Compounds in Nitric Phosphates

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The water-insoluble compounds in nitric phosphates were identified and their amounts determined by quantitative x-ray analysis. The apatite formed on ammoniation of the initial acidulate was fluorapatite, and both the amount and the solubility of the apatite in ammonium citrate solutions increased with a rise in the pH at which it was formed. The citrate solubility of the apatite was inversely related to its crystallite size and to the ratio of sample to citrate solution. The apatite in granular nitric phosphates is very finely divided and is significantly soluble in citrate solution, but the relationship between the citrate solubility of an apatite and its agronomic value has not been demonstrated.

Nitric phosphate fertilizers produced from phosphate ore, nitric acid, and ammonia may gain in commercial importance because of the shortage of sulfur. Solid nitric phosphate fertilizers have been produced in several countries for some 30 years, and nitric phosphate slurry fertilizers have been developed recently (Grace, 1965; Nabiev and Ibragimova, 1963; Silverberg *et al.*, 1966). When a nitric acid acidulate of phosphate ore is ammoniated, calcium from the ore leads to formation of dicalcium phosphate and apatite, and the relative amounts of these compounds depend upon the manner and degree of ammoniation as well as upon the initial composition of the acidulate.

When tested alone, apatite was a very poor source of phosphorus for plants on acid soils and its effectiveness decreased with rising pH until it was not significantly better than the no-phosphorus control on alkaline soils (Terman *et al.*, 1958). In tests of nitric phosphates, however, particularly those containing considerable amounts of water-soluble phosphates, the effects of the water-soluble phosphates almost completely mask those of the water-insoluble phosphates in the same fertilizer (Terman and Lancaster, 1965). The agronomic value of the apatite in a nitric phosphate thus has not been conclusively evaluated. Although the agronomic value may be related inversely to the crystallite size, as is the citrate solubility, this relationship has not been demonstrated.

In a study of the ammoniation reactions of nitric phosphate extracts of phosphate rocks, Brosheer and Lenfesty (1958) relied almost entirely on chemical analysis in estimating the amounts of the different water-insoluble compounds; properties of the apatite were not studied thoroughly. In the study described here, the solid-phase compositions of the water-insoluble portions of slurry and granular nitric phosphate fertilizers were determined by quantitative x-ray analysis (Ando *et al.*, 1965b), supplemented by petrographic and infrared examinations and chemical analyses. As the products contained apatites of different crystal sizes and citrate solubilities, synthetic apatites were prepared in the laboratory, and composition, crystal size, and citrate solubility, as affected by conditions of preparation, were studied for comparison with the properties of the apatites separated from the nitric phosphates.

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METHODS AND MATERIALS

Quantitative x-ray analysis was made by the method of Ando *et al.* (1965b). The approximate crystal sizes of the apatite were determined by the method of Rau (1962). Citrate solubility was measured both by the AOAC method (Association of Official Agricultural Chemists, 1965) and by the alkaline citrate method of Brabson and Burch (1964).

Slurry Fertilizers. The nitric phosphate slurry fertilizers described in Table I were prepared in the laboratory. In each preparation, 1200 grams of minus 20-mesh Florida pebble phosphate ore (47.5% CaO, 33.0% P_2O_5, 4.0% F, 1.5% Fe_2O_3, 1.2% Al_2O_3, 3.1% CO_2, and 5.7% SiO_2) was treated with 42% nitric acid in the amount to provide a mole ratio HNO_3:CaO of either 1.9 (tests SN, SK, SD, SP) or 1.1 (test SS). In most preparations, sulfuric or phosphoric acid was added to decrease the effective ratio of calcium to phosphate. The acidulates were ammoniated batchwise to pH 7.8 in 20 to 30 minutes with anhydrous ammonia; the maximum temperature ranged from 88° to 98° C.

The slurries were sampled at different degrees of ammoniation, and the pH was measured on samples cooled to room temperature. The slurries were filtered, and the water-insoluble fractions were washed with water and dried at 80° C. Most of the water-insoluble solids were separated from the slurries within 1 hour of their preparation, but some of the slurries were allowed to stand at room temperature for 42 days to study the changes during storage.

Table I. Composition of Nitric Phosphate Slurries

No.	Material[a]	Grade	Mole Ratio CaO : P_2O_5	Mole Ratio (CaO–SO_3) : P_2O_5
SN	None	10–10–0	3.65	3.65
SK	KCl, H_3PO_4	9–9–9	2.91	2.91
SD	H_2SO_4	12–10–0	3.65	3.28
SS	H_2SO_4	9–11–0	3.65	2.00
SP	H_3PO_4	12–16–0	2.00	2.00

[a] In addition to phosphate rock, HNO_3, and NH_3.

