moles of phosphoric oxide requires 14 moles of ammonia. Since the precipitation of apatite, or other calcium phosphates more basic than dicalcium phosphate, cannot be prevented entirely, neutralization of an extract requires more ammonia than is indicated by Equation 1 or 2.

Complete extraction of a rock phosphate with nitric acid is obtained with an acid ratio of 0.90 to 0.95. When the acid ratio in an unadjusted extract is 0.95, the first permanent precipitate ap-

Table I. Composition of Rock Phosphates

Rock Phosphate	Composition, %					
	P_2O_5	CaO	Al_2O_3	Fe_2O_3	SiO_2	F
Tennessee brown	28.1	37.1	2.4	2.0	22.0	3.1
Florida pebble	31.6	45.5	1.4	1.9	8.5	3.7
Florida hard	34.5	48.3	1.8	1.1	6.8	4.0
Western (Idaho)	32.7	46.5	1.4	0.6	8.1	3.2
Ocean Island	39.2	52.8	0.4	0.4	0.1	2.9

pears at about 30% neutralization; most of the iron, aluminum, and fluorine are precipitated at about 45% neutralization. With good conditions of ammoniation, almost all the phosphorus is precipitated at about 105% neutralization. Under poor conditions of ammoniation, however, all the phosphorus is precipitated and neutrality is obtained at about 150% neutralization.

The precipitates formed in the different stages and under different conditions of ammoniation contain calcium phosphates ranging in basicity from dicalcium phosphate to apatite. Fluorine in the precipitates occurs largely as calcium fluoride and fluor- and fluorhydroxyapatites of unknown and presumably variable composition. Iron and aluminum in the precipitates are present largely as phosphates, also of unknown compositions.

Citrate solubility is unsuitable as a measure of the effect of changes in conditions of ammoniation on the properties of the precipitates, because the citrate solubility is sensitive to conditions other than those of the precipitation. Petrographic and x-ray examinations are invaluable in determining the mineralogical compositions of the precipitates, but the methods are not quantitative. A precipitate is evaluated most conveniently through a calculation of its basicity.

A precipitate that contains little iron and aluminum is evaluated on the basis of its net lime ratio. In calculating this ratio, all the fluorine is assumed to be combined as calcium fluoride:

$$\text{Net lime ratio} = (\text{CaO} - \text{F}_2)/\text{P}_2\text{O}_5 \quad (5)$$

where the chemical formulas represent moles of the components. A net lime ratio of 2 indicates that the precipitate is composed wholly of calcium fluoride and dicalcium phosphate, whereas a net lime ratio of 3 indicates that all the phosphate in the precipitate may be present as fluorapatite when the fluorine content is high enough; hydroxyapatite has a net lime ratio of 3.33. A net lime ratio between 2 and 3 indicates that the phosphate is a mixture of dicalcium phosphate and apatite. Results of petrographic and x-ray examinations agreed well with mineralogical compositions deduced from net lime ratios. Net mole ratios of bases to phosphoric oxide in precipitates that contained much iron or aluminum, however, were of little value.

Procedure

The compositions of the rock phosphates are shown in Table I. The nitric acid (43% HNO_3) was obtained directly from plant production. Other chemicals used in preparing simulated extracts and in treatment of extracts were of reagent grade.

Nitric acid extracts of rock phosphate usually were prepared at 90° C. Extracts that were to be ammoniated continuously were filtered free of gangue. Filtered extracts of Florida pebble phosphate deposited sediments of calcium fluoride overnight, which were removed by filtration or decantation.

Simulated extracts usually were prepared from calcium carbonate, phosphoric acid, and nitric acid. Fluorine was added as fluosilicic acid; iron, aluminum, and magnesium, as the nitrates.

The ammoniation tank was a cylindrical vessel with four vertical baffles and, for continuous ammoniations, an overflow spout one tank diameter above the bottom (9). The contents were agitated by either a propeller or a four-bladed turbine at the bottom of the tank. The speed of the impeller was not critical, if agitation was fairly vigorous. The tank could be placed on a hot plate.

The ammonia was introduced just above the impeller, close to the shaft. To prevent the sucking of liquor into the inlet tube when the flow of ammonia was stopped, air was passed continuously through the tube. The input gas to the ammoniation tank contained 90 to 95% ammonia. In continuous ammoniations, the input liquor was introduced through a tube similar to the ammonia inlet tube.

