

Ammoniation Reactions of Superphosphates

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Ordinary and concentrated commercial superphosphates were ammoniated to different degrees in a pilot-plant ammoniator, and the compounds in the products were identified and their amounts determined by quantitative x-ray and chemical analyses. At high degrees of ammoniation, more of the P_2O_5 was converted to apatite in ordinary superphosphate than in concentrated superphosphate because the calcium sulfate supplied calcium for the conversion. The apatite was fluorapatite, and its solubility in ammonium citrate solution was related inversely to its crys-

tallite size. Ammoniation reactions of the concentrated superphosphates were affected adversely by the relatively high content of complex iron and aluminum phosphates. An empirical basicity index aids in correlation of the products of ammoniation with the chemical compositions and amounts of the superphosphate and the ammoniating agent. Results of ammoniation in large-scale equipment were reproduced in laboratory apparatus when the temperature and moisture content of the superphosphate on the two scales were the same.

Investigators of the reactions that occur in the ammoniation of superphosphate have relied almost entirely on chemical analyses (including determinations of citrate solubility) in interpretation of their results (Hardesty and Ross, 1937; Hardesty *et al.*, 1943; Holmes, 1941; Keenen, 1930; Kumagai *et al.*, 1954; MacIntire and Hardin, 1940; MacIntire *et al.*, 1944; Panfilov, 1938; Payne and Webber, 1960; Taylor and Gurney, 1965; White *et al.*, 1935; Yates *et al.*, 1954). The products of ammoniation were assumed to be a few well-characterized crystalline phases that were formed by relatively simple reactions.

In the work described here, commercial superphosphates were ammoniated to different degrees in a pilot plant, and the products were examined by quantitative x-ray analysis (Ando *et al.*, 1965) to identify solid phases and determine their amounts. The examinations were supplemented by petrographic and infrared examinations, as well as by chemical analyses. From the results, an empirical basicity index was derived for correlating the chemical composition of the ammoniated superphosphate with the distribution of the compounds present at any degree of ammoniation.

In the course of this study, the authors discovered that concentrated superphosphates from current commercial production differ considerably from earlier materials, mainly in the higher content of complex iron and aluminum phosphates that are introduced in the wet-process phosphoric acids with which the superphosphates are prepared (Frazier and Lehr, 1967). The behavior of these complex phosphates during ammoniation and the factors affecting the formation of apatite were of particular interest in the study.

Superphosphates for examination were ammoniated in a pilot plant to ensure that the results of the ammoniations would be the same as those in commercial equipment. The difficulty of reproducing these results in

the laboratory is well known, and a study was made to determine the conditions under which laboratory ammoniations would yield the same results as large-scale ammoniations. Addition of supplemental heat and moisture in the laboratory apparatus yielded results comparable to those obtained in the pilot plant.

Material and Methods

Five superphosphates, all currently produced, commercial, nongranular materials were selected for ammoniation. The two ordinary superphosphates (A,B) contained about 20% P_2O_5 and 1.4% R_2O_3 ($Al_2O_3 + Fe_2O_3$), and the three concentrated superphosphates (C,D,E) contained about 46% P_2O_5 and 4% R_2O_3 . Chemical compositions of the superphosphates are shown in Table I.

The pilot-plant rotary-drum ammoniator (Yates *et al.*, 1954) was 3 feet in diameter and 6 feet long. Superphosphate was fed continuously to maintain a constant depth of bed with continuous discharge, and the ammoniating agent was introduced beneath the surface of the bed of superphosphate. All the ammoniated products were discharged through a rotary cooler; four of the

Table I. Chemical Compositions of Superphosphates

Composition, Wt. %	Ordinary Super- phosphate		Concentrated Superphosphate		
	A	B	C	D	E
P_2O_5					
Total	19.9	20.7	45.5	46.8	46.8
H ₂ O-sol. ^a	17.5	18.0	37.0	41.0	39.2
Cit.-insol. ^a	0.3	0.5	0.5	0.3	0.4
Free acid ^a	2.4	...	0.6	3.3	2.7
CaO	27.1	28.4	19.0	18.8	19.7
SO ₃	28.4	28.2	5.1	3.8	3.3
Fe ₂ O ₃	0.7	0.7	1.8	2.0	1.9
Al ₂ O ₃	0.6	0.7	2.5	1.3	1.9
Moisture	5.9	6.1	1.9	4.2	3.7

^a Determined by AOAC procedures (Assoc. Offic. Agr. Chemists, 1965).

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ammoniated superphosphates were not dried or granulated, but one, superphosphate E, was granulated in a rotary dryer and the cooled fines were recycled. The conditions of the ammoniations are shown in Table II.

Solid-phase compositions of the superphosphates and their ammoniated products were determined by quantitative x-ray analysis through application of previously reported calibration data (Ando *et al.*, 1965) and the calibrations of selected diffraction peaks of new compounds shown in Table III. Approximate crystallite sizes of the apatites were determined by the x-ray diffraction method of Rau (1962).

A pH value for each product was determined by suspending 10 grams of the solid in 90 ml. of water, allowing the mixture to settle for 15 or 20 minutes, and measuring the pH of the supernatant solution with a glass electrode and a commercial meter.

Composition of Superphosphates

The solid-phase compositions of the superphosphates are shown in Table IV. The ordinary superphosphates contained about 32% monocalcium phosphate monohydrate and 50 to 55% calcium sulfate, mainly anhydrite, CaSO₄. The concentrated superphosphates contained 60 to 65% monocalcium phosphate monohydrate and 15 to 20% iron and aluminum phosphates.

The relatively large amounts of iron and aluminum phosphates in the concentrated superphosphates apparently were introduced mainly in the unclarified wet-process phosphoric acid or acid sludges used in their preparation; (Fe,Al)₃KH₁₄(PO₄)₈·4H₂O is a major component and (Fe,Al)₃KH₈(PO₄)₆·6H₂O a minor component of the sludge in wet-process acid (Lehr *et al.*, 1966). The compound (Fe,Al)₃KH₈(PO₄)₆·6H₂O also forms in ordinary superphosphate from the iron and aluminum compounds in the phosphate ore, and the substitution of H₃O⁺ for K⁺ in this material is useful in identifying its source. The compound Ca(Fe,Al)H(PO₄)₂·4H₂O appears to be a product of the reaction of the acidic calcium phosphate solution with the iron and aluminum sludge phases (Frazier and Lehr, 1967). All these complex iron and aluminum phosphates are insoluble in water but soluble in neutral ammonium citrate solution.