Granular Fertilizers. The granular nitric phosphates were products of two different processes that were under current study in TVA pilot and demonstration plants. The samples, which were taken at random from current production or from storage, were selected on the basis of their nominal grade without knowledge or control of the exact conditions of their preparation. The formulations of these materials are shown in Table II.

The major difference between the two processes, which had most effect on the composition of the products, was in the methods of ammoniation; the methods of granulation differed also, but these were presumed to have had no significant effect on the composition of the products. In one process, designated for convenience the multistage ammoniation process, the acidulate was ammoniated continuously and completely in a series of four neutralizer tanks from which it was discharged to a pug mill for granulation. In the other process, the two-stage ammoniation process, the acidulate was ammoniated to a pH below 2 in a single neutralizer tank from which it was discharged to a TVA drum ammoniator (Young *et al.*, 1962) where the ammoniation was completed abruptly and the product was granulated.

In general, the multistage process was operated slightly on the acid side to minimize the formation of citrate-insoluble phosphate, and the two-stage process was operated to yield a less acidic product that dried more readily in the drum granulator.

All the multistage products (samples A, B, and C) were produced in a pilot plant. Of the two-stage products, samples designated D were produced in a demonstration plant and those designated E and F were produced in a pilot plant.

The pH of each granular nitric phosphate was measured on a slurry of 10 grams of the product in 90 ml. of water.

Synthetic Apatites. Synthetic apatites that differed in composition and crystal size were prepared by the method described by Ando (1957) from 1*M* solutions of diammonium phosphate, ammonium fluoride, calcium nitrate, and ammonium nitrate. A mixture of 120 ml. of the phosphate solution, 0 to 50 ml. of the fluoride solution, and 5 to 25 ml. of concentrated aqueous ammonia was diluted to 200 ml. This solution and 200 ml. of the calcium nitrate solution were introduced simultaneously and at the same rate into ammonium nitrate solution (100 ml.). The temperature was kept at 80° C. in most preparations, and the mixture was stirred constantly. In one preparation, the precipitation was carried out at 25° C.

The crystal size of the apatite was influenced by the pH, rate of mixing of the reagents, and temperature of the precipitation. The pH of the product slurry ranged from 2.5 to 8.9, and the time in which the reagents were mixed ranged from 3 seconds to 20 minutes. The slurries were filtered, and the precipitates were washed with water and dried at 110° C., and the products (about 20 grams) were analyzed chemically and by x-ray. Apatites that had the largest crystallite size (Table III) dried as very fine powders; those that precipitated in the smallest crystals were colloidal and dried as hard caked masses. These caked precipitates and a sample of Florida phosphate ore were ground to minus 100-mesh for determinations of their citrate solubility and bulk volume.

The relative bulk volume was determined empirically by placing 3 to 4 grams of sample in a 10-ml. graduate and measuring the volume after tapping the cylinder lightly 30 times. The neutral-citrate solubility of the P_2O_5 was determined by treating 0.1-, 0.3-, and 1.0-gram samples with 100 ml. of neutral ammonium citrate solution.

Table II. Formulation of Granulated Nitric Phosphates

	Multistage Product			Two-Stage Product		
Material[a]	A	B	C	D	E	F
H_3PO_4[b]	X			X		X
H_2SO_4	X	X	X		X	
KCl		X			X	X
K_2SO_4			X			

[a] In addition to phosphate rock, HNO_3, and NH_3.
[b] Electric-furnace acid.

Table III. Synthetic Apatites

	Preparation			Composition, Wt. %			Moles/ Mole P_2O_5		Unit-Cell Dimensions, A.		Av. Crystal Size, A.		Bulk Volume,	Cit.-Sol. P_2O_5,[a] % of Total, Detd. on Indicated Wt. of Sample, G.		
No.	Temp., ° C.	Time, min.	pH	CaO	P_2O_5	F	CaO	F	a_0	c_0	a_0	c_0	Ml./G.	0.1	0.3	1.0
HA	80	20	8.7	53.2	41.2	0.0	3.28	0.00	9.43	6.88	450	1100	2.8	99.7	64.7	26.4
FA-1	80	10	8.8	52.7	39.9	3.6	3.34	0.68	9.39	6.88	300	670	2.6	86.6	45.0	17.2
FA-7	80	10	4.5	53.8	41.1	3.7	3.33	0.67	9.38	6.87	530	1000	1.7	55.2	24.6	10.2
FA-9	80	10	3.0	53.3	41.4	3.8	3.27	0.68	9.39	6.87	500	1100	1.7	48.0	24.4	10.4
FA-12[b]	80	0.05	3.8	53.4	40.8	3.7	3.33	0.68	9.38	6.88	200	500	1.2	63.6	35.3	11.8
FA-12[c]														87.9	51.8	27.6
FA-12[c]														84.1[d]	42.6[d]	...
FA-13[b]	25	0.05	7.0	52.0	40.9	3.6	3.23	0.66	9.38	6.88	100[e]	340	1.8	89.0	49.3	20.0
FA-13[c]														99.9	80.3	28.5
FA-13[c]														98.3[d]	51.9[d]	...
FA-14[b]	80	10	8.9	54.2	40.4	4.2	3.41	0.78	9.38	6.88	210	520	1.6	68.0	32.4	13.0
$Ca_5(PO_4)_3F$, stoichiometric				55.6	42.2	3.8	3.33	0.67	...	...	...	...	...	...	...	...
Florida phosphate rock				47.5	33.0	4.0	3.66	0.91	9.33	6.90	450	800	1.1	37.6	20.9	11.2

