



Figure 1. Stirring device and cuvette

Other modifications to the original procedure were the use of a green filter in the colorimeter, and the technique of setting to zero using distilled water in the second cell. It was considered that any errors, owing to the dilution by titrant of the background color in the process acids, would be minimized by using a green filter rather than a colorless matt filter. In actual practice, this final background is slight, but varies (in intensity and color) with the origin of the phosphate rock used in the process.

This possible source of error is not eliminated by the use of a second aliquot in the reference cell, as in the Russian

article. In fact, when the aliquot is made up to final volume with ethanol and water, entrapped bubbles appear from time to time on the optical surfaces of the cells. A stirring action is necessary to remove these bubbles, and this effect is achieved only in the titration cell. Thus, the use of distilled water in the reference cell was adopted.

For the purposes of calibration, synthetic standards were made up from phosphoric acid and standard sulfate solution to cover the range from 0 to 7%. The use of synthetic standards has the advantage that the final results on the assays are not dependent on the accuracy of gravimetric determinations. The calibration graph obtained appears to be linear over the range investigated, and the reaction between titrant and sulfate ions is, to all intents, stoichiometric.

Samples of process acid made from Nauru rock were analyzed by this method, and the results obtained were in close agreement to those obtained by the classical gravimetric procedure. Results of tests by the authors showed that the method is tolerant of impurities found in wet-process acid. The calcium oxide, fluoride, iron oxide, and aluminum oxide contents can vary over a wider range than would be normally encountered, without any significant effect on the results of the sulfate determination. The results are also independent of the phosphorus pentoxide contents of the filtrate acid.

In the early stages of the study, some work was done using protective agents, not to achieve repro-

ducible particle size but to minimize layering effects at the higher ranges. Use of these agents is necessary for turbidimetric measurements where absorbance is related to sulfate content (7, 2, 6), but as pointed out earlier, this method does not depend on reproducible particle size. The early work showed that, with the stirrer design and speed used, no advantage was gained by using these protective agents, and accordingly their use was not incorporated in the method.

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## IMPURITIES FROM PHOSPHORIC ACID

# Precipitated Impurities in Fertilizers Prepared from Wet-Process Phosphoric Acid

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Ammoniation of wet-process phosphoric acid precipitates the metallic elements that were dissolved from the phosphate rock or added as micronutrients. The nature and solubility of the precipitates change as the acid is concentrated to the superphosphoric acid range and condensed phosphate species are introduced. The optical properties and x-ray patterns of 26 of the most common precipitates are described.

WET-PROCESS phosphoric acid contains soluble impurities, mostly iron and aluminum, that were dissolved from the gangue minerals in the phosphate rock from which the acids were prepared. In the concentration of these acids to merchant-grade (24% P, 54%  $P_2O_5$ ) or superphosphoric acid (about 33% P, 75%  $P_2O_5$ ), some of the impurities precipitate during storage as crystalline compounds (9) that interfere seriously with mechanical handling of the acid and immobilize some of the

phosphate. Considerable amounts of these impurities—iron, aluminum, calcium, and magnesium—remain in solution or as suspended solids, particularly when additives are introduced during production of the acid to stabilize suspended solids or delay their formation until the acid is processed into other fertilizers.

The preparation of fertilizers from wet-process phosphoric acid usually entails ammoniation of the acid; the acid or its ammoniation product often is concen-

trated, and many of the products thus contain condensed phosphates as well as orthophosphate. Addition of salts of potassium to prepare complete fertilizers and of micronutrients increases the amount of metal cations that may take part in precipitation processes.

The change in pH during ammoniation and the introduction of condensed phosphate species by concentration steps result in precipitation of the dissolved metallic impurities; these crystallization processes usually require an induc-

tion period of several days and may be accelerated by temperature changes during storage of the product. Un-ammoniated, concentrated acids yield precipitates that are mainly orthophosphates or tripolyphosphates (9), but the precipitates in ammoniated concentrated acids are mainly pyrophosphates. The identification and characterization of precipitated impurities isolated from a wide variety of experimental fertilizers prepared from ammoniated wet-process phosphoric acids are reported here. Some of these compounds have been identified previously as products of the reaction of phosphates with soil minerals (7, 10), but many of the compounds have not been reported before or have been incompletely characterized.

In addition to the metallic impurities in phosphoric acid and added micronutrient metals such as zinc, manganese, and copper, impurities are added by corrosion of process equipment, such as ferrous iron if the processing equipment is mild steel. The micronutrients, like the metallic impurities, form insoluble phosphates which alter the rates at which the micronutrients become available to plants in the soil. In liquid fertilizers, the precipitates settle out with resultant segregation of micronutrients and interference with mechanical handling of the solutions.

Because of the wide variations in conditions under which ammonium polyphosphate fertilizers are prepared, no attempts were made to determine the solubilities of the compounds in any of their mother liquors. The amounts of precipitates that form in the preparation of a solid or liquid fertilizer depend on so many variables—composition of the acid, amounts of other fertilizer salts added, temperature attained during ammoniation, etc.—that no generalizations can be made about the difficulties the precipitates will introduce in subsequent use of the fertilizers. The information presented here is intended to assist fertilizer producers in identifying the undesirable solid phases in their products so that means may be devised to prevent their formation.