Ammoniated Ordinary Superphosphate. The chemical compositions of the ammoniated ordinary superphosphates are shown in Table V, and the solid-phase compositions are shown in Table VI. The distributions of the phosphorus compounds are shown in Figure 1,

Table III. Calibration of X-Ray Diffraction Peaks of Fertilizer Compounds

(Pattern determined with CuK α radiation, $\lambda = 1.5405$ A.)

Compound	$2\theta^\circ$	I/I_s^a
Ca(H ₂ PO ₄) ₂ ·H ₂ O	7.4	0.45
	22.8	0.41
Ca ₂ H ₇ NH ₄ (PO ₄) ₄ ·2H ₂ O	7.3	0.41
	20.9	0.35
Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	24.0	0.26
(Fe,Al) ₃ KH ₁₄ (PO ₄) ₈ ·4H ₂ O	10.0	2.78
(Fe,Al) ₃ KH ₈ (PO ₄) ₆ ·6H ₂ O	12.3	0.38
Ca(Fe,Al)H(PO ₄) ₂ ·4H ₂ O	14.0	0.60

^a Ratio of height of peak to height of 36.8° peak of spinel in mixtures containing equal weights of compound and spinel.

Table IV. Solid-Phase Compositions of Superphosphates

	Composition, Weight %				
	Ordinary		Concentrated		
	A	B	C	D	E
Ca(H ₂ PO ₄) ₂ ·H ₂ O	31	33	63	64	63
CaHPO ₄	0	0	2	1	1
Apatite	0	0	1	1	1
(Fe,Al) ₃ KH ₁₄ (PO ₄) ₈ ·4H ₂ O	0	0	4	5	3
(Fe,Al) ₃ KH ₈ (PO ₄) ₆ ·6H ₂ O	2	5	10	2	1
Ca(Fe,Al)H(PO ₄) ₂ ·4H ₂ O	0	0	2	8	14
CaSO ₄	40	41	2	3	3
CaSO ₄ ·0.5H ₂ O	11	7	4	4	2
CaSO ₄ ·2H ₂ O	3	5	2	0	0
Total	87	91	90	88	88

and those of the sulfur compounds are shown in Figure 2.

In the first stage of the ammoniation of superphosphate A with anhydrous ammonia, monocalcium phosphate monohydrate was converted rapidly to Flatt's salt, Ca₂NH₄H₇(PO₄)₄·2H₂O (Flatt and Brunisholz, 1951), which on further ammoniation decomposed into a mixture of monoammonium phosphate, anhydrous dicalcium phosphate, and apatite. As ammoniation continued, the amount of dicalcium phosphate remained constant, but the amount of monoammonium phosphate decreased and that of apatite increased in direct proportion to the amount of ammonia added. The decrease in monoammonium phosphate resulted from its reaction with calcium sulfate to form apatite. The hydrated

Table II. Conditions of Ammoniation

Condition	Ordinary Superphosphate		Concentrated Superphosphate		
	A	B	C	D	E
Particle size, mesh, of feed	-10	-10	-10	-6	-6
Bed depth, inches	9	9	4	9	9
Ammoniating agent	NH ₃	Soln. ^a	NH ₃	NH ₃	NH ₃
H ₂ O added, % of charge	0	0	2-3 ^b	2-3 ^b	20-60 ^c
Granulation	No	No	No	No	Yes

^a Ammoniating solution containing 25% NH₃, 69% NH₄NO₃, 6% H₂O.

^b Added when ammoniation was 3.5 lb. NH₃/unit P₂O₅ or more, to minimize loss of ammonia.

^c Added to dryer, to which cooled fines were recycled, for granulation.

Table V. Chemical Composition of Ammoniated Superphosphates

Composition, Weight %								
N	P ₂ O ₅			Moisture	Degree of Ammoniation ^b	pH ^c	Basicity Index	
	Total	W.S. ^a	C.I. ^a					
Ordinary superphosphate plus anhydrous ammonia								
A	...	19.9	17.5	0.3	5.9	...	2.7	2.9
A-1	1.4	20.0	14.8	0.3	4.5	1.7	3.4	3.5
A-2	2.0	20.0	13.2	0.3	4.6	2.5	3.8	3.8
A-3	2.7	19.5	11.1	0.6	4.9	3.4	4.3	4.2
A-4	3.4	19.8	9.0	1.3	3.6	4.2	4.6	4.5
A-5	4.0	20.3	8.4	2.0	2.0	4.9	4.9	4.8
A-6	4.8	19.5	5.4	2.3	1.9	6.1	5.1	5.2
A-7	5.2	19.7	3.9	2.3	1.7	6.5	5.3	5.4
Ordinary superphosphate plus ammoniating solution								
B	...	20.7	18.0	0.5	6.1	...	2.7	2.9
B-4	6.9 ^d	18.0	7.8	1.4	4.0	4.9	4.4	4.7
B-6	8.7 ^e	17.5	5.1	1.7	2.9	6.1	4.6	4.9
Concentrated superphosphates plus anhydrous ammonia								
C	...	45.5	37.0	0.5	1.9	...	2.8	2.6
C-1	1.9	44.8	32.3	0.8	1.4	1.0	3.3	3.3
C-2	4.0	44.6	25.0	0.9	1.3	2.2	3.6	4.3
C-3	5.5	44.6	19.9	1.0	1.3	3.0	5.2	5.2
C-4	6.8	42.8	20.4	1.3	2.0	3.9	6.2	6.0
C-5	7.3	41.9	20.3	1.4	3.2	4.3	6.4	6.3
D	...	46.8	41.0	0.3	4.2	...	2.6	2.3
D-2	4.1	47.3	27.4	0.8	1.4	2.1	3.9	4.2
D-4	6.6	45.9	22.3	0.9	1.6	3.5	5.9	5.5
E	...	46.8	39.2	0.4	3.7	...	2.7	2.4
E-1	3.4	45.7	28.7	0.5	3.2	1.8	3.7	4.1
E-3	5.0	45.7	21.3	0.6	1.4	2.7	4.8	4.7
E-4	6.0	45.4	22.1	1.0	1.8	3.2	5.7	5.3

^a Water-soluble and citrate-insoluble P₂O₅ determined by AOAC procedures (Assoc. Offic. Agr. Chemists, 1965).

^b Pounds of NH₃ per unit of P₂O₅.