[a] Neutral-citrate solubility (Assoc. Offic. Agr. Chemists, 1965); each sample treated with 100 ml. of citrate solution.
[b] Caked on drying, ground to minus 100-mesh.
[c] Citrate solubility determined on undried sample.
[d] Alkaline-citrate solubility (Brabson and Burch, 1964).
[e] Approximate value.

To study the effect of caking on the citrate solubility, tests were made also on two samples of the small-crystal apatite that were recovered by decantation to avoid the caking and treated with citrate solution without drying. Aliquots of the slurries of these apatites that contained 0.1, 0.3, and 1.0 gram of apatite were filtered, washed with water, and treated with 100 ml. of neutral or alkaline ammonium citrate solution.

RESULTS

Nitric Phosphate Slurries. The distributions of the phosphate in the slurry fertilizers are shown in Table IV. Most of the P_2O_5 was present as anhydrous dicalcium phosphate and apatite, and the rest was present as water-soluble phosphates and gelatinous iron and aluminum phosphates. The effect of increasing ammoniation on the amount of apatite in the fresh slurries is shown in Figure 1.

Slurry SN, in which no adjustment was made of the ratio of lime to phosphate, was sampled at five degrees of ammoniation, and the water-insoluble compounds were filtered off about 40 minutes after sampling. At pH 2, 77% of the P_2O_5 was present as anhydrous dicalcium phosphate in 3- to 5-micron crystals, and no apatite was detected. The amount of dicalcium phosphate decreased markedly on further ammoniation to the pH range 3.0 to 3.7 with concomitant formation of apatite. Above pH 3.7, nearly all the P_2O_5 was in the form of apatite. The composition of the slurry ammoniated to pH 7.8 did not change appreciably during storage.

In slurry SK, to which potassium chloride and a small amount of phosphoric acid had been added, the formation of apatite was less rapid than in slurry SN; apatite formed gradually as the pH was raised from 3.5 to 8.2. The lower ratio of calcium to phosphate seemed to retard the conversion of dicalcium phosphate to apatite, and the presence of potash may also have delayed the conversion.

The formation of apatite was still slower when a small amount of sulfuric acid was added as in slurry SD, and a considerable amount of dicalcium phosphate was present

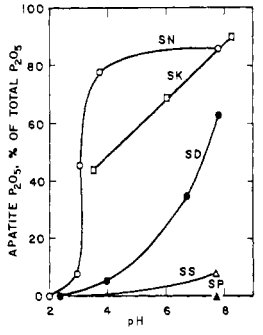

Figure 1. Formation of apatite on ammoniation of nitric phosphate slurries

Slurries sampled 30 minutes after preparation

Table IV. Phosphate Compounds in Nitric Phosphate Slurries

Sample	Age, Days	Age, Min.	pH	Composition, Wt. %: P_2O_5	Composition, Wt. %: $CaHPO_4$	Composition, Wt. %: Apatite	Distribution, %, of P_2O_5: $CaHPO_4$	Distribution, %, of P_2O_5: Apatite	Distribution, %, of P_2O_5: Other[a]	Cit.-Sol.[b] P_2O_5, % of Total
SN-1	...	40	2.0	10.1	15	0	77	0	23	100
SN-2	...	40	3.0	10.3	15	2	76	8	16	93
SN-3	...	40	3.1	10.3	8	11	41	46	13	87
SN-4	...	40	3.7	10.4	2	19	10	78	12	86
SN-5	...	40	7.8	10.3	1	21	5	86	9	85
SN-5	42	...	7.6	10.3	0	22	0	90	10	...
SK-1	...	60	3.5	9.6	8	10	44	44	12	91
SK-2	...	60	6.0	9.3	5	15	28	69	3	90
SK-3	...	60	8.2	9.9	0	21	0	90	10	81
SD-1	...	30	1.3	9.8	9	0	48	0	52	...
SD-2	...	30	1.9	9.8	15	0	80	0	20	...
SD-3	...	30	2.4	9.8	17	0	91	0	9	100
SD-4	...	30	4.0	9.9	16	1	85	4	11	100
SD-5	...	30	6.7	9.8	11	8	59	35	7	100
SD-6	...	30	7.8	10.1	6	15	31	63	6	100
SD-6	2	...	4.8	10.1	4	18	21	75	4	...
SD-6	42	...	3.8	10.1	2	20	10	83	7	...
SS	...	30	7.7	10.6	16	2	78	8	14	...
	1	...	6.4	10.6	13	6	64	24	12	90
	7	...	5.7	10.6	11	9	54	36	10	...
	21	...	5.5	10.6	10	10	49	40	11	...
	42	...	5.4	10.6	10	11	49	44	7	...
SP	...	30	7.7	16.5	29	0	92	0	8	100
	7	...	6.3	16.5	27	2	86	5	9	...
	21	...	6.0	16.5	25	4	79	11	10	...
	42	...	5.7	16.5	24	5	76	13	11	...