In a batch ammoniation, ammonia was introduced into a portion of an extract at a measured constant rate for a measured time to obtain a desired degree of ammoniation. The ammonia was shut off, and a sample of the agitated slurry was pipetted. When desired, the ammoniation was resumed, with sampling at desired degrees of ammoniation.

With a constant rate of input of ammonia in a batch ammoniation, the degree of neutralization of the extract was increased at a constant rate. The rate of ammoniation then was expressed in terms of per cent of the ammonia requirement per minute and was calculated by dividing the change in degree of

neutralization by the time during which the ammonia was added.

In a continuous ammoniation, confluent streams of ammonia and a filtered extract were metered to an ammoniation tank filled with water at the run temperature. Conditions were assumed to be at steady state after the equivalent of four changes in the contents of the tank. A 3- to 5-minute grab sample of the effluent was taken for analysis.

When a second stage of continuous ammoniation was wanted, the run was continued until the feed tank was empty. All the slurry was filtered (the constant-head feed device would not handle suspensions), and the filtrate was ammoniated in the same way as the initial extract.

In a few runs in which a liquor was ammoniated in two continuous stages, the effluent from the first tank was wasted until conditions were steady state. The effluent then was introduced into the second tank, where steady-state conditions were assumed to exist after four fillings.

Analytical samples were diluted with 2 to 4 volumes of water and filtered. The washed and dried precipitates usually were analyzed for phosphorus, calcium, and fluorine—sometimes for aluminum, iron, and magnesium. The filtrates usually were analyzed for phosphorus, calcium, fluorine, total nitrogen, and ammonium nitrogen (nitrate nitrogen was determined by difference). Best material balances usually were obtained on the basis of phosphorus.

Results of Ammoniation

Most of the ammoniations were made with extracts of the Florida pebble phosphate (Table I) and 43% nitric acid or with simulated extracts containing about the same concentrations of phosphorus, calcium, and nitrate as the actual extracts. When such an extract was ammoniated at room temperature, crystals of monocalcium phosphate were formed ahead of principal precipitation reactions, and some of the extracts were diluted to prevent this crystallization. Dilution of an extract had no significant effect on the course of the precipitation reactions or their extent at a given degree of ammoniation, but it did raise the pH of the partially ammoniated slurry at early stages of ammoniation so that pH was suitable as a method of control only in the final stages.

Except for the effect on the crystallization of monocalcium phosphate from the undiluted extracts, variation of the temperature from ambient to boiling generally had little effect on the course and extent of the precipitation reactions. In fluorine-free simulated extracts, however, dicalcium phosphate dihydrate was precipitated at temperatures below

50° C. and anhydrous dicalcium phosphate at higher temperatures.

Most of the extracts were unadjusted. Adjustment of the lime ratio to 2 or less decreased considerably the formation of apatite in the final stages of batch ammoniation under favorable conditions but did not prevent the formation of apatite under adverse conditions of either batch or continuous ammoniation.

Batch Ammoniation. The results of a batch ammoniation of an unadjusted extract (acid ratio, 0.93) of the Florida pebble phosphate (Table I) are shown in Figure 1. The curves were affected by changes in the composition of the extract, but were highly reproducible for a given extract. The point of initial precipitation depended upon the initial acid ratio. The rock phosphate was relatively low in iron and aluminum; increase in their amounts raised the initial portion of the phosphorus curve above that in Figure 1, but did not change the iron and aluminum curves significantly. Abrupt breaks in both the phosphorus and fluorine curves at about 90% precipitation of the fluorine were characteristic.

Adjustment of the extract with phosphoric acid brought the calcium curve closer to the phosphorus curve, and overadjustment reversed the positions of the calcium and phosphorus curves in Figure 1.

Unadjusted extracts of the five rock phosphates in Table I were ammoniated batchwise to obtain precipitates containing 90% of the fluorine from each extract. The extracts contained most of the iron and aluminum from the rock phosphates, and precipitation of both was practically complete along with the first 90% of the fluorine. The ratios of calcium to fluorine in the precipitates were near those in calcium fluoride. The mole ratios of iron oxide plus aluminum oxide (R_2O_3) to phosphoric oxide in the precipitates were in the narrow range from 0.60 to 0.66, which indicated that the iron and aluminum were precipitated initially as the secondary phosphates, $R_2(HPO_4)_3$. The mole ratios R_2O_3 to

P_2O_5 in the five rock phosphates ranged from 0.02 to 0.18, and the phosphorus precipitated with the first 90% of the fluorine from an extract was close to 1.5 times the mole ratio R_2O_3 to P_2O_5 in the corresponding rock phosphate.