Many of the compounds reported here occur in fertilizers in particle sizes too small for detailed optical characterization. These compounds were prepared also in the laboratory from reagent chemicals under conditions resembling those in which they were formed in the production of the fertilizer material but which yielded well crystallized products. The laboratory preparations, whose optical properties agreed with those determined on the materials isolated from fertilizers, were used for measurements of the optical and crystallographic properties of the compounds. During the preparations, other salts of related composition were sometimes obtained that were not found in fertilizers; their

properties are reported also, since they were formed under conditions that may be encountered in the ammoniation of different concentrations of wet-process phosphoric acid.

Most of the laboratory preparations were made at room temperature by adding a soluble salt of the metal to a saturated solution, prepared from reagent chemicals, of ammonium phosphates similar to the fertilizer solution in which the desired compound had been observed. Most of the compounds precipitated rapidly, and addition of the soluble metal salt was continued only until the amount of precipitate was sufficient for optical and x-ray examinations and for chemical analysis.

Two compounds, however, required a different method of preparation. The compound  $\text{Fe}(\text{NH}_4)_3\text{HPO}_4\text{P}_2\text{O}_7$  was prepared from a mixture of 2 grams of  $\text{FePO}_4$  and 15 grams of ammonium polyphosphate that contained 14% N and 26% P (60%  $\text{P}_2\text{O}_5$ ) and in which half the phosphorus was ortho- and half pyrophosphate. The mixture was heated in a sealed glass tube at 230° C. for 1 to 2 hours; the cooled product was washed with water to remove the excess ammonium phosphate, washed briefly with acetone, and air dried.

Members of the series  $(\text{Al,Fe})\text{NH}_4\text{P}_2\text{O}_7$  were prepared similarly from mixtures of 2 grams of the appropriate mixture of  $\text{AlPO}_4$  and  $\text{FePO}_4$  and 15 grams of the same ammonium polyphosphate. The mixtures were heated in sealed glass tubes at 250° C. for 16 hours, and the cooled products were washed and dried as above.

Complex phosphates, such as those discussed here, usually dissolve incongruently in water or any solvent that differs significantly from the mother liquors in which they were formed. Most of these compounds are very slowly soluble, however, and the adhering mother liquor was washed off without detectable decomposition of the compounds. The methods of chemical analysis were the same as those used in the study of the precipitates in wet-process phosphoric acid (9). The compositions of the crystalline compounds are listed in Table I, their optical properties and morphology are described in Table II, and their x-ray powder diffraction patterns are shown in Table III. The compounds listed in the tables either have not been reported previously in the literature or have been incompletely characterized.

### Calcium Salts

Wet-process phosphoric acids usually contain small amounts of calcium. In the ammoniation of acids that contain no condensed phosphates, calcium precipitates as  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH,F})_2$  (apatite),  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , or as the dimorphs of  $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  (4).

In more concentrated acids (about 33% P, 75%  $\text{P}_2\text{O}_5$ ) that contain about equal amounts of ortho- and pyrophosphate, ammoniation to pH 4 to 6 precipitates calcium as  $\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$ ; above pH 6,  $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$  is precipitated (7, 2). In still more concentrated acids that contain considerably more pyro- than orthophosphate,  $\text{Ca}(\text{NH}_4)_4\text{H}_2(\text{P}_2\text{O}_7)_2$  is precipitated at pH 4 to 6.

The formation of calcium salts in ammoniated wet-process acid is not a major problem, since most wet-process acids contain an excess of sulfate over that required to combine with the calcium as calcium sulfate, and only a small amount of calcium remains dissolved in the acid.

### Magnesium Salts

Wet-process acids frequently contain magnesium dissolved chiefly from dolomite in the phosphate rock; magnesium also is added to liquid fertilizers as a secondary nutrient and in attapulgite clay, a stabilizing agent. Ammoniation of merchant-grade acids (22–24% P, 50–54%  $\text{P}_2\text{O}_5$ ) precipitates magnesium as  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  (struvite) or its monohydrate, depending on the temperature, and sometimes as  $\text{Mg}_3(\text{NH}_4)_2\text{H}_4(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$  (hannayite) and  $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  (3). When potassium is present, magnesium may precipitate as  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  (14) which is isomorphous with struvite.

If aluminum is present, magnesium precipitates as  $\text{MgAl}(\text{NH}_4)_5\text{H}_2(\text{PO}_4)_4 \cdot 6\text{H}_2\text{O}$ , a salt frequently found in ammoniated merchant-grade wet-process phosphoric acid; and in ammonium polyphosphate liquid fertilizers prepared from wet-process phosphoric acid; its iron analog has not been observed.

On ammoniation to pH 3.5 to 6.0 of solutions of orthophosphoric and pyrophosphoric acids that contain magnesium, the magnesium precipitates preferentially as pyrophosphate, the monoclinic dimorph of  $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$  in highly concentrated solutions, and the orthorhombic dimorph in less concentrated solutions. In solutions that contain more ortho- than pyrophosphate, as in most ammonium polyphosphate liquid fertilizers, the orthorhombic dimorph precipitates from concentrated solutions. In ammonium pyrophosphate solutions with pH above 6, magnesium precipitates as  $\text{Mg}(\text{NH}_4)_6(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$  and in those with pH 2 to 3, as  $\text{Mg}(\text{NH}_4)_2\text{H}_4(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ .

Precipitated magnesium compounds are a source of considerable trouble during storage and handling of liquid fertilizers prepared from ammoniated wet-process phosphoric acid. The salts are quite insoluble, but tend to supersaturate and precipitate slowly over several days or weeks, forming large, well developed plate or acicular crystals that

Table I. Solids in Ammoniated Concentrated Wet-Process Phosphoric Acid

Compound	Composition, Weight %					Moles/Mole P				
	Ca, Mg, Fe, Mn, or Zn	Al	N or K	P	H <sub>2</sub> O (diff.)	Ca, Mg, Fe, Mn, or Zn	Al	N or K	H <sub>2</sub> O	
Ca(NH <sub>4</sub> ) <sub>4</sub> H <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>	8.93	...	11.74	26.42	5.2	0.26	...	0.98	0.34	
Stoichiometric	8.66	...	11.58	26.85	3.9	0.25	...	1.00	0.25	
MgNH <sub>4</sub> PO <sub>4</sub> ·H <sub>2</sub> O	15.32	...	8.88	19.95	12.4	0.98	...	0.99	1.07	
Stoichiometric	15.74	...	9.05	20.08	11.1	1.00	...	1.00	1.00	
MgKPO <sub>4</sub> ·6H <sub>2</sub> O	9.23	...	13.77	11.75	41.2	1.01	...	0.93	6.05	
Stoichiometric	9.13	...	14.65	11.64	40.6	1.00	...	1.00	6.00	
Mg(NH <sub>4</sub> ) <sub>2</sub> H <sub>4</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	5.31	...	6.30	27.16	17.3	0.25	...	0.51	1.10	
Stoichiometric	5.43	...	6.25	27.68	16.1	0.25	...	0.50	1.00	
Mg(NH <sub>4</sub> ) <sub>6</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	3.98	...	13.84	21.05	19.5	0.25	...	1.46	1.59	
Stoichiometric	4.13	...	14.27	21.09	18.4	0.25	...	1.50	1.50	
Mg(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ·4H <sub>2</sub> O I	7.86	...	9.05	20.26	23.8	0.50	...	0.99	2.02	
Mg(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ·4H <sub>2</sub> O II	7.78	...	8.99	20.08	24.4	0.50	...	0.99	2.09	
Stoichiometric	7.94	...	9.14	20.22	23.5	0.50	...	1.00	2.00	
MgAl(NH <sub>4</sub> ) <sub>3</sub> H <sub>2</sub> (PO <sub>4</sub> ) <sub>4</sub> ·6H <sub>2</sub> O	3.80	4.18	10.93	19.78	20.2	0.25	0.24	1.22	1.76	
Stoichiometric	4.01	4.40	11.42	20.22	20.0	0.25	0.25	1.25	1.75	
Al(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ·OH·2H <sub>2</sub> O	...	9.53	9.69	21.44	14.9	...	0.51	1.00	1.20	
Stoichiometric	...	9.31	9.65	21.38	15.5	...	0.50	1.00	1.25	
Al <sub>0.33</sub> Fe <sub>0.67</sub> NH <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	14.04	3.23	5.82	25.85	3.8	0.30	0.14	0.50	0.60	
Stoichiometric	15.65	3.77	5.87	26.02	0.0	0.33	0.17	0.50	0.00	
Al <sub>0.3</sub> Fe <sub>0.3</sub> KP <sub>2</sub> O <sub>7</sub>	9.29	4.18	15.18	24.58	4.2	0.21	0.20	0.49	0.60	
Stoichiometric	10.79	5.20	15.03	23.89	0.0	0.25	0.25	0.50	0.00	
Fe(NH <sub>4</sub> ) <sub>3</sub> HPO <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	14.33	...	10.82	23.99	4.4	0.33	...	1.00	0.32	
Stoichiometric	14.74	...	11.04	24.45	2.4	0.33	...	1.00	0.17	
Fe(NH <sub>4</sub> ) <sub>3</sub> HPO <sub>4</sub> P <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O	13.96	...	10.39	23.27	7.4	0.33	...	0.99	0.55	
Stoichiometric	14.04	...	10.55	23.36	6.8	0.33	...	1.00	0.50	
Fe(NH <sub>4</sub> ) <sub>6</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	8.39	...	13.68	20.02	17.9	0.23	...	1.51	1.54	
Stoichiometric	8.87	...	13.34	19.68	17.1	0.25	...	1.50	1.50	
Fe(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	17.64	...	8.78	20.17	14.8	0.49	...	0.96	1.26	
Stoichiometric	18.50	...	9.28	20.54	11.9	0.50	...	1.00	1.00	
Mn(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	17.74	...	9.15	20.65	12.8	0.49	...	0.98	1.07	
Stoichiometric	18.27	...	9.30	20.60	12.0	0.50	...	1.00	1.00	
ZnNH <sub>4</sub> H <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	21.49	...	4.77	20.87	16.6	0.49	...	0.51	1.37	
Stoichiometric	22.21	...	4.75	21.05	15.3	0.50	...	0.50	1.25	
ZnNH <sub>4</sub> PO <sub>4</sub> A	36.4	...	7.75	17.33	0.6	1.00	...	0.99	0.06	
ZnNH <sub>4</sub> PO <sub>4</sub> B	36.32	...	7.81	17.33	0.6	0.99	...	1.00	0.06	
Stoichiometric	36.67	...	7.85	17.38	0.0	1.00	...	1.00	0.00	
Zn <sub>2</sub> KH(PO <sub>4</sub> ) <sub>2</sub>	36.07	...	11.20	17.25	2.1	0.99	...	0.52	0.21	
Stoichiometric	36.32	...	10.79	17.20	2.5	1.00	...	0.50	0.25	
Zn <sub>2</sub> KH(PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	31.98	...	9.96	15.46	12.8	0.98	...	0.51	1.43	
Stoichiometric	32.94	...	9.79	15.63	11.3	1.00	...	0.50	1.25	
ZnKPO <sub>4</sub>	32.70	...	19.80	15.63	-0.3	0.99	...	1.00	-0.03	
Stoichiometric	32.79	...	19.61	15.55	0.0	1.00	...	1.00	0.00	
Zn(NH <sub>4</sub> ) <sub>2</sub> H <sub>4</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	13.40	...	5.71	25.19	15.0	0.25	...	0.50	1.03	
Stoichiometric	13.59	...	5.82	25.76	13.3	0.25	...	0.50	1.00	
Zn(NH <sub>4</sub> ) <sub>6</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	10.04	...	13.6	19.93	16.6	0.24	...	1.52	1.43	
Stoichiometric	10.39	...	13.35	19.70	17.2	0.25	...	1.50	1.50	
Zn(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O	22.42	...	9.35	20.98	6.7	0.51	...	0.99	0.55	
Stoichiometric	22.29	...	9.54	21.13	6.1	0.50	...	1.00	0.50	
Zn <sub>3</sub> (NH <sub>4</sub> ) <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	30.69	...	4.58	20.35	6.7	0.72	...	0.50	0.57	
Stoichiometric	31.82	...	4.54	20.13	5.8	0.75	...	0.50	0.50	