[a] Water-soluble phosphates and gelatinous iron and aluminum phosphates, by difference.
[b] Determined by AOAC procedure (Assoc. Offic. Agr. Chemists, 1965).

even at pH 7.8. Presumably, veneers of calcium sulfate on the dicalcium phosphate crystals delayed their conversion to apatite. During storage, the pH of the slurry (SD-6) dropped from 7.8 to 4.8 in 2 days and to 3.8 in 42 days with an increase of apatite and a decrease of dicalcium phosphate, and the apatite content approached that of SN-5, as shown in Figure 2.

Addition of a large amount of sulfuric acid to lower the mole ratio ($CaO–SO_3$):P_2O_5 to 2.00 (slurry SS) further delayed the conversion of dicalcium phosphate to apatite. On ammoniation to terminal pH 7.7, 78% of the P_2O_5 was present as dicalcium phosphate and only 8% as apatite; the sulfate was present as calcium sulfate hemihydrate. During storage, the pH fell gradually and some of the dicalcium phosphate was converted to apatite; the calcium sulfate hemihydrate altered to gypsum in the first few days and thereafter supplied calcium for formation of apatite from dicalcium phosphate. The aged slurry, however, contained only about half as much apatite as slurries SN-5 and SD-6, as shown in Figure 2.

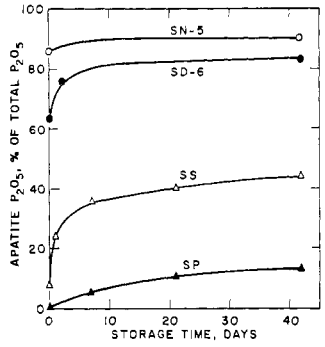

Figure 2. Increase of apatite content on storage of slurries initially ammoniated to pH 7.7

In slurry SP, where the mole ratio $CaO:P_2O_5$ was adjusted to 2.00 by addition of phosphoric acid, the crystals of dicalcium phosphate were larger (5 to 10 microns) than those in slurry SS (1 to 2 microns) and in slurry SN (3 to 5 microns); no apatite formed on ammoniation of slurry SP to pH 7.7, and only a small amount of apatite formed during storage.

Granular Nitric Phosphates. The chemical compositions and pH of the granular nitric phosphates are shown in Table V. The P_2O_5 in samples D-1 to -3 and F, which had mole ratios $CaO:P_2O_5$ of about 1.5, was 37 to 49% water-soluble and 0.6% or less neutral-citrate-insoluble. The alkaline-citrate insolubility of the P_2O_5 in samples D-1 and D-2 was 13.6 and 13.4%, respectively. The other samples had higher ratios $CaO:P_2O_5$, lower water solubility (17 to 29%), and higher neutral-citrate insolubility (2.5 to 5.1%) of the P_2O_5. The pH of the samples, as measured on 10% aqueous suspensions, ranged from 3.8 to 6.9; those made in the new demonstration plant (D-1 to -3) had the highest pH.

The compounds in the potash-free granular nitric phosphates are shown in Table VI. All the nitrate was present as ammonium nitrate (form IV) except in sample A which contained sulfate and in which a part of the nitrate was present as $2NH_4NO_3 \cdot (NH_4)_2SO_4$. Sample A had the lowest pH (4.6) and contained the largest amount of dical-