The curves in Figure 1 show that when an unadjusted extract is ammoniated past the point at which all the phosphorus is precipitated, additional calcium is precipitated. The ammoniation of the extract in Figure 1 was repeated. In one series of runs, the ammoniation was stopped when 90% of the fluorine was precipitated; the precipitate was removed, and the ammoniation was continued with the filtrate. In the other series, the ammoniation was carried to completion without removal of precipitate (Table II).

Petrographic examinations of the first-stage precipitates showed that most of the fluorine was present as calcium fluoride. Simulated extracts containing no iron or aluminum yielded similar precipitates whose chemical compositions indicated that 90% of the fluorine was present as calcium fluoride and 10% as fluorapatite.

Although precipitated as compounds generally considered to be inert, the fluorine had a marked effect in later stages of ammoniation. Thus, when the precipitated fluorine was removed, precipitation of the phosphorus was complete on addition of 111% of the ammonia requirement, the pH rose rapidly as ammoniation neared completion, and nearly all the phosphorus in the precipitate was present as dicalcium phosphate. When the precipitated fluorine was not removed, its adverse effect became apparent between 80 to 90% of the ammonia requirement. Only 87% of the phosphorus was precipitated with 107% of the ammonia requirement, and a considerable fraction of the precipitated phosphorus was in the form of a phosphate more basic than dicalcium phosphate. On further ammoniation, the pH rose slowly, calcium continued to precipitate, and the precipitated dicalcium phosphate was converted to apatite, apparently as rapidly as the ammonia was added.

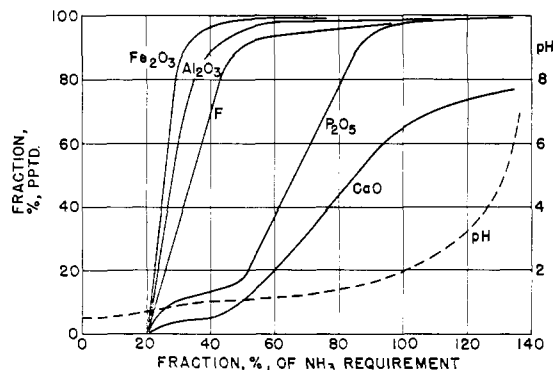


Figure 1. Batch ammoniation of nitric acid extract of Florida pebble phosphate

Table II. Effect of First-Stage Precipitate on Subsequent Precipitates

(Batchwise ammoniation at 95° C. of unadjusted nitric acid extract of Florida pebble phosphate)

Stage	Cumulative %				pH	Net Mole Ratio CaO:P ₂ O ₅ in Cum. 2nd-Stage and Later Ppts.
	NH ₃ reqd.	P ₂ O ₅ pptd.	CaO pptd.	F pptd.		
First-stage precipitate removed before subsequent ammoniation						
1	45	20	17	91	0.5	...
2	92	83	52	96	1.4	1.99
3	111	100	63	97	7.1	2.04
First-stage precipitate left in slurry during subsequent ammoniation						
1	43	18	16	92	0.5	...
2	81	59	41	99	1.5	2.05
3	90	74	48	98	1.1	2.14
4	107	87	58	99	2.5	2.14
5	136	100	75	99	3.6	2.71
6	149	100	82	99	5.4	2.99
7	168	100	89	100	7.6	3.19

Table III. Ammoniation of Solutions in the System CaO-P₂O₅-F-N₂O₅-H₂O(Initial net mole ratio CaO:P₂O₅, 2.0. Continuous ammoniation at 95° C. Precipitates removed between stages. Retention time, 7 minutes each stage)

Initial Wt. Ratio F:P ₂ O ₅	Stage	Fraction, %				pH of Filtrate	Net Mole Ratio CaO:P ₂ O ₅ in Ppt.
		NH ₃ reqd.	P ₂ O ₅ pptd.	CaO pptd.	F pptd.		
0.037	1	69	35	46	93.9	1.4	2.46
	2	22	31	29	3.2	1.9	1.99
	3	8	21	20	1.1	3.0	2.01
	4	10	4	5	0.3	7.5	2.76
	Total	109	91	100	98.5		
0.136	1	63	21	41	97.8	1.2	2.69
	2	22	34	27	1.5	1.7	2.06
	3	13	18	14	0.2	2.3	2.00
	4	15	16	18	0.1	7.2	2.87
	Total	113	89	100	99.6		

Although calcium fluoride was a major component of the first-stage precipitate, addition of reagent calcium fluoride to a fluorine-free simulated extract had no significant effect on the precipitation reactions. The form of the precipitated fluorine that had the adverse effect on subsequent precipitation reactions was not determined.