^c Includes 2.2% NO₂ nitrogen.

^d Includes 1.7% NO₂ nitrogen.

^e Determined on 10% aqueous suspension.

double salt Ca(NH₄)₂(HPO₄)₂·2H₂O, which appeared toward the end of the ammoniation, was replaced by diammonium phosphate in the final stage as moisture was lost by evaporation. The maximum degree of ammoniation of the ordinary superphosphate obtainable without considerable (10%) loss of ammonia was 6.5 pounds of ammonia per unit of P₂O₅.

The anhydrous calcium sulfate in the ordinary superphosphate was present as very small (1-micron), highly reactive crystals. As shown in Figure 2, the amount of anhydrite began to decrease when apatite appeared (Figure 1). Ammonium syngenite, Ca(NH₄)₂(SO₄)₂·H₂O, appeared rather late in the ammoniation but then decreased as water was lost by evaporation and reacted to form ammonium sulfate and apatite. Calcium sulfate hemihydrate appeared to be stable during the ammoniation, but gypsum disappeared early in the ammoniation, presumably by conversion to apatite and ammonium syngenite.

The sequence of reactions when superphosphate B was treated with ammoniating solution was practically the same as that when superphosphate A was treated

with anhydrous ammonia, but a higher degree of ammoniation with the solution than with anhydrous ammonia was required to produce a given solid-phase composition. Thus, ammoniation with anhydrous ammonia to 4.2 and 4.9 pounds of ammonia per unit of P₂O₅ gave practically the same distribution of phosphate compounds as ammoniation with the solution to 4.9 and 6.5 pounds of ammonia per unit of P₂O₅, respectively.

The difference in the results with the two ammoniating agents was primarily the behavior of the sulfate compounds. In ammoniation with the solution, nearly all the ammonium nitrate combined with ammonium sulfate to form the double salts 3NH₄NO₃·(NH₄)₂SO₄ and 2NH₄NO₃·(NH₄)₂SO₄. Anhydrite was more reactive when the solution was used, and a larger amount of Ca(NH₄)₂(SO₄)₂·H₂O was formed from the water added with the solution.

Ammoniated Concentrated Superphosphate. The chemical compositions of the ammoniated concentrated superphosphates are shown in Table V, and the solid-phase compositions are shown in Table VI. The dis-

Table VI. Compounds in Ammoniated Superphosphates

	Composition, Weight %																		
	Ordinary Superphosphates								Concentrated Superphosphates										
	A-1	A-2	A-3	A-4	A-5	A-6	A-7	B-4	B-6	C-1	C-2	C-3	C-4	C-5	D-2	D-4	E-1	E-3	E-4
Ca(H ₂ PO ₄) ₂ ·H ₂ O	3	0	0	0	0	0	0	0	23	0	0	0	0	0	0	4	0	0	
Ca ₂ NH ₄ H ₇ (PO ₄) ₄ ·2H ₂ O	20	13	0	0	0	0	0	0	24	9	0	0	0	11	0	15	0	0	
NH ₄ H ₂ PO ₄	5	9	15	13	10	4	2	11	6	9	28	28	18	12	31	26	24	32	30
(NH ₄) ₂ HPO ₄	0	0	0	0	0	1	3	0	0	0	0	12	19	0	9	0	0	4	
Ca(NH ₄) ₂ H(PO ₄) ₂ ·H ₂ O	0	0	0	1	3	2	1	0	3	0	0	2	4	2	0	4	0	4	3
CaHPO ₄	2	4	7	8	7	8	8	9	8	12	29	31	26	23	29	30	23	32	32
Apatite	0	3	9	12	17	21	27	12	17	2	4	7	12	14	4	8	3	4	6
(NH ₄) ₂ SO ₄	0	0	0	2	6	11	15	0	0	0	0	2	4	6	3	4	0	1	1
Ca(NH ₄) ₂ (SO ₄) ₂ ·H ₂ O	0	3	5	11	8	6	4	13	18	0	0	0	0	0	0	0	1	2	
CaSO ₄	40	37	36	33	29	23	20	25	18	2	2	1	0	2	1	2	1	1	
CaSO ₄ ·0.5H ₂ O	9	10	9	8	10	10	9	6	3	4	3	2	1	0	3	2	1	1	
CaSO ₄ ·2H ₂ O	3	2	1	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	
NH ₄ NO ₃	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	
3NH ₄ NO ₃ ·(NH ₄) ₂ SO ₄	0	0	0	0	0	0	0	12	11	0	0	0	0	0	0	0	0	0	
2NH ₄ NO ₃ ·(NH ₄) ₂ SO ₄	0	0	0	0	0	0	0	9	0	0	0	0	0	0	0	0	0	0	
(Fe,Al) ₃ KH ₃ (PO ₄) ₈ ·4H ₂ O	0	0	0	0	0	0	0	0	0	3	1	0	0	0	1	0	1	0	
(Fe,Al) ₃ KH ₃ (PO ₄) ₆ ·6H ₂ O	0	0	0	0	0	0	0	0	0	5	0	0	0	0	0	0	0	0	
Ca(Fe,Al)H(PO ₄) ₂ ·4H ₂ O	0	0	0	0	0	0	0	0	0	1	0	0	0	0	5	3	8	4	
Total	82	81	82	88	90	86	89	90	93	86	77	74	78	76	89	87	81	82	83

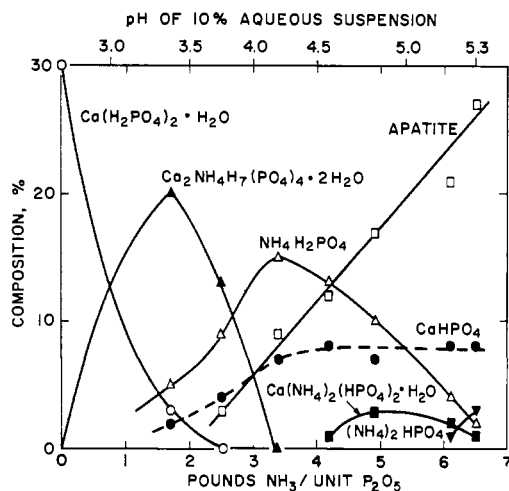


Figure 1. Phosphorus compounds in ammoniated ordinary superphosphate

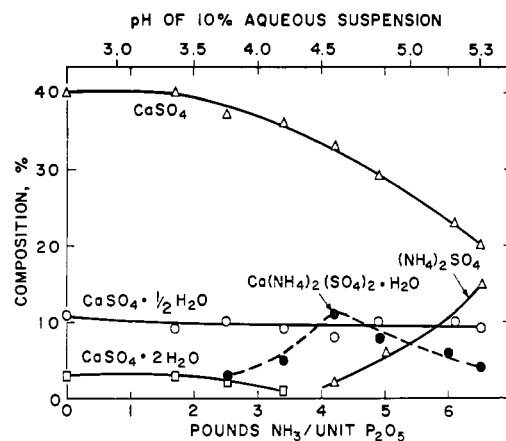


Figure 2. Sulfur compounds in ammoniated ordinary superphosphate

tributions of the compounds in the ammoniation of superphosphate C are shown in Figure 3. The maximum amount of ammoniation of the concentrated superphosphates without considerable loss of ammonia was about 4 pounds of NH₃ per unit of P₂O₅.