are difficult to pump or handle in distributor equipment.

**Zinc Salts**

Zinc, an increasingly important micro-nutrient, is sparingly soluble in many phosphatic liquid fertilizers. When a soluble zinc salt is added to ammonium orthophosphate solutions, the zinc forms supersaturated solutions and precipitates as ZnNH<sub>4</sub>H<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O at pH 3, as the hexagonal dimorph of ZnNH<sub>4</sub>PO<sub>4</sub> at pH 3.5 to 5.5, and as the orthorhombic dimorph of ZnNH<sub>4</sub>PO<sub>4</sub> at pH 6 and above. Zinc added to potassium orthophosphate solutions precipitates at pH 4 as Zn<sub>2</sub>KH(PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (which slowly dehydrates in the mother liquor to the anhydrous salt), and as ZnKPO<sub>4</sub> at pH 5 to 7.

Hopeite, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, has not been found in high-analysis ammonium or potassium phosphate fertilizers, but it

forms over a wide pH range in diluted fertilizer solutions and in superphosphate fertilizers to which zinc oxide has been added. Although hopeite is highly insoluble, it is an effective source of zinc for plants, particularly when it is finely divided (16).

Zinc added in excess to solutions of ammonium polyphosphate precipitates as Zn(NH<sub>4</sub>)<sub>2</sub>H<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·2H<sub>2</sub>O at pH's below 4, as Zn<sub>3</sub>(NH<sub>4</sub>)<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·2H<sub>2</sub>O at pH 4 to 6, and as Zn(NH<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O at pH 6 to 8. The solubility of zinc in concentrated ammonium polyphosphate solutions with pH's of 6 and above increases markedly with increase in the ratio of pyro- to orthophosphate. In concentrated ammonium pyrophosphate solutions with pH's of 6 and above, a solution saturated with zinc has a mole ratio of Zn to P<sub>2</sub>O<sub>5</sub> of about 0.5, and this ratio must be exceeded before a zinc salt will crystallize. Under these conditions, zinc crystallizes as Zn(NH<sub>4</sub>)<sub>6</sub>

(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·6H<sub>2</sub>O, but this salt is congruently soluble in water and would not be a troublesome constituent of a fertilizer. Measurements of solubility in the system NH<sub>3</sub>-ZnO-H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>O are being prepared for publication (17).

Unlike calcium and magnesium, which selectively precipitate as pyrophosphates from solutions of any concentration that contain both ortho- and pyrophosphate, zinc precipitates as Zn<sub>3</sub>(NH<sub>4</sub>)<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·2H<sub>2</sub>O from a concentrated (25% or more) ammonium polyphosphate solution and as ZnNH<sub>4</sub>PO<sub>4</sub>, dimorph A, when the same solution is diluted.

**Manganese Salts**

The behavior of manganese in liquid fertilizers was studied only briefly. In the amounts usually added as a micro-nutrient, trivalent manganese remains dissolved in ammonium polyphosphate solutions. Divalent manganese, how-