In a study of the effect of the rate of batch ammoniation on the composition of the precipitate, portions of simulated extracts containing no iron or aluminum and having a fluorine ratio (weight ratio F to P₂O₅) of 0.12 were ammoniated to 65 to 90% of the ammonia requirement at 30° to 40° C. The reproducibility of the results was poor, but, in general, precipitates formed at ammoniation rates higher than 1.3% of the ammonia requirement per minute had net lime ratios of 2.6 or higher, as compared with ratios between 2.1 and 2.2 for precipitates formed at ammoniation rates of 0.5 to 0.8% per minute.

Similar results were obtained in ammoniations at 85° C., except that ammoniation rates as high as 1.3% per minute yielded precipitates in which the net lime ratio usually was less than 2.2.

Continuous Ammoniation. In batch ammoniation, the degree of neutralization

is increased gradually at a measurable rate, and the precipitation reactions proceed in at least three successive phases. In the ammoniation of an unadjusted extract, the iron, aluminum, and fluorine are precipitated in the first phase, dicalcium phosphate is precipitated in the second phase, and excess calcium is precipitated and dicalcium phosphate is converted to apatite in the third phase.

In continuous ammoniation on the other hand, the neutralization is carried out in successive stages, the degree of neutralization in each being increased abruptly. The rate of ammoniation in a stage has no practical relation to the time the slurry is retained in that stage. When the stages of continuous ammoniation are proportioned so that each stage is within one of the successive phases encountered in batch ammoniation, the results of the two types of ammoniation are essentially the same. Overlapping of two phases in a single stage of continuous ammoniation results, however, in extension of the less desirable phase over the entire stage.

Fluorine-free simulated extracts were ammoniated in successive continuous stages with removal of the precipitate between stages. When the terminal pH was 3.5 or below, and less than 90% of

the phosphorus was precipitated, the precipitate was dicalcium phosphate. The composition of the precipitate was not affected significantly by variation in the initial lime ratio of the extract from 2 to 3, variation in the increment of ammoniation in any stage, or variation of the retention time in any stage.

When the terminal pH was between 3.5 and 5.5, the precipitate contained octacalcium phosphate, Ca₈H(PO₄)₃·xH₂O (2); at higher pH's, apatite was a major constituent of the precipitate.

Fluorine-containing simulated extracts were prepared by adding fluosilicic acid to solutions of calcium nitrate and phosphoric acid. The solutions remained clear. Addition of hydrofluoric acid instead of fluosilicic acid yielded an immediate precipitate of calcium fluoride that contained as much as 70% of the added fluorine. The fluorine that remained in solution from the two sources behaved exactly the same when the solutions were ammoniated.

Results of four-stage continuous ammoniations of fluorine-containing simulated extracts, with removal of the precipitate between stages, are shown in Table III. Most of the fluorine was precipitated before much of the phosphorus was precipitated, but fluorine precipitation was never complete. The small amount of fluorine remaining in solution after the first stage, however, had no significant effect on the precipitates in subsequent stages.

Petrographic examination of the first-stage precipitates in Table III showed that each was composed of particles that were complex aggregates (mostly <15 microns in diameter) of two or more phases that did not lend themselves to mechanical separation. The core of each particle was calcium fluoride, and some cores were covered with crystals of anhydrous dicalcium phosphate. Nearly all the particles were covered with a dense overgrowth of apatite.

On the assumption that each of the first-stage precipitates in Table III was composed wholly of calcium fluoride, dicalcium phosphate, and fluorapatite, it was calculated that about 15% of the phosphorus in each solution was precipitated as apatite. The fluorine ratio in most domestic rock phosphates ranges from 0.10 to 0.12 (8). The data in Table III show that removal of two thirds of the fluorine from an extract of rock phosphate would not decrease significantly the adverse effect of fluorine on the composition of the first-stage precipitate.