In the ammoniation of concentrated superphosphates, the sequence of reactions involving monocalcium phosphate monohydrate was the same as that in the ammoniation of ordinary superphosphate, but a given reaction occurred at a lower degree of ammoniation (pounds of NH₃ per unit of P₂O₅) of the concentrated superphosphate than with the ordinary superphosphate. Since the concentrated superphosphate contained only very small amounts of calcium sulfate, the relative amounts of ammonium phosphate, anhydrous dicalcium phos-

phate, and apatite differed markedly from those in ammoniated ordinary superphosphate. For example, in the ammoniation of concentrated superphosphate the weight ratio CaHPO₄ to apatite decreased from 6.0 initially to 1.6 at the end, whereas with ordinary superphosphate this ratio started at 1.3 and decreased to 0.3.

The behavior of the complex iron and aluminum phosphates during ammoniation of the concentrated superphosphates is shown in Figure 4. These compounds were decomposed by the ammoniation to form gelatinous iron and aluminum phosphates of about the composition of (Fe,Al)PO₄·nH₂O and the usual phosphates of the other ions.

Of the three major complex phosphates, (Fe,Al)₃KH₃(PO₄)₆·6H₂O was present as the smallest crystals,

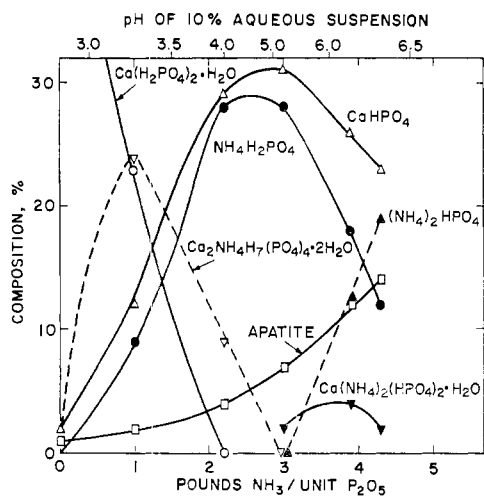


Figure 3. Compounds in ammoniated concentrated superphosphate

usually only a few microns in size, and these were decomposed by the time the ammoniation had been carried to 2 pounds of NH_3 per unit of P_2O_5 . The other potassium salt, $(\text{Fe,Al})_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$, was present as platelike crystals 20 to 50 microns wide and 2 to 5 microns thick; these were decomposed on ammoniation to 3 pounds of NH_3 per unit of P_2O_5 . The calcium salt, $\text{Ca}(\text{Fe,Al})\text{H}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, was present as aggregates of blade crystals that were 10 to 30 microns in diameter in superphosphate C, 80 microns in diameter in superphosphate D, and 100 microns in diameter in superphosphate E. The aggregates in superphosphate C were decomposed on ammoniation to 2 pounds of NH_3 per unit of P_2O_5 , but those in superphosphates D and E were not completely decomposed at 3.5 pounds of NH_3 per unit of P_2O_5 . The compound $(\text{Fe,Al})\text{K}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, a trace constituent of superphosphate C, decomposed on ammoniation to 3 pounds of NH_3 per unit of P_2O_5 .

The amorphous gels of $(\text{Fe,Al})\text{PO}_4 \cdot n\text{H}_2\text{O}$ that are formed on decomposition of the complex iron and aluminum phosphates react with alkalis to form insoluble compounds, and addition of potassium chloride to ammoniated superphosphates that contain these gels may result in formation of water-insoluble potassium compounds. The gels cannot be determined by x-ray analysis, and this may explain, to some extent, the low totals of the analyses in Table VI.

Results

As shown in Figures 1 and 3, the ammoniation reactions in the two types of superphosphate occur at different degrees of ammoniation, expressed as pounds of ammonia per unit of P_2O_5 , so that the degree of ammoniation is not satisfactory as a basis for comparison of the results. The authors observed, however, that the pH, measured on a 10% aqueous suspension of the product, was a satisfactory basis for correlating the composition of the products. The relations between pH and the degree of ammoniation for the different types of superphosphate are shown in Figure 5. Ordinary

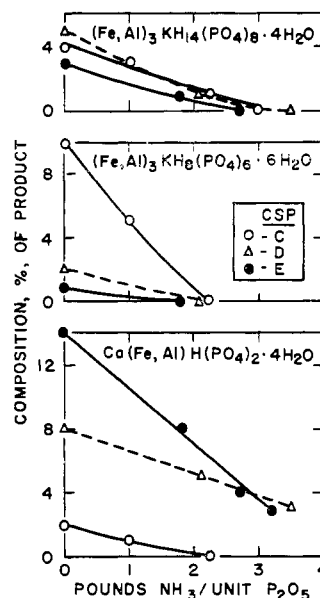


Figure 4. Decomposition of complex iron and aluminum phosphates during ammoniation of concentrated superphosphates

nary superphosphate can react with about 6.5 pounds of ammonia per unit of P_2O_5 without excessive loss of ammonia, and the pH of the product is about 5.5. Concentrated superphosphate can react with about 4 pounds of ammonia per unit of P_2O_5 , and the pH of the product is about 6.5.

Although pH is useful as a basis for comparison of results, it cannot be used to predict the degree of ammoniation that would yield a desired result with a given superphosphate. For this purpose, a more useful parameter is the basicity index which is calculated as

$$\text{Basicity index} = \frac{25(\text{NH}_3\text{-N}) + 5\text{CaO} + 6\text{R}_2\text{O}_3}{\text{P}_2\text{O}_5 + 1.1\text{SO}_3 + 6(\text{NO}_3\text{-N})}$$

in which the formulas represent weights (or weight per cent) of the constituents of a superphosphate or its ammoniated product. This formula was derived empirically to express the numerical value of the pH in terms of the chemical composition of an ammoniated product, which can be estimated from the compositions and amounts of the initial superphosphate and the ammoniating agent. The basicity index of each ammoniated product is shown with the pH in Table V.