**Table II. Morphological and Optical Properties**

Compound	Crystal System, Class, and Habit	Refractive Indices	Optical Properties <sup>a</sup>
Ca(NH <sub>4</sub> ) <sub>4</sub> H <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>	Monoclinic, 2/ <i>m</i> . Highly modified prisms tabular on (100)	$\alpha = 1.538$ $\beta = 1.558$ $\gamma = 1.565$	Biaxial (-), 2 <i>V</i> = 60° (60.5°). OAP $\perp$ (010), $X \wedge c = 53^\circ$ in acute $\beta$ . $\beta = 107.5^\circ$ , $b = Z$ , $d = 2.05$
MgNH <sub>4</sub> PO <sub>4</sub> · H <sub>2</sub> O	Orthorhombic, <i>mmm</i> . Plate crystals containing <i>Y-Z</i> elongated along <i>Z</i>	$\alpha = 1.549$ $\beta = 1.569$ $\gamma = 1.571$	Biaxial (-), 2 <i>V</i> = 40° (35°). OAP $\perp$ tabular plane, <i>Z</i> $\parallel$ elongation. $d = 2.15$
MgKPO <sub>4</sub> · 6H <sub>2</sub> O	Orthorhombic, hemimorphic, <i>mm</i> . Prisms exhibiting (001), prominent (00 $\bar{1}$ ), (101), ( $\bar{1}01$ ), (011), and (0 $\bar{1}1$ )	$\alpha = 1.477$ $\beta = 1.481$ $\gamma = 1.487$	Biaxial (+), 2 <i>V</i> = (78°). OAP = (001), $X = b$ , $Y = c$ , $Z = a$ . $d = 1.91$
Mg(NH <sub>4</sub> ) <sub>2</sub> H <sub>4</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	Triclinic, 1. Rhombic prisms and tablets with contact and polysynthetic twinning	$\alpha = 1.487$ $\beta = 1.502$ $\gamma = 1.522$	Biaxial (+), 2 <i>V</i> = (82°). $d = 2.01$
Mg(NH <sub>4</sub> ) <sub>6</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	Monoclinic, 2/ <i>m</i> . Prisms tabular on (100), modified by {110}, (010), and {111}	$\alpha = 1.497$ $\beta = 1.501$ $\gamma = 1.504$	Biaxial (-), 2 <i>V</i> = (75°). OAP = (010), $b = Y$ , $Z \wedge c = 40^\circ$ in obtuse $\beta$ . $\beta = 107^\circ$ , $d = 1.66$
Mg(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · 4H <sub>2</sub> O I	Orthorhombic, hemimorphic, <i>mm</i> . Blades tabular on <i>X-Y</i> plane	$\alpha = 1.5005$ $\beta = 1.502$ $\gamma = 1.504$	Biaxial (+), 2 <i>V</i> = 75° (82°). OAP $\perp$ tabular plane, <i>X</i> $\parallel$ elongation. $d = 1.79$
Mg(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · 4H <sub>2</sub> O II	Monoclinic, 2/ <i>m</i> . Plates tabular on (010) and (100)	$\alpha = 1.488$ $\beta = 1.502$ $\gamma = 1.503$	Biaxial (-), 2 <i>V</i> = 30° (30°). OAP = (010), $b = Y$ , $Z \wedge c \sim 16^\circ$ on (010) in acute $\beta$ . $\beta = 120^\circ$ , $d = 1.77$
MgAl(NH <sub>4</sub> ) <sub>3</sub> H <sub>2</sub> (PO <sub>4</sub> ) <sub>4</sub> · 6H <sub>2</sub> O	Needle to blade crystals, with orthorhombic or higher symmetry	$N_1 = 1.486$ $N_2 = 1.488$	Parallel extinction, <i>X</i> $\perp$ elongation. $d = 1.78$
Al(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · OH · 2H <sub>2</sub> O	Orthorhombic. Thin needle crystals	$\alpha = 1.490$ $\gamma = 1.500$	<i>Z</i> $\parallel$ length, $d = 1.84$
Al <sub>0.33</sub> Fe <sub>0.67</sub> NH <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	Monoclinic, fusiform aggregates of small needle crystals	$\alpha = 1.648$ $\beta = 1.662$ $\gamma = 1.677$	Biaxial (+), 2 <i>V</i> = (89°), <i>Z</i> almost $\parallel$ length. $d = 2.64$
Al <sub>0.5</sub> Fe <sub>0.5</sub> KP <sub>2</sub> O <sub>7</sub>	Monoclinic, 2/ <i>m</i> . (100) tablets modified by (111), ( $\bar{1}11$ ), ( $\bar{1}\bar{1}\bar{1}$ ), and ( $\bar{1}\bar{1}\bar{1}$ )	$\alpha = 1.593$ $\beta = 1.601$ $\gamma = 1.612$	Biaxial (+), 2 <i>V</i> = (82°), OAP = (010), $b = Y$ . $d = 2.89$
Fe(NH <sub>4</sub> ) <sub>3</sub> HPO <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	Orthorhombic, <i>mmm</i> . Needles and blades containing <i>X-Z</i>	$\alpha = 1.587$ $\beta = 1.590$ $\gamma = 1.630$	Biaxial (+), 2 <i>V</i> = (30°). OAP = plane of tabularity, <i>Z</i> $\parallel$ length. $d = 2.14$