In a study of the effect of the amount of fluorine on the composition of the first-stage precipitate, different amounts of fluosilicic acid were added to a simulated unadjusted extract. Each portion was ammoniated to about 65% of the ammonia requirement in a single continuous

Table IV. Effect of Amount of Fluorine on Composition of First-Stage Precipitate(Initial mole ratio CaO:P₂O₅, 3.12. Continuous ammoniation at 97° C. Retention time 6 minutes)

Initial Wt. Ratio F:P ₂ O ₅	Fraction, %					pH of Filtrate	Net Mole Ratio CaO:P ₂ O ₅ in Ppt.	Fraction, % of Total P ₂ O ₅ Pptd. as Apatite ^a
	NH ₃ reqd.	P ₂ O ₅ pptd.	CaO pptd.	F pptd.	F			
0.007	66	48	33	79	1.0	2.05	2	
0.013	69	48	35	90	1.1	2.17	9	
0.023	68	38	33	92	1.0	2.52	19	
0.046	61	24	27	93	1.0	2.83	20	
Cl ^b	73	35	21	..	1.0	1.97	0	

^a Calculated on assumption that precipitate is composed wholly of calcium fluoride, dicalcium phosphate, and fluorapatite.^b Hydrochloric acid equivalent to hydrofluoric acid in amount to give weight ratio F:P₂O₅ of 0.125.**Table V. Effect of Amount of Ammonia Added in First Stage of Continuous Ammoniation**(Solution contained P₂O₅ 71, CaO 126, F 9, nitrate-N 57 g.p.l. Ammoniation at 98° C. Retention time, 6 minutes)

NH ₃ reqd.	Fraction, %				pH	Net Mole Ratio CaO:P ₂ O ₅ in Ppt.	Fraction, % of Total Constituent Pptd. as Apatite ^a		
	P ₂ O ₅ pptd.	CaO pptd.	F pptd.	F			P ₂ O ₅	CaO	F
50	21	22	97	0.9	2.56	12	8	8	
64	32	29	97	1.1	2.75	24	18	17	
83	47	40	98	1.2	2.83	39	29	26	
103	68	55	97	1.4	2.91	62	45	39	

^a Assuming that precipitate consists of only calcium fluoride, dicalcium phosphate, and fluorapatite.

stage. The results (Table IV) show that the effect of the fluorine was appreciable even with an initial fluorine ratio of 0.007, but was serious only when the initial ratio exceeded 0.013. Only dicalcium phosphate was obtained upon ammoniation of a portion of the fluorine-free solution to which chlorine was added instead of fluorine.

Results similar to those in Table IV were obtained by similar treatment of a fluorine-free simulated adjusted extract. Adjustment of the extract does not significantly affect the precipitation reactions in the first stage. The results indicate that at least 90% of the fluorine should be removed from an extract of rock phosphate if the adverse effect of fluorine is to be held to a practical minimum. The fluorine ratio in the low-fluorine filtrate should be no higher than 0.015.

Portions of a simulated, unadjusted extract (fluorine ratio, 0.13) were ammoniated to different degrees in single continuous stages. The results (Table V) show that an increase in the addition of ammonia in the first stage led to an increased precipitation of phosphorus and fluorine as apatite instead of dicalcium phosphate and calcium fluoride. These results are in marked contrast to those in Table II, where dicalcium phosphate was precipitated in batch ammoniations after most of the fluorine had been precipitated. Thus, even in a nitric phosphate process in which the first-stage

precipitate is not removed, the degree of neutralization in the first stage of ammoniation should be that at which about 90% of the fluorine is precipitated. Addition of less ammonia leaves in solution fluorine which forms apatite during its precipitation in the next stage, and addition of more ammonia precipitates more phosphorus, as apatite, than is necessary.

Effects of Added Ions. Andrès (7) reported that ammoniation of a nitric acid extract of a Morocco rock phosphate to a pH above 3 yielded considerable amounts of citrate-insoluble phosphate, but that addition of a small amount of magnesium sulfate to the extract permitted ammoniation to a pH as high as 9 without formation of citrate-insoluble phosphate. Salts of aluminum, cobalt, nickel, manganese, and other metals were said to have similar, but less pronounced effects.

Sulfate was the most effective anion that Andrès found for maintaining high citrate solubility of the precipitated phosphate. Unpublished data on TVA pilot plant studies of nitric phosphate process IV (11), in which an unadjusted extract is ammoniated, indicated that sulfate was effective in preventing the precipitation of citrate-insoluble phosphate. On the other hand, neither TVA process II (16) nor III (10), in both of which large amounts of sulfate are used, is free from trouble with citrate-insoluble phosphate in the product.