Table V. Chemical Composition of Granulated Nitric Phosphates

	Multistage Process			Two-Stage Process					
Sample	A	B	C	D-1	D-2	D-3	E-1	E-2	F
Grade ($N–P_2O_5–K_2O$)	17–20–0	11–11–11	12–11–12	20–20–0	20–20–0	20–20–0	11–11–11	11–11–11	15–15–15
Composition, wt. %									
N									
Total	17.7	11.5	12.2	22.1	22.5	23.0	11.1	11.9	15.2
NH_3–N	9.1	6.0	4.6	12.6	12.5	13.0	5.8	6.1	8.8
P_2O_5									
Total	20.9	11.9	11.7	20.6	19.4	19.3	11.9	11.9	16.2
W.S.[a]	3.6	2.1	2.3	10.0	7.4	7.8	3.3	3.4	6.0
C.I.[a]	0.8	0.5	0.6	<0.1	0.1	<0.1	0.4	0.3	0.1
K_2O	...	11.1	12.1	...	...	...	11.1	12.9	15.9
CaO	16.7	17.6	16.8	11.0	11.1	11.0	15.7	15.8	9.6
SO_3	4.9	10.1	11.1	...	...	...	9.8	10.1	...
Mole ratio									
$CaO:P_2O_5$	2.0	3.8	3.6	1.4	1.5	1.5	3.4	3.4	1.5
$(CaO–SO_3):P_2O_5$	1.6	2.2	2.0	1.4	1.5	1.5	1.9	1.9	1.5
pH[b]	4.6	4.6	4.9	6.3	6.6	6.9	3.8	4.5	5.3
Distribution of P_2O_5, %									
$CaHPO_4$	78	66	76	35	43	40	71	44	45
Apatite	8	21	15	18	15	20	18	25	13
Other[c]	14	13	9	47	42	40	11	31	42
Fraction, %, of apatite									
P_2O_5 cit.-insol.[a]	48	21	34	<3	3	<3	19	10	5

[a] Determined by AOAC procedures (Assoc. Offic. Agr. Chemists, 1965).
[b] Measured on 10% aqueous suspension.
[c] By difference.

Table VI. Compounds in Potash-Free Granulated Nitric Phosphates

Sample Grade (N–P_2O_5–K_2O)	A 17–20–0	D-1 20–20–0	D-2 20–20–0	D-3 20–20–0
Compound, wt. %				
NH_4NO_3, form IV	43	51	53	52
$2NH_4NO_3 \cdot (NH_4)_2SO_4$	3	0	0	0
$(NH_4)_2SO_4$	2	0	0	0
$NH_4H_2PO_4$	6	6	4	3
$(NH_4)_2HPO_4$	0	8	10	12
$CaHPO_4$	31	14	16	15
Apatite	4	9	7	9
$CaSO_4 \cdot 2H_2O$	4	0	0	0
	93	88	90	91

cium phosphate and the smallest amount of apatite. Samples D-1, D-2, and D-3 had pH values of 6.3, 6.6, and 6.9, respectively, and contained diammonium phosphate in amounts that increased as the pH was raised. All three samples contained considerable amounts of apatite.

The compounds in the granular nitric phosphates containing potassium are shown in Table VII. Most of the potassium chloride had reacted with ammonium salts to form ammonium chloride, potassium nitrate, and the solid solutions ammonium potassium nitrate, ammonium potassium sulfate, and monoammonium monopotassium phosphate. The double salt $NH_4NO_3 \cdot 2KNO_3$ was present in all these nitric phosphates.

Sulfate was present mainly as calcium sulfate and partly as ammonium potassium sulfate and $2NH_4NO_3 \cdot (NH_4)_2SO_4$. The double salt $NH_4H_2PO_4 \cdot 4CaSO_4$ (Ando *et al.*, 1965a) was present in products B and C, both of which were made by the multistage process. Dicalcium phosphate comprised 10 to 17% and apatite 4 to 17% of the samples. The pH of all the samples was below 5.3 and no diammonium phosphate was present.

Synthetic Apatites. The compositions and properties of a sample of hydroxyapatite (HA) and six samples of fluorapatite (FA-1 to -14) are shown in Table III with those of stoichiometric fluorapatite, $Ca_5(PO_4)_3F$, and a sample of Florida phosphate rock.

An excess of fluorine was used in the preparation of FA-14. All the other precipitates had nearly the stoichiometric compositions of the apatites, except that they contained 3 to 4% of water which could be driven off gradually by heating to 600° C. All the preparations consisted only of apatite except FA-14 in which a trace of calcium fluoride was detected petrographically.

Fluorapatite and hydroxyapatite can be distinguished by the small but significant differences in their unit-cell dimen-

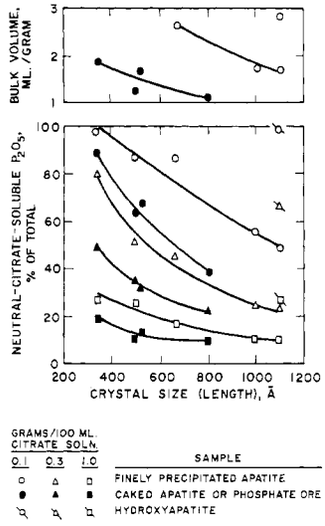

Figure 3. Effects of crystal size and bulk volume on neutral-citrate solubility of apatites