Fe(NH <sub>4</sub> ) <sub>3</sub> HPO <sub>4</sub> P <sub>2</sub> O <sub>7</sub> · H <sub>2</sub> O	Orthorhombic, intergrown blade crystals tabular on <i>Y-Z</i>	$\alpha = 1.551$ $\beta = 1.577$ $\gamma = 1.600$	Biaxial (-), 2 <i>V</i> = (85°). OAP $\perp$ tabular plane, <i>Z</i> $\parallel$ length. $d = 2.01$
Fe(NH <sub>4</sub> ) <sub>6</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	Monoclinic, 2/ <i>m</i> . (100) tablets modified by {011}, {110}, and small (101), ( $\bar{1}01$ ), and {110}	$\alpha = 1.510$ $\beta = 1.5146^b$ $\gamma = 1.515$	Biaxial (-), 2 <i>V</i> = 25°. OAP $\perp$ (010), $X \wedge c = 43^\circ$ in obtuse $\beta$ . $b = Z$ . $d = 1.75$
Fe(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · 2H <sub>2</sub> O	Hexagonal, rosette aggregates of interpenetrated blade crystals	$\epsilon = 1.556$ $\omega = 1.598$	Uniaxial (-). $d = 2.24$
Mn(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · 2H <sub>2</sub> O	Hexagonal, interpenetrated blade crystals tabular on (0001)	$\epsilon = 1.541$ $\omega = 1.581$	Uniaxial (-). $d = 2.17$
ZnNH <sub>4</sub> H <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> · H <sub>2</sub> O	Triclinic, 1. Highly modified tabular crystals	$\alpha = 1.518$ $\beta = 1.521$ $\gamma = 1.541$	Biaxial (+), 2 <i>V</i> = 39° (43°). $d = 2.29$
ZnNH <sub>4</sub> PO <sub>4</sub> A	Orthorhombic, <i>mmm</i> . Prisms tabular on <i>X-Y</i> plane; <i>Y-Z</i> view shows pseudo-hexagonal symmetry	$\alpha = 1.582$ $\beta = 1.589$ $\gamma = 1.591$	Biaxial (-), 2 <i>V</i> = 45° (50°). OAP $\perp$ tabular plane. $d = 2.54$
ZnNH <sub>4</sub> PO <sub>4</sub> B	Hexagonal, 62. Bipyramids and rod crystals	$\epsilon = 1.586$ $\omega = 1.589$	Uniaxial (-). $d = 2.54$
Zn <sub>2</sub> KH(PO <sub>4</sub> ) <sub>2</sub>	Triclinic, 1. Highly modified rod crystals	$\alpha = 1.515$ $\beta = 1.524$ $\gamma = 1.546$	Biaxial (+), 2 <i>V</i> = 70° (67°). $d = 2.99$
Zn <sub>3</sub> KH(PO <sub>4</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	Triclinic, 1. Rhombic tablets	$\alpha = 1.536$ $\beta = 1.541$ $\gamma = 1.548$	Biaxial (+), 2 <i>V</i> = 80° (81°). $d = 2.83$
ZnKPO <sub>4</sub>	Hexagonal, 62. Needle crystals	$\epsilon = 1.553$ $\omega = 1.574$	Uniaxial (-). $d = 3.25$
Zn(NH <sub>4</sub> ) <sub>2</sub> H <sub>4</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	Triclinic, 1. Plates containing <i>X'</i> and <i>Z'</i>	$\alpha = 1.507$ $\beta = 1.516$ $\gamma = 1.540$	Biaxial (+), 2 <i>V</i> = 60° (63°). OAP $\wedge$ length = 15°, and inclined to plate by 37°; $X \wedge$ length = 15°, and inclined to plate by 1°. $d = 2.16$
Zn(NH <sub>4</sub> ) <sub>6</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	Monoclinic, 2/ <i>m</i> . Prisms tabular on (100) with prominent {110} and smaller {011}	$\alpha = 1.507$ $\beta = 1.513$ $\gamma = 1.514$	Biaxial (-), 2 <i>V</i> = 40° (45°), OAP $\perp$ (010), $Y \wedge c = 47^\circ$ in acute $\beta$ . $b = Z$ , $\beta = 108^\circ$ . $d = 1.77$
Zn(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · H <sub>2</sub> O	Orthorhombic, scalar blades tabular on <i>Y-Z</i> plane, elongated along <i>Z</i>	$\alpha = 1.567$ $\beta = 1.600$ $\gamma = 1.606$	Biaxial (-), 2 <i>V</i> = (45°). OAP $\perp$ plane of tabularity, <i>Z</i> $\parallel$ elongation. $d = 2.42$
Zn <sub>3</sub> (NH <sub>4</sub> ) <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	Orthorhombic needles and blades	$\alpha = 1.593$ $\beta = 1.596$ $\gamma = 1.601$	Biaxial (+), 2 <i>V</i> = (85°). <i>X</i> $\parallel$ length. $d = 2.85$