The correlation of the water-soluble and citrate-insoluble P_2O_5 contents of the products with the basicity index is shown in Figure 6. The differences in the results with the two types of superphosphate reflect the release of calcium from the calcium sulfate in the ordinary superphosphate for the formation of apatite in the later stages of ammoniation when the pH exceeds 4 at an ammoniation of about 3 pounds of ammonia per unit of P_2O_5 . The sharp break in the curve of water-soluble P_2O_5 in ammoniated concentrated superphosphate at pH 4.8 (2.7 pounds of NH_3 per unit of P_2O_5)

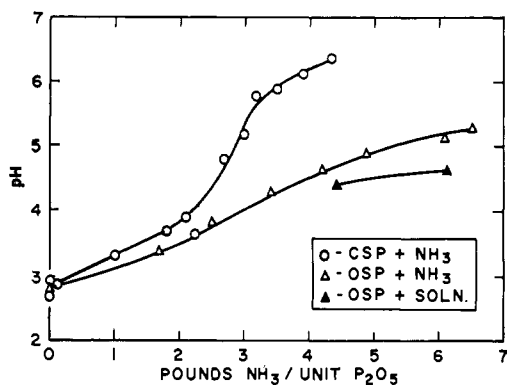


Figure 5. Relation between degree of ammoniation and pH of 10% aqueous suspensions of ammoniated superphosphates

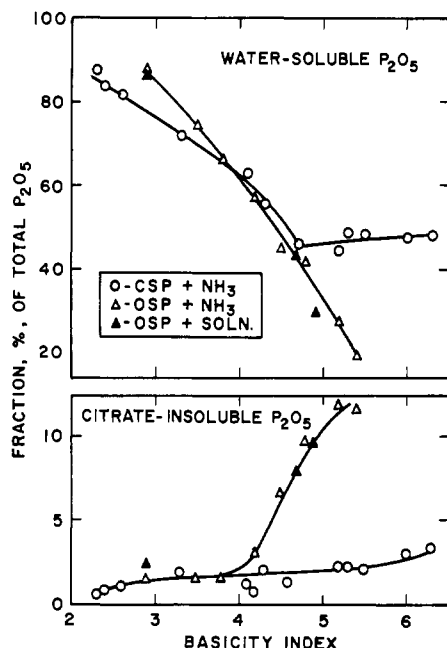


Figure 6. Correlation of solubility of ammoniated superphosphates with basicity index

reflects the conversion of monoammonium phosphate to diammonium phosphate and the conversion of dicalcium phosphate to apatite and more diammonium phosphate.

The correlations of the distribution of P_2O_5 in different compounds with the degree of ammoniation as expressed by the basicity index are shown in Figure 7 for both ordinary and concentrated superphosphates.

Monocalcium phosphate disappears at basicity index about 4. Flatt's salt, $Ca_2NH_4H_7(PO_4)_4 \cdot 2H_2O$, appears at index about 2.5, reaches a maximum at index 3.5, and disappears at index about 4.5. Monoammonium phosphate reaches a maximum at index 4.3 in ordinary superphosphate and index 4.8 in concentrated superphosphate; it disappears at index 5.5 in ordinary superphosphate but persists at index 6.3 in concentrated superphosphate. Diammonium phosphate appears at

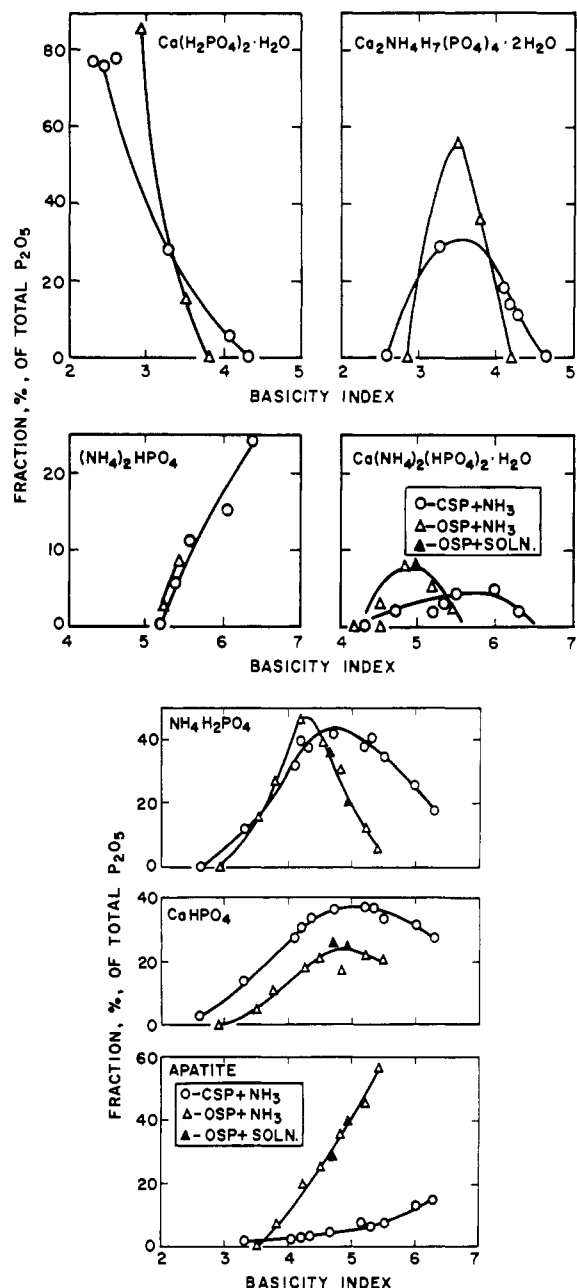


Figure 7. Correlation of distribution of P_2O_5 in ammoniated superphosphates with basicity index

index 5 and increases rapidly on further ammoniation. Small amounts of $Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$ appear at index 4 to 5, but disappear rapidly on further ammoniation.