Table VII. Compounds in Granulated Nitric Phosphates Containing Potassium

Sample Grade (N–P_2O_5–K_2O)	B 11–11–11	C 12–11–12	E-1 11–11–11	E-2 11–11–11	F 15–15–15
Compound, wt. %					
NH_4Cl	17	0	11	12	20
KCl	2	0	4	0	2
$(NH_4,K)NO_3$[a]	0	34[b]	20[c]	10[c]	5[c]
$NH_4NO_3 \cdot 2KNO_3$	17	18	16	12	30
KNO_3	10	0	4	7	6
$2NH_4NO_3 \cdot (NH_4)_2SO_4$	0	0	3	5	0
$(NH_4,K)_2SO_4$	0	0	3[d]	8[d]	0
$(NH_4,K)H_2PO_4$	2[e]	2[e]	2[e]	3[f]	8[f]
$NH_4H_2PO_4 \cdot 4CaSO_4$	8	4	0	0	0
$CaHPO_4$	15	17	16	10	14
Apatite	6	4	5	7	5
$CaSO_4$	2	0	5	7	0
$CaSO_4 \cdot 0.5H_2O$	0	0	8	3	0
$CaSO_4 \cdot 2H_2O$	8	15	0	0	0
Total	87	94	97	84	90

[a] Present as NH_4NO_3 form III.
[b] 65% NH_4NO_3, 35% KNO_3, by weight.
[c] 70% NH_4NO_3, 30% KNO_3, by weight.
[d] 50% $(NH_4)_2SO_4$, 50% K_2SO_4, by weight.
[e] 90% $NH_4H_2PO_4$, 10% KH_2PO_4, by weight.
[f] 95% $NH_4H_2PO_4$, 5% KH_2PO_4, by weight.

sions. The unit-cell dimensions of the apatites precipitated in the presence of fluorine are those of fluorapatite, regardless of the pH at which they were formed. Lowering of the pH of precipitation, however, increased the crystal size of the fluorapatite, as shown by samples FA-1, -7, and -9. Another sample prepared at pH 2.5 had the average crystal size a = 800 A. and c = 1700 A. When prepared rapidly at high pH and low temperature, the crystals were small, as in FA-13. Samples FA-12, -13, and -14 which had crystals smaller than about 500 by 200 A. were colloidal and caked into hard masses on drying at 110° C.

As shown in Figure 3, both the bulk volume and the neutral-citrate solubility increased with decrease in crystal size of the apatite. Hydroxyapatite had a larger bulk volume and higher citrate solubility than fluorapatite with about the same crystal size (FA-9). Caked samples of fluorapatite had smaller bulk volumes and lower citrate solubilities than uncaked samples of the same preparation and showed good agreement with phosphate ore in the relationships of the crystal size to bulk volume and citrate solubility.

The neutral-citrate solubility is related also to the ratio of the sample to citrate, as is shown in Figure 3. The citrate solubility of a sample with average crystal length 340 A., as

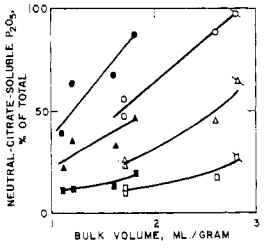

Figure 4. Effect of bulk volume on neutral-citrate solubility of apatites

Symbols same as in Figure 3

determined on undried material, was practically 100% with 0.1 gram of sample, but about 80% with 0.3 gram and about 45% with 1.0 gram of sample.

Although the alkaline-citrate solubility of fluorapatite is lower than the neutral-citrate solubility, that of sample FA-13 was 98% when 0.1 gram was treated with citrate solution without drying.

The citrate solubility increased with increase of the bulk volume, as shown in Figure 4. Hydroxyapatite and fluorapatite which did not cake fall on practically the same curve, and caked fluorapatite and phosphate ore fall on another curve. These relationships show that the bulk volume, which reflects the effective surface area, correlates better than the chemical composition with the neutral-citrate solubility of an apatite. The higher citrate solubility of the caked samples than of the fine-powder samples with the same bulk volume results from the marked difference in crystal size—for example, when the bulk volume was 1.8, the average length of the crystals of caked fluorapatite was 340 A. and that of the crystals of uncaked fluorapatite was 1000 A.

Formation and Properties of Apatite in Nitric Phosphates. The chemical compositions of the water-insoluble fractions of a nitric phosphate slurry at different stages of ammoniation are shown in Table VIII, together with the dicalcium phosphate and apatite contents as determined by x-ray analysis. As shown in previous studies of the ammoniation of nitric phosphates (Brosheer and Lenfesty, 1958), practically all the fluorine, iron, and aluminum was precipitated early in the ammoniation while considerable calcium and phosphate remained in solution. The form in which the fluorine was precipitated initially could not be determined, but apparently the fluorine was present as a reactive amorphous compound and participated in formation of apatite in later stages of the ammoniation. The amount of fluorine in phosphate rock is in excess of that required to form fluorapatite with all the phosphate.