<sup>a</sup> Calculated values for 2*V* are in parentheses. All values for densities are calculated by the Gladstone-Dale equation (8).

<sup>b</sup> Calculated from 2*V* measurement.

**Table III. Powder X-Ray Diffraction Patterns<sup>a</sup>**

d, A.	I	d, A.	I	d, A.	I	d, A.	I	d, A.	I	d, A.	I	d, A.	I
<b>Ca(NH<sub>4</sub>)<sub>4</sub>H<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub></b>				<b>Mg(NH<sub>4</sub>)<sub>2</sub>H<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·2H<sub>2</sub>O</b>				<b>Mg(NH<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·4H<sub>2</sub>O II</b>					
10.09	73	2.65	7	3.02	30	1.737	7	2.970	7	1.966	2		
5.38	11	2.63	8	2.992	12	1.731	5	2.930	2	1.940	5		
5.24	17	2.53	7	2.861	7	1.704	4	2.877	16	1.865	2		
5.06	100	2.41	13	2.815	5	1.673	4	2.832	5	1.821	4		
4.70	35	2.37	4	2.774	12	1.661	4	2.685	4	1.787	4		
4.39	5	2.20	4	2.654	16	1.623	5	2.677	4	1.778	2		
4.21	10	2.17	5	2.580	21	1.602	4	2.663	5	1.773	2		
4.16	11	2.13	5					2.614	4	1.723	2		
3.57	13	2.08	7	<b>Mg(NH<sub>4</sub>)<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·6H<sub>2</sub>O</b>				2.583	13	1.603	5		
3.35	26	2.05	3	8.63	24	3.05	9	2.553	1	1.573	3		
3.31	13	2.03	4	8.07	14	2.99	35	2.510	2	1.560	2		
3.28	12	1.932	3	7.81	55	2.98	39	2.449	1				
3.18	39	1.887	4	7.22	27	2.93	52						
3.12	12	1.861	4	6.53	72	2.78	7	<b>MgAl(NH<sub>4</sub>)<sub>3</sub>H<sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>·6H<sub>2</sub>O</b>					
3.07	10	1.819	4	6.18	37	2.66	4	8.72	87	2.74	6		
3.05	9	1.776	4	5.96	6	2.63	5	8.31	3	2.73	9		
2.93	8	1.760	4	5.34	100	2.60	6	7.42	100	2.68	6		
2.78	14	1.726	4	5.04	7	2.59	9	7.03	8	2.58	4		
2.76	8			4.99	9	2.53	11	6.44	4	2.52	2		
				4.94	11	2.45	9	6.10	12	2.48	3		
				4.84	5	2.36	6	5.49	43	2.45	7		
				4.65	13	2.32	6	5.00	5	2.42	2		
				4.45	20	2.27	8	4.51	6	2.38	6		
				4.32	26	2.19	9	4.27	5	2.33	3		
				4.18	5	2.172	10	4.18	4	2.32	5		
				4.04	15	2.167	18	4.11	2	2.29	5		
				3.96	12	2.093	3	3.72	3	2.23	3		
				3.91	6	2.066	9	3.65	7	2.15	3		
				3.50	18	2.017	4	3.53	9	2.14	4		
				3.32	59	1.974	5	3.49	2	2.04	3		
				3.28	9	1.849	5	3.30	2	1.970	3		
				3.22	22	1.821	5	3.24	8	1.953	2		
				3.16	24	1.806	5	3.19	8	1.933	2		
				3.10	12	1.603	6	3.15	28	1.906	2		
				<b>Mg(NH<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·4H<sub>2</sub>O I</b>				2.99	10	1.865	3		
				8.26	3	2.439	5	2.95	15	1.827	2		
				7.47	100	2.385	9	2.90	7	1.768	3		
				6.27	54	2.365	2	2.88	5	1.751	2		
				6.09	12	2.289	16	2.81	5	1.653	2		
				5.78	31	2.219	3	2.78	5				
				5.39	43	2.204	3	<b>Al(NH<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·OH·2H<sub>2</sub>O</b>					
				5.28	10	2.158	3	9.46	100	2.817	22		
				4.89	5	2.141	2	8.10	18	2.748	7		
				4.58	4	2.099	5	7.71	97	2.677	3		
				4.44	11	2.090	3	7.48	52	2.609	21		
				4.31	4	2.071	3	6.85	7	2.567	12		
				4.13	2	2.033	2	6.21	4	2.538	20		
				3.81	5	2.006	8	5.63	65	2.497	8		
				3.74	79	1.965	6	5.13	43	2.412	16		
				3.56	18	1.947	2	4.91	19	2.326	6		
				3.52	16	1.918	4	4.75	3	2.245	5		
				3.43	6	1.900	3	4.40	4	2.194	4		
				3.24	18	1.870	11	4.15	6	2.098	15		
				3.19	9	1.854	2	4.03	10	2.011	12		
				3.16	13	1.810	2	3.92	5	1.981	5		
				3.11	3	1.800	5	3.86	5	1.925	9		
				3.05	15	1.763	9	3.75	4	1.877	4		
				2.930	35	1.750	3	3.56	17	1.857	5		
				2.897	24	1.715	3	3.50	19	1.810	3		
				2.825	10	1.684	3	3.39	10	1.778	4		
				2.761	15	1.660	2	3.30	8	1.752	5		
				2.712	5	1.651	3	3.17	6	1.704	5		
				2.656	13	1.618	2	3.13	10	1.652	3		
				2.641	16	1.595	3	3.06	39	1.624	4		
				2.494	14	1.588	3	2.902	33	1.568	5		
				<b>Mg(NH<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·4H<sub>2</sub>O II</b>				2.857	26				
				6.30	60	2.421	3	<b>Al<sub>0.33</sub>Fe<sub>0.67</sub>NH<sub>4</sub>P<sub>2</sub>O<sub>7</sub></b>					
				5.96	53	2.399	2	5.82	100	2.98	44		
				5.22	8	2.326	4	5.29	31	2.95	62		
				4.63	23	2.182	2	4.96	11	2.92	10		
				4.01	19	2.157	6	4.17	11	2.63	12		
				3.57	4	2.137	2	3.95	61	2.48	7		
				3.55	5	2.105	2	3.41	12	2.42	21		
				3.46	14	2.082	3	3.12	17	1.98	7		
				3.37	2	2.062	7	3.09	12	1.75	15		
				3.20	100	2.007	5	3.00	38				
				3.16	16	1.993	4						
				3.11	4	1.982	4						

<sup>a</sup> Patterns obtained with an x-ray diffractometer, CuK<sub>α</sub> radiation, λ = 1.5405 Å. Intensities measured as peak heights above background and expressed as per cent of strongest line.