Dicalcium phosphate appears early in the ammoniation and reaches a maximum at about basicity index 5, which corresponds to about 5 pounds of ammonia per unit of P_2O_5 in ordinary superphosphate or to about 3 pounds of ammonia per unit of P_2O_5 in concentrated superphosphate. Apatite appears at index 3.5 (2 pounds of NH_3 per unit of P_2O_5 in ordinary, 1.5 pounds of NH_3 per unit of P_2O_5 in concentrated superphosphate) and increases regularly on further ammoniation more rapidly in ordinary than in concentrated superphosphate.

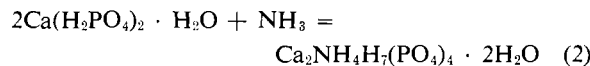
These results agree in general but differ considerably in detail from those of previous investigators (Holmes, 1941; Keenen, 1930; Panfilov, 1938; Taylor and Gurney, 1965; White *et al.*, 1935) who had to rely almost entirely on chemical analysis and citrate solubility for estimation of the amounts of the different compounds in the ammoniated products. Some of the differences result from the fact that the previous investigators were unaware of the existence of the calcium ammonium phosphates, syngenite, and the complex alkali iron and aluminum phosphates. Other differences can be ascribed to the errors introduced by taking citrate solubility as a reliable measure of the amount of apatite present.

Discussion

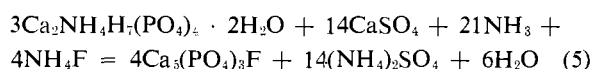
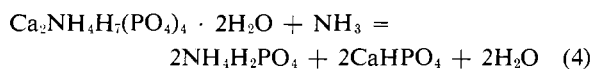
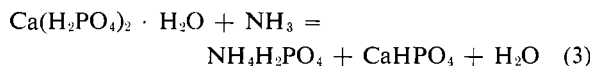
Ammoniation Reactions. As shown in Figures 1, 2, and 3, the reactions involved in the ammoniation of superphosphate occur in overlapping steps. The following reactions were selected arbitrarily to illustrate the formation of intermediate compounds and their subsequent conversion to the final compounds in accordance with the results of the x-ray and chemical examinations of the ammoniated superphosphates. The reactions are grouped to represent the initial, intermediate, and final stages of ammoniation, although there is evidently considerable overlap between stages. For example, apatite, a major final product, is formed at all stages of the ammoniation.

In these equations the fluorine is assumed to be present as ammonium fluoride when the ammoniation reaction is initiated. In the summary equations, the fluorine is assumed to be present initially as hydrofluoric acid for convenience in calculating the total ammonia requirement.

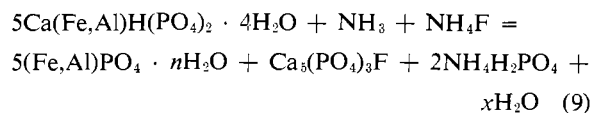
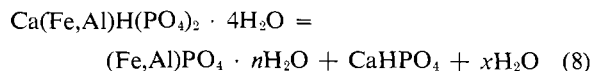
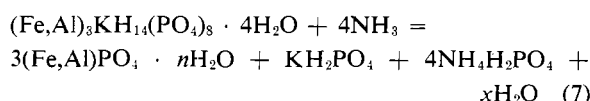
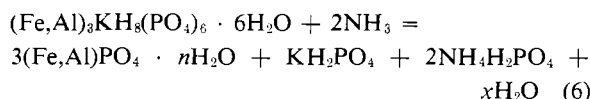
At the start of the ammoniation, below basicity index 3.5, free acid and monocalcium phosphate are ammoniated.



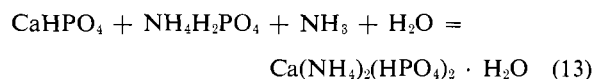
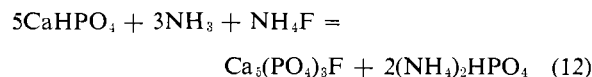
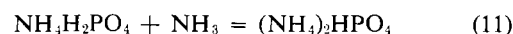
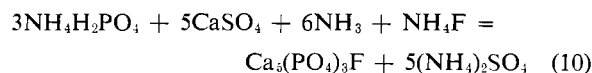
From index 3.5 to 4.5, there is extensive formation of monoammonium phosphate, dicalcium phosphate, and, in ordinary superphosphate, apatite.



In the index range 3.5 to 4.5, the complex iron and aluminum phosphates are decomposed also.

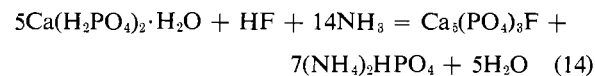


In the final stages of ammoniation beyond index 4.5 the predominant reactions are the formation of apatite in ordinary superphosphate and of diammonium phosphate in concentrated superphosphate.



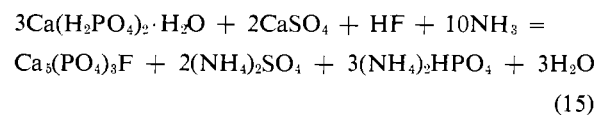
Ammonia Requirements. Equations 1 to 13 are useful in describing the reactions that take place at different stages of ammoniation, but summary equations are required for calculation of the ammonia requirements.

Ammoniation of monocalcium phosphate monohydrate to monoammonium phosphate and dicalcium phosphate, as in Equation 3, requires 2.4 pounds of NH_3 per unit of P_2O_5 , and further ammoniation to form diammonium phosphate would require a total of 4.8 pounds of ammonia. Still further ammoniation to convert the dicalcium phosphate to apatite, as in the over-all reaction



would require a total of 6.7 pounds of ammonia. The fact that concentrated superphosphate is ammoniated with difficulty past 4 pounds of ammonia per unit of P_2O_5 indicates that the reaction in Equation 12 does not take place readily.

Ordinary superphosphate, however, is ammoniated readily to 6.5 pounds of ammonia per unit of P_2O_5 . This high degree of ammoniation is not the result of the reaction of Equation 14, but of a reaction with calcium sulfate, such as



which requires 8.0 pounds of ammonia. Apparently, neither of the reactions in Equation 14 or 15 is taken to completion in a practicable ammoniation process.