Additions of magnesium, aluminum,

iron, sodium, potassium, boron, and sulfate in the present study had too little effect on the precipitation reactions to warrant their addition to the system.

An addition of magnesium to a simulated extract appeared to accelerate the precipitation of fluorine in the early stages of ammoniation and to delay the precipitation of phosphorus. Magnesium altered the crystal habit of the precipitated calcium phosphate somewhat, but the beneficial effect of magnesium on the precipitation reactions disappeared in continuous ammoniations where the conditions were markedly unfavorable or in batch ammoniations as neutrality was approached.

Aluminum forms complexes with fluorine, the most stable being AlF₂⁺ (15). When aluminum nitrate is added to a solution of calcium nitrate and phosphoric acid, hydrofluoric acid can be added until the mole ratio of fluorine to aluminum is 2 before calcium fluoride is precipitated. The complex is stable in acid solution, but decomposes with precipitation of aluminum phosphate and calcium fluoride when an alkali is added.

The presence of aluminum or iron in an extract has a slight beneficial effect in that citrate-soluble aluminum or iron phosphates, instead of apatite, are precipitated during the precipitation of fluorine as calcium fluoride. This effect disappears, however, as a batch ammoniation is carried to completion. The addition of iron or aluminum in a nitric phosphate process cannot be recommended.

Removal of Fluorine

It was concluded that nitric phosphate processes could be improved by removing about 90% of the fluorine from the system to leave a fluorine ratio in the treated extract of 0.015 or less. The precipitation of fluorine as sodium or potassium fluosilicate from acid extracts of rock phosphate is described in the literature (3, 17), but even relatively large amounts of potassium chloride precipitated less than 75% of the fluorine from nitric acid extracts of Florida pebble phosphate.

By partial ammoniation of the extracts, 90% of the fluorine was precipitated along with a fraction of the phosphorus that depended upon the amounts of iron and aluminum in the extract. In filtrations at 80° C., however, the unwashed precipitate contained a water-soluble solid phosphate, presumably monocalcium phosphate, in addition to the water-insoluble phosphates. The phosphorus in the water-soluble phosphate ranged from one third that in the washed precipitate from an unadjusted extract to the same as that in the washed precipitate from an adjusted extract.

The washed precipitates were composed of uniform rosettes or spheroidal aggregates, usually 5 to 15 microns in diameter, comprising very small particles

of calcium fluoride, iron and aluminum phosphates, and apatite. Mechanical separation of the components was impossible. The washed filter cakes (30 to 40% solids when sucked dry) were thixotropic. Although the cakes washed fairly well, a volume of wash water 0.5 to 1.0 times that of the filtrate was required for 99% recovery of the filtrate when the cakes were washed by immersion. About two thirds of the total filtrate was recovered before dilution with wash water became significant.

Filtration tests were made with a test leaf filter (Eimco Corp.). Clear filtrates were obtained with a monofilament polyethylene cloth (National Filter Media Corp. No. P-2201; 1/1 plain weave; thread count, 112 by 48). All the tests reported here were made with this cloth.

The slurry from an unadjusted extract of Florida pebble phosphate that had been ammoniated to 40% was filtered at 80° C. to yield the results shown in Table VI. The precipitate contained 18% of the phosphorus and 90% of the fluorine; the density of the filtrate was 1.4 grams per cc. and the viscosity 2.3 centipoises, both at 80° C. The slurry was stirred by hand during the tests, and considerable variation in the results was caused by the poor agitation. The results reported are averages of at least three tests.

When the filter cake was washed with a spray of water or by immersion, the flow of liquid through the cake became very rapid as the filtrate was displaced. In a typical run with a vacuum of 15 inches of mercury, a 6-mm. cake was formed in 20 seconds. The rate of filtration during the form time and for the first 15 seconds of washing was 30 gal./ (sq. ft.) (hr.), after which the wash water passed through the cake at a rate of 70 gal./ (sq. ft.) (hr.). In this run, complete removal of the filtrate was obtained with a volume of wash water equal to that of the filtrate, and the over-all rate of filtration of all the filtrate, calculated as undiluted filtrate, in 70 seconds of form, wash, and dry times was 23 gal./ (sq. ft.) (hr.).