Table VIII. Chemical Composition of Water-Insoluble Fractions of Nitric Phosphates

		Composition, Wt. %						
No.	pH	CaO	P_2O_5	F	Fe_2O_3	Al_2O_3	$CaHPO_4$[a]	Apatite[a]
SN-1	2.0	37.9	39.1	5.1	2.0	2.1	66	0
SN-2	3.0	38.7	39.5	4.7	1.8	1.8	61	8
SN-3	3.1	44.1	38.0	4.5	1.7	1.7	32	44
SN-4	3.7	44.8	36.6	4.1	1.7	1.7	7	69
SN-5	7.8	46.5	35.3	4.1	1.6	1.6	3	71

[a] Determined by x-ray analysis. These fractions also contain gelatinous iron and aluminum phosphates and calcium fluoride.

Table IX. Properties of Apatites Separated from Nitric Phosphates

	Unit-Cell Dimensions, A.		Average Crystal Size, A.			
No.	a_0	c_0	a	c	pH when Formed	Cit.-Sol. P_2O_5,[a] % of Total
SN-4	9.38	6.88	210	420	3.0–3.7	81
SN-5	9.38	6.88	<200	360	3.0–7.8	83
SN-5[b]	9.38	6.88	200	400	...	...
SN-5[c]	9.38	6.89	230	480	...	...
SD-6	9.38	6.88	<200	300	4.0–7.8	100

[a] Determined by procedure of Assoc. Offic. Agr. Chemists (1965).
[b] Alkaline-citrate-insoluble fraction (Brabson and Burch, 1964).
[c] Neutral-citrate-insoluble fraction (Assoc. Offic. Agr. Chemists, 1965).

The unit-cell dimensions, average crystal size, and neutral-citrate solubility of the apatites in several nitric phosphate slurries are shown in Table IX. The unit-cell dimensions are those of fluorapatite, and this identification was confirmed by infrared examination. Since the apatites in all the nitric phosphates were essentially fluorapatite, differences in their citrate solubilities cannot be ascribed to differences in composition.

The neutral citrate solubility of apatite increased with decrease in crystal size. Although the difference between the citrate solubilities of samples SN-4 and SN-5 is small, the data in Tables VIII and IX show that all the apatite that was formed in the ammoniation from the stage of SN-4 to that of SN-5 was citrate soluble. Since the amount of apatite in SN-4 was 91% of that in SN-5, the crystals of the last 9% of the apatite in SN-5, which were formed between pH 3.7 and pH 7.8, had to be extremely small to lower the average crystal size from that of SN-4 to SN-5. The average crystals of the apatite in sample SD-6, all of which were formed above pH 4, were smaller than those of SN-5 and were completely citrate soluble. Although the average crystal size of SD-6 does not differ much from that of SN-5, probably SD-6 contained no large crystals that formed at low pH and were less soluble.

Further evidence that the citrate solubility of apatite is related to its crystal size is provided by the crystal sizes of the citrate-insoluble fractions of sample SN-5. Alkaline-citrate extraction dissolves the smallest apatite crystals first, so that the average crystal size of the residue is larger than that of the initial sample. Neutral-citrate extraction also dissolves the smallest crystals first, even when it follows an alkaline-citrate extraction, so that there is further increase in average crystal size. Throughout these extractions, however, the chemical composition and crystallographic properties of the residue remain the same as those of the initial sample.

The crystals of apatite in the granular material produced in the two-stage process were much smaller than those of the apatite in the nitric phosphate slurries or in the granular material produced in the multistage process, and this difference reflects the difference in the ammoniation steps of the different processes. The crystals of the apatite in nitric phosphate D-1 (Table V), for example, were smaller than 200 A. and were about 97.5% soluble in neutral ammonium citrate solution. The much larger crystals of apatite in the multistage products were only 55 to 80% soluble in neutral ammonium citrate solution.

The effect of the pH of formation on the citrate solubility of the apatite in the two-stage products is shown in Figure 5. The increase in citrate solubility with rise in the pH of formation presumably reflects a decrease in the crystal size of the apatite.

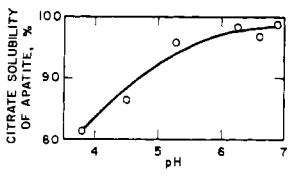

Figure 5. Effect of pH of formation on neutral-citrate solubility of apatites in two-stage nitric phosphates

As shown in Figure 6, the fraction of the P_2O_5 present as apatite or as citrate-insoluble P_2O_5 increases with increase in the ratio $(CaO–SO_3):P_2O_5$. Products prepared in the two-stage process contained more apatite than products with the same effective ratio $CaO:P_2O_5$ that were prepared at the same pH in the multistage process, but the neutral citrate-insoluble P_2O_5 in the products of the two-stage process was less than that in the products of the multistage process.