The adverse effect of the complex iron and aluminum phosphates on the ammoniation characteristics of superphosphates is indicated by their relatively low capacities for ammonia. The reaction of Equation 6 shows that $(\text{Fe,Al})_3\text{KH}_8(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$ can react with

only 1.6 pounds of ammonia per unit of P_2O_5 , or 3.2 pounds if diammonium phosphate is formed. The corresponding amounts of ammonia for $(Fe,Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$ (Equation 7) are 2.4 and 4.8 pounds of ammonia per unit of P_2O_5 . The calcium salt, $Ca(Fe,Al)H(PO_4)_2 \cdot 4H_2O$, which constitutes a considerable fraction of some commercial concentrated superphosphates, requires no ammonia for the reaction in Equation 8, only 0.96 pound of ammonia per unit of P_2O_5 for Equation 9, and 1.92 pounds of ammonia if diammonium phosphate is formed. This small capacity for ammonia, together with the sluggish reactivity of the complex phosphate, may explain some of the difficulties that have been encountered in attempts to ammoniate commercial concentrated superphosphates that contain considerable amounts of iron and aluminum.

Apatite in Ammoniated Superphosphates. Comparison of the amounts of apatite found by x-ray analysis of ammoniated superphosphates (Table VI) with the corresponding citrate-insoluble P_2O_5 contents (Table V) shows that 60 to 80% of the apatite was soluble in neutral ammonium citrate solution as determined by the official procedure (Association of Official Agricultural Chemists, 1965). The apatite fractions of two ammoniated superphosphates, A-7 and C-5, were separated by extraction of dicalcium phosphate, iron and aluminum phosphates, and calcium sulfate with relatively small amounts of alkaline ammonium citrate solutions (300 to 400 ml. of solution for 14 grams of sample), and the residues were characterized by chemical analysis and by x-ray and infrared examinations. The results are shown in Table VII with those of similar examinations of the neutral ammonium citrate-insoluble fractions of the ammoniated superphosphates and two laboratory preparations of fluorapatite.

The apatite in the ammoniated superphosphates was fluorapatite present as very small crystallites (average length, 200 A.) with the same unit-cell dimensions as synthetic fluorapatites that were precipitated rather slowly at pH 4.5 or rapidly at pH 7.0. The crystallites of the residues from the neutral ammonium citrate extraction were somewhat larger (average length, 300 A.) than those in the unextracted samples of apatite,

indicating that the smaller crystallites are dissolved preferentially in the citrate extraction. Further evidence of the preferential dissolution of the smaller crystallites was obtained by extracting 0.3-gram samples of the two synthetic apatites with 100 ml. of neutral ammonium citrate solution; 80% of sample FA-13, but only 25% of sample FA-7, was dissolved.

The citrate-insoluble fraction of sample C-5 contained a small amount of unreacted phosphate rock, and that of sample A-7 an even smaller amount.

Bench-Scale Ammoniation. The laboratory drum ammoniator was 10 inches in diameter and 8 inches long and was rotated at 30 r.p.m. One end of the ammoniator was closed, and the ammoniations were made batchwise. A 1-kg. charge of concentrated superphosphate D (Tables I and IV) ground to minus 10 mesh formed a bed 1 inch deep, and ammonia was admitted below the surface of the bed for 13 minutes at the rate of 3.3 grams of N per minute. Absorption of all the ammonia would have provided 2.2 pounds of ammonia per unit of P_2O_5 , or 4.3% N in the product, about that obtained in sample D-2 (Table V) in the pilot plant. At the end of the ammoniation, the product was allowed to cool in the rotating drum for 3 minutes; the pilot-plant product passed through the plant cooler in 9 minutes. The results of the laboratory tests are compared with those obtained in the pilot plant in Table VIII.

In the laboratory test with no supplemental heat (DA-1) the maximum temperature was 77° C., whereas a temperature of 99° C. was reached in the pilot plant (D-2). Although the chemical compositions of the two products were nearly the same, there were marked differences in their solid-phase compositions. The laboratory product contained considerable amounts of unreacted $Ca(H_2PO_4)_2 \cdot H_2O$ and the basic phosphate $Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$, neither of which was detected in the pilot-plant product. There was much less monoammonium phosphate and dicalcium phosphate in the laboratory product than in the pilot-plant product. Furthermore, the complex iron and aluminum phosphates in the laboratory product were largely unaltered, and the laboratory product apparently contained a

Table VII. Compositions and Properties of Apatites

		Composition, Weight %			Moles/Mole P_2O_5		Unit-Cell Dimension, A.		Crystal Size, A.	
		CaO	P_2O_5	F	CaO	F	a_0	c_0	a	c
Apatites Recovered from Ammoniated Superphosphates										
A-7	A ^a	43.7	33.5	3.9	3.31	0.87	9.38	6.87	<200	200
A-7	N ^b	9.38	6.88	<200	300
C-5	A ^a	40.7	33.9	3.5	3.05	0.77	9.38	6.87	<200	200
C-5	N ^b	9.38	6.88	<200	350
Laboratory Preparations of Apatite										
FA-7		53.8	41.1	3.7	3.33	0.67	9.38	6.87	550	1000
FA-13		52.0	40.9	3.6	3.23	0.66	9.38	6.88	<200	350
$Ca_5(PO_4)_3F$		55.6	42.2	3.8	3.33	0.67

^a Alkaline citrate-insoluble fraction.

^b Neutral citrate-insoluble fraction.

Table VIII. Comparison of Products of Laboratory and Pilot-Plant Ammoniation of Concentrated Superphosphate

	Pilot Plant	Laboratory				
	D-2	DA-1	DA-2	DA-3	DA-4	DA-5
Conditions of ammoniation						
Bed depth, inches	9	1	1	1	1	1
Time of ammoniation, min.	13	13	13	13	13	13
Heat addition	No	No	Yes	Yes	Yes	Yes
Maximum temp., ° C.	99	74	99	99	99	99
Water addition, %	0	0	0	7	15	Steam
Composition of product, wt. %						
Moisture	1.4	1.4	0.3	1.0	1.4	0.9
N	4.1	3.8	3.7	4.0	4.2	4.1
P ₂ O ₅						
Total	47.3	46.8	47.4	47.3	46.4	46.9
W.S. ^a	19.9	18.4	16.7	17.0	17.6	18.7
C.I. ^a	0.8	0.6	0.6	0.6	0.8	0.6
pH	3.9	3.8	3.8	3.9	3.9	3.9
Ca(H ₂ PO ₄) ₂ ·H ₂ O	0	12	11	5	3	4
Ca ₂ NH ₄ H ₇ (PO ₄) ₄ ·2H ₂ O	11	12	10	13	8	10
NH ₄ H ₂ PO ₄	31	15	16	20	24	22
CaHPO ₄	29	11	13	18	20	19
Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	0	4	2	4	2	3
Ca ₃ (PO ₄) ₃ F	4	6	6	7	8	6
(Fe,Al) ₃ KH ₁₄ (PO ₄) ₈ ·4H ₂ O	1	4	4	3	2	2
(Fe,Al) ₃ KH ₈ (PO ₄) ₅ ·6H ₂ O	0	1	1	1	0	0
Ca(Fe,Al)H(PO ₄) ₂ ·4H ₂ O	5	7	7	6	5	5
CaSO ₄	2	2	2	2	2	2
CaSO ₄ ·0.5H ₂ O	3	3	3	3	3	3
(NH ₄) ₂ SO ₄	3	1	3	0	0	2
Ca(NH ₄) ₂ (SO ₄) ₂ ·H ₂ O	0	0	0	2	3	0
Total	89	78	78	84	80	78