Slurries for the filtration tests were prepared by batch ammoniation at a rate of about 0.7% per minute of the total ammonia requirement. Increase of the rate of ammoniation to 3% per minute caused a marked decrease in the filterability of the slurry. Ammoniation somewhat less than that to precipitate 90% of the fluorine did not decrease the filterability of the slurry significantly, and higher ammoniation increased the filterability, because of the more granular dicalcium phosphate that was precipitated.

In an attempt to prevent formation of the crystalline water-soluble phosphate, ammonium nitrate solution of the same normality as the 43% nitric acid was added to double the volume of the

Table VI. Filtration of First-Stage Precipitate at 80° C.

(Cake not washed. Filtration rates based on form times only)

Vacuum, Inches Hg	Filtration Rate, Gal./ (Sq. Ft.) (Hr.), at Indicated Form Time			Cake Thickness, Mm., at Indicated Form Time		
	10 sec.	20 sec.	30 sec.	10 sec.	20 sec.	30 sec.
10	39	32	27	3	5	6
15	50	37	30	3	6	7
20	59	42	39	5	7	8

Table VII. Compositions of First-Stage Precipitates

Code	Rock Phosphate Used in Extract	Composition, %				
		P ₂ O ₅	CaO	Al ₂ O ₃	Fe ₂ O ₃	F
Precipitates mixed with gangue						
FG	Florida pebble	18.4	20.7	3.2	4.9	8.0
TG	Tennessee brown	15.0	9.8	5.9	4.6	5.7
Gangue-free precipitates						
FO	Florida pebble	29.7	28.9	5.0	7.2	14.7
TO	Tennessee brown	35.6	17.3	10.6	9.0	12.6

Table VIII. Defluorinated First-Stage Precipitates

Code ^a	Temp., °C.	Time, Min.	Composition, % ^b				Fraction, % of F Removed	Fraction, % ^b of Total P ₂ O ₅	
			Total P ₂ O ₅	W. S. P ₂ O ₅	C. I. P ₂ O ₅	F		W. S.	C. I.
FG	220	90	16.8	7.9	1.5	0.60	92	47	9
	320	70	17.7	0.3	1.8	0.43	94	1	10
FO	240	90	23.5	6.0	0.0	0.54	95	26	0
	320	75	24.0	0.3	0.2	0.51	96	1	1

^a As in Table VII. FG contained gangue, FO contained no gangue.

^b W. S. = water-soluble; C. I. = citrate-insoluble.

slurry. The diluted slurry filtered less rapidly (calculated on the basis of undiluted filtrate) than the undiluted filtrate. The crystallized water-soluble phosphate apparently makes the precipitate more readily filterable.

Most of the filtration tests were made on slurries prepared by ammoniation of unfiltered extracts of rock phosphate that had been prepared with 43% nitric acid. The unammoniated extracts were virtually unfilterable. An extract prepared with a mixture of nitric and sulfuric acids of the same normality as 43% nitric acid in the proportions to adjust the net lime ratio of the extract to 2.0 filtered slowly. Another extract prepared with the same proportions of nitric and sulfuric acids, but with addition of the sulfuric acid after the nitric acid was about spent, filtered at a rate of 41 gal./ (sq. ft.) (hr.).

When gangue-free extracts were ammoniated to precipitate about 90% of the fluorine, the slurries filtered initially at a rate of 80 gal./ (sq. ft.) (hr.), but the cloth tended to blind and the rate decreased to 24 gal./ (sq. ft.) (hr.).

Recovery of Fluorine

First-stage precipitates containing about 90% of the fluorine from extracts of Florida and Tennessee rock phosphates had the compositions shown in Table VII. The most feasible method for re-

covery of fluorine from these precipitates was to mix them with sulfuric acid and to heat the mixtures at 200° to 300° C. in a current of air containing steam. The requirement of sulfuric acid was an amount to convert all the calcium to the sulfate, all the phosphorus to the primary phosphates of iron and aluminum, and the remainder of the iron and aluminum to the sulfates. The amount of sulfuric acid was about 40% of that required to adjust the lime ratio in the initial extract to 2.0.

When 5-gram portions of the acidulated mixtures were heated in a current of air, 80% of the fluorine was volatilized in 60 minutes at 200° C. When steam was added to the air, 95% of the fluorine was volatilized in 60 minutes at 200° C., in 30 minutes at 250° C., or in 15 minutes at 300° C. In an atmosphere containing steam, the fluorine was volatilized as readily from gangue-free precipitates as from the precipitates that contained the siliceous gangues or added silica gel.