In the multistage process, the initial acidulate slurry was ammoniated in stages in a series of four tanks to prevent local overammoniation and to minimize the formation of apatite. The reaction time was fairly long, and the crystals of apatite, although small in amount, grew relatively large and were insoluble in neutral citrate solution. In the two-stage process, however, the acidulate slurry was ammoniated in a preneutralizer only to pH 2, at which apatite is not formed, and then abruptly ammoniated to a terminal pH of 4 or above. The amount of apatite formed was relatively large, but the effective pH of precipitation was so high, and the ammoniation was so rapid, that the crystals of apatite were very small and were readily soluble in citrate solution.

DISCUSSION

The amount of apatite in a nitric phosphate is decreased by decreasing the effective ratio of lime to phosphate in the initial acidulate. Addition of phosphoric acid to lower the mole ratio $CaO:P_2O_5$ to 2.00 prevented the formation of apatite in a bench-scale batch ammoniation to pH 7.8. Sulfuric acid was less effective than phosphoric acid because the initially precipitated calcium sulfate slowly redissolved to supply calcium for the conversion of dicalcium phosphate to apatite when the ammoniation had been carried to a high pH.

In the granular nitric phosphates produced in the continuous plant-scale operations, a considerable amount of

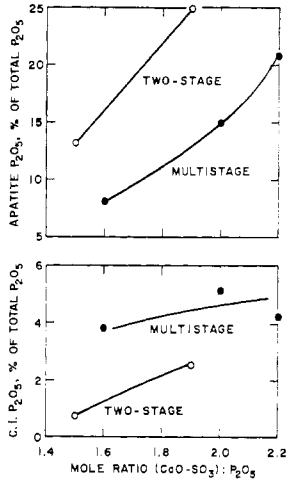

Figure 6. Effect of mole ratio $(CaO–SO_3):P_2O_5$ on amount of apatite and citrate solubility of granulated nitric phosphates prepared at pH 4.5 to 5.3

apatite formed even when the mole ratio $CaO:P_2O_5$ was adjusted to less than 2.0 by adding phosphoric acid and the acidulate was ammoniated to a pH in the range 4 to 7. There apparently were some factors in the plant-scale operations that promoted the formation of apatite. In the multistage process, the reaction time was much longer than in the laboratory batch ammoniations. The reaction temperature also was higher in the multistage process, and there was some indication that apatite is formed more readily at higher temperatures. The continuous operation of the plants may also be a factor: Apatite once formed acts as seeds which promote the formation of apatite during ammoniation in the neutralizer tanks of the multistage process and also in the two-stage process in which a large amount of fines is recycled to the ammoniator-granulator drum.

The rapid ammoniation in the drum of the two-stage process formed very small crystals of apatite that were almost completely citrate soluble. In the production of the nitric phosphate slurries, additions of small amounts of sulfuric acid also decreased the crystal size, thereby increasing the citrate solubility of the apatite.

The citrate solubility of very small crystals of synthetic apatite was decreased by the caking of the apatite during drying. The small crystals then tended to form hard lumps, as would occur on the drying of granular nitric phosphate fertilizer in the plant dryer. There was some indication that the neutral citrate solubility of apatite in the granular products was a little lower than that of apatite of the same crystal size in nitric phosphate slurry fertilizers that were not dried. The caking of the small crystals of apatite in fertilizers, however, should be less pronounced than that of synthetic apatites because of the presence of other crystalline compounds, and small crystals of apatite in fertilizers are usually highly soluble in neutral citrate solution.

Alkaline citrate solution dissolves less apatite than does neutral citrate solution, but the alkaline-citrate solubility was nearly 100% when 0.1 gram of fine crystals of apatite FA-13 that was not dried was treated with 100 ml. of the citrate solution. The alkaline-citrate solubility, however, is depressed by the presence of dicalcium phosphate (Brabson and Burch, 1964). The test with two samples, D-1 and -2, showed that only 20% of the apatite was dissolved in alkaline citrate solution although the crystals were very small and less than 0.2 gram of apatite (in 2 grams of sample) was treated. The low solubility apparently reflected the presence of dicalcium phosphate and the caking on drying.

The citrate solubility of apatite is a function of not only the crystal size and caking but also the ratio of apatite plus dicalcium phosphate to citrate solution. The apatite and dicalcium phosphate contents of fertilizers usually range from 0 to 30%. Citrate solubility therefore is a poor measure of the amount and reactivity of the apatite in a fertilizer when the water-insoluble residue from a standard amount of fertilizer is treated with a standard amount of the citrate solution. A more significant comparison would be obtained if the water-insoluble residues taken for the citrate extraction contained a standard amount of water-insoluble P_2O_5, a conclusion reported also by Brabson and Burch (1964).

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Received for review January 29, 1968. Accepted March 21, 1968.