^a Water-soluble and citrate-soluble P₂O₅ determined by AOAC procedures (Assoc. Offic. Agr. Chemists, 1965).

considerable amount of amorphous calcium ammonium phosphate. Water extracts of the laboratory product deposited precipitates of CaHPO₄·2H₂O which were formed by hydrolysis of the monocalcium phosphate monohydrate; only E-1 (Table VI) of the pilot-plant series behaved similarly.

When the laboratory ammoniator was heated with a burner flame impinging on the outside of the cylindrical wall of the drum to raise the temperature to that obtained in the pilot plant (DA-2), the amounts of Ca(H₂PO₄)₂·H₂O and Ca₂NH₄H₇(PO₄)₄·2H₂O were decreased slightly and those of NH₄H₂PO₄ and CaHPO₄ were increased slightly, but the composition still differed markedly from that of D-2. Product DA-2 contained 0.3% moisture, whereas D-2 contained 1.4%.

To increase the moisture content of the ammoniated product, the open end of the ammoniator was closed with a sheet of fiberboard in which a central hole was provided for the ammonia inlet tube and for introduction of water as spray or as steam. When the drum was heated as before, spraying water in the amount of 7% of the superphosphate (test DA-3) increased the reaction rate considerably, and increasing the water spray to 15% of the superphosphate (test DA-4)

brought the moisture content of the product up to that in D-2. This increase in moisture content increased the uptake of ammonia, promoted the ammoniation reactions (including the decomposition of the crystalline iron and aluminum phosphates), and produced a solid-phase composition much like that of D-2, except for the presence of a small amount of unreacted Ca(H₂PO₄)₂·H₂O and less NH₄H₂PO₄ and CaHPO₄ than in D-2. Addition of steam, as in test DA-5, apparently was as effective as addition of water spray in promoting the ammoniation reactions.

Similar results were obtained in batch laboratory ammoniations of superphosphate C. The solid-phase composition of the product was not affected significantly by change of the particle size of the superphosphate from 6 to 10 to 20 mesh, by change of the ammoniation time from 7 to 13 to 20 minutes, or by increasing the agitation markedly during ammoniation. These results indicate that temperature and moisture content are the controlling factors in laboratory-scale ammoniations.

The differences between the results of uncontrolled laboratory ammoniations and those obtained in the pilot plant result from the rapid loss of water—present

as free moisture in the superphosphate and as water of crystallization of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ —from the shallow bed in the laboratory ammoniator. In the large continuous pilot-plant ammoniator, escape of moisture is hindered by the greater depth of the bed and by condensation on the cold feed material. In spite of the higher temperature in the pilot-plant operation, the material remains moist enough to permit rapid completion of the ammoniation reactions. In the laboratory ammoniator, the dry granules are ammoniated largely on their surfaces, and penetration of the ammonia is hindered by the lack of moisture and by the shells of reaction products. The same results can be obtained in the laboratory as in pilot-plant or larger-scale operation only if the proper conditions of temperature and moisture content are maintained throughout the ammoniation.

Acknowledgment

R. S. Meline, G. C. Hicks, and M. M. Norton prepared the ammoniated superphosphates in the pilot plant.

Literature Cited

Ando, J., Smith, J. P., Siegel, M. R., Jordan, J. E., *J. AGR. FOOD CHEM.* **13**, 186–95 (1965).
Association of Official Agricultural Chemists, "Official Methods of Analysis," 10th ed., p. 14, 1965.

- Flatt, R., Brunisholz, G., Chapuis-Gottreux, S., *Helv. Chim. Acta* **34**, 884–94 (1951).
Frazier, A. W., Lehr, J. R., *J. AGR. FOOD CHEM.* **15**, 348–9 (1967).
Hardesty, J. O., Ross, W. H., *Ind. Eng. Chem.* **29**, 1283–90 (1937).
Hardesty, J. O., Ross, W. H., Adams, J. R., *J. Assoc. Offic. Agr. Chemists* **26**, 203–11 (1943).
Holmes, J. B. S., *Am. Fertilizer* **95**, No. 9, 5–7, 22 (1941).
Keenen, F. G., *Ind. Eng. Chem.* **22**, 1378–82 (1930).
Kumagai, R., Rapp, H. F., Hardesty, J. O., *J. AGR. FOOD CHEM.* **2**, 25–30 (1954).
Lehr, J. R., Frazier, A. W., Smith, J. P., *J. AGR. FOOD CHEM.* **14**, 27–33 (1966).
MacIntire, W. H., Hardin, L. J., *J. Assoc. Offic. Agr. Chemists* **23**, 388–98 (1940).
MacIntire, W. H., Marshall, H. L., Shank, R. C., *J. Assoc. Offic. Agr. Chemists* **27**, 413–25 (1944).
Panfilov, V. N., *Trans. Sci. Inst. Fertilizers Insectofungicides (USSR)* **141**, 179–97 (1938).
Payne, J. H., Jr., Webber, R. T., *J. AGR. FOOD CHEM.* **8**, 164–72 (1960).
Rau, R. C., "Advances in X-Ray Analyses," Vol. **5**, pp. 104–16, Univ. of Denver, Plenum Press, New York, 1962.
Taylor, A. W., Gurney, E. L., *J. AGR. FOOD CHEM.* **13**, 92–9 (1965).
White, L. M., Hardesty, J. O., Ross, W. H., *Ind. Eng. Chem.* **27**, 562–7 (1935).
Yates, L. D., Nielsson, F. T., Hicks, G. C., *Farm Chem.* **117**, No. 7, 38–48; No. 8, 34–41 (1954).

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