When 100-gram portions of the acidulated mixtures were heated in vertical glass tubes through which a mixture of air and steam was passed, defluorination was practically complete in 70 to 90 minutes at either 220° or 320° C. The compositions of the residues are shown in Table VIII.

The decrease in the water-soluble phos-

phate in the residues as the temperature of defluorination was raised from 220° to 320° C. probably reflects the conversion of the primary orthophosphates to metaphosphates. The presence of the gangue from the rock phosphate in FG probably is the cause of the larger fraction of citrate-insoluble phosphate in defluorinated FG than in defluorinated FO.

These residues could be returned to the ammoniation step at any point subsequent to the removal of the high fluorine precipitate, and the phosphorus in the precipitate then would appear in the final product.

Ammoniation of Low-Fluorine Filtrates

When an extract of rock phosphate is completely ammoniated without removal of any intermediate precipitate, the precipitate at any degree of ammoniation is very finely divided and settles slowly from the mother liquor. When the precipitate that contains 90% of the fluorine is removed, however, subsequent precipitates are so granular and settle so rapidly that, in bench-scale work, homogeneous slurries were not maintained with vigorous agitation. The solids contents of grab samples of the effluent slurries from continuous ammoniations ranged from one-half to three times that in a homogeneous slurry.

Although troublesome in bench-scale work, the rapid settling of the precipitates from low-fluorine filtrates might be useful in large-scale operation. Intermediate precipitates could be removed by sedimentation between stages of ammoniation, and removal of the precipitates would facilitate control of the final stage of ammoniation and also minimize reversion of the precipitated dicalcium phosphate to more basic phosphates.

A low-fluorine filtrate (fluorine ratio, 0.011) that had been overadjusted with phosphoric acid to a net lime ratio of 1.8 was ammoniated completely in a single continuous stage with precipita-

tion of all the calcium and formation of only dicalcium phosphate when the correct amount of ammonia was added and the terminal pH was 4. Addition of more than the correct amount of ammonia in either one or two continuous stages also precipitated all the calcium, but the precipitate contained less phosphorus—much of it present as calcium phosphates more basic than dicalcium phosphate.

Similar results were obtained with an adjusted filtrate in which the net lime ratio was 2.03 and the fluorine ratio was 0.015. With an adjusted filtrate in which the net lime ratio was 2.05 and the fluorine ratio was 0.036, however, significant amounts of basic calcium phosphates were formed when the terminal pH was raised above 2 and more than 60% of the phosphorus was precipitated. A slurry from this filtrate that had been ammoniated to pH 2 was ammoniated to pH 3.5 in a second continuous stage to precipitate the rest of the phosphorus without formation of much basic phosphate.

An unadjusted extract with a net lime ratio of 4.04 and a fluorine ratio of 0.013 could not be ammoniated in a single continuous stage past a pH of 1.5 without precipitation of basic calcium phosphate. At pH 1.5 90% of the ammonia requirement had been added and 80% of the phosphorus was precipitated. The slurry was ammoniated in one more continuous stage to precipitate the rest of the phosphorus at pH 4 by addition of a total of 110% of the ammonia requirement, but 10 to 20% of the phosphorus in the combined precipitate was in the form of basic calcium phosphates. Addition of carbon dioxide during the second stage did not prevent the precipitation of basic phosphates.

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FERTILIZER NITROGEN ANALYSES

Apparent Loss of Organic Nitrogen in Fertilizers Containing Urea and Natural Organics

SPECIALTY FERTILIZERS with a fixed percentage of organic nitrogen, such as 10-6-4 fertilizer, used for golf courses, usually contain organic by-products known as natural organics. The latter are the source of both the

water-insoluble organic and of the water-soluble organic nitrogen. Urea is used to increase the content of the water-soluble organic nitrogen.

Explanations were sought for the unexpectedly low percentages of organic nitrogen reported frequently by one company making such fertilizers. Erroneous weighing of the ingredients or

segregation was not considered a sufficient reason for the analyses consistently lacking a few tenths of a per cent of organic nitrogen. Fertilizer grade urea is known to be practically free from mineral nitrogen as supplied by nitrates and ammonium salts. It had to be determined, whether the results indicated errors in the analytical procedure, or

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