**Table III. Continued**

d, A.	l	d, A.	l	d, A.	l	d, A.	l	d, A.	l	d, A.	l
$\text{Al}_{0.5}\text{Fe}_{0.5}\text{KP}_2\text{O}_7$				$\text{Mn}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$				$\text{Zn}_2\text{KH}(\text{PO}_4)_2$			
5.74	54	2.61	15	7.80	94			9.04	100	2.42	5
5.24	13	2.47	8	7.47	100			5.60	96	2.35	5
4.19	16	2.41	7	6.20	30			4.81	3	2.31	4
3.92	46	2.38	18	4.89	30			4.60	12	2.26	16
3.64	11	2.28	9	4.76	48			4.52	14	2.22	4
3.52	11	2.26	9	2.83	58			4.34	18	2.20	4
3.38	26	2.19	9					4.16	72	2.18	6
3.24	6	2.13	11					3.80	16	2.08	21
3.08	26	2.09	15					3.68	26	2.04	3
3.04	13	2.04	11					3.59	7	1.958	3
2.99	35	2.03	9					3.40	12	1.945	7
2.95	40	1.96	12					3.35	2	1.875	4
2.92	100	1.72	15					3.12	26	1.852	9
$\text{Fe}(\text{NH}_4)_3\text{HPO}_4\text{P}_2\text{O}_7$				$\text{ZnNH}_4\text{H}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$				$\text{Zn}_2\text{KH}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$			
7.85	100	2.94	10	7.18	100	2.82	4	3.01	10	1.842	9
7.31	33	2.92	8	6.88	6	2.75	6	2.95	12	1.810	4
6.58	59	2.88	5	6.61	4	2.69	7	2.90	10	1.764	11
5.13	12	2.78	6	5.97	88	2.66	7	2.81	16	1.725	4
4.67	6	2.76	4	5.64	74	2.62	8	2.74	14	1.700	5
4.06	10	2.67	4	5.24	8	2.55	7	2.70	16	1.684	3
3.94	8	2.61	13	5.02	4	2.51	7	2.59	14	1.607	5
3.68	5	2.51	4	4.76	2	2.50	5	2.53	5	1.575	10
3.50	15	2.31	6	4.16	6	2.44	2	2.51	4	1.553	10
3.45	16	2.25	5	3.99	13	2.40	6				
3.39	8	2.14	4	3.91	2	2.29	3				
3.30	15	2.03	4	3.70	5	2.20	2				
3.22	3	1.968	5	3.60	24	2.12	5				
3.12	5	1.915	5	3.55	8	2.004	9				
3.07	5	1.862	4	3.43	6	1.991	5				
3.01	19	1.776	5	3.32	41	1.883	5				
2.97	15			3.20	6	1.861	5				
$\text{Fe}(\text{NH}_4)_3\text{HPO}_4\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$				$\text{ZnNH}_4\text{PO}_4 \text{ A}$				$\text{Zn}_2\text{KH}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$			
8.29	64	2.83	8	9.24	5	2.24	30	12.87	33	3.25	30
7.64	100	2.77	12	8.91	4	2.20	3	8.15	21	3.22	28
5.19	12	2.66	6	6.27	64	2.17	5	7.74	43	3.17	11
4.68	15	2.62	6	5.14	3	2.13	2	7.66	58	3.12	42
4.57	7	2.59	4	4.65	100	2.07	4	7.46	17	2.93	19
4.35	6	2.53	6	4.47	48	2.04	5	6.67	16	2.91	17
3.92	12	2.50	3	4.38	73	2.01	4	6.33	18	2.85	91
3.87	7	2.23	4	4.10	8	1.990	4	6.27	11	2.81	10
3.81	5	2.17	6	3.98	6	1.945	20	5.81	35	2.79	32
3.71	14	2.15	5	3.93	6	1.877	4	5.68	15	2.72	13
3.50	12	2.12	7	3.46	7	1.827	4	5.07	15	2.69	14
3.43	21	2.10	5	3.42	8	1.779	7	4.90	11	2.68	14
3.24	10	2.09	7	3.21	62	1.745	4	4.71	35	2.65	10
3.05	14	2.03	5	3.20	52	1.736	5	4.63	14	2.63	38
3.02	15	1.94	5	3.14	19	1.718	7	4.41	19	2.61	25
2.95	5	1.86	5	3.12	21	1.688	17	4.34	15	2.44	14
2.92	6	1.79	5	2.98	13	1.679	13	4.30	28	2.38	12
2.88	9			2.78	27	1.660	6	4.20	12	2.32	10
$\text{Fe}(\text{NH}_4)_6(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$				$\text{ZnNH}_4\text{PO}_4 \text{ B}$				$\text{ZnKPO}_4$			
8.70	100	2.93	24	2.72	56	1.641	9	3.82	51	2.18	11
7.82	23	2.80	7	2.67	11	1.625	4	3.76	13	2.15	19
6.57	26	2.67	2	2.62	57	1.612	3	3.68	28	2.10	10
6.16	13	2.61	3	2.55	4	1.607	4	3.62	100	2.05	10
5.34	21	2.59	3	2.50	21	1.590	2	3.58	26	2.04	11
4.64	3	2.52	3	2.48	11	1.569	5	3.52	12	1.989	19
4.48	4	2.50	3	2.46	7	1.564	8	3.47	30	1.950	14
4.36	17	2.45	3	2.44	4	1.550	11	3.34	30	1.895	11
4.08	3	2.31	5	2.31	4			3.29	10	1.767	17
4.03	6	2.26	2								
3.96	5	2.24	2								
3.52	11	2.22	5								
3.34	17	2.19	3								
3.22	4	2.17	3								
3.16	4	2.13	2								
3.04	10	2.10	3								
3.01	18	2.07	3								
2.97	9	1.85	3								
$\text{Fe}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$				$\text{ZnNH}_4\text{PO}_4 \text{ B}$				$\text{Zn}(\text{NH}_4)_2\text{H}_4(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$			
9.24	47			6.33	65	2.17	11	7.30	100	2.786	12
7.47	100			5.12	2	2.12	5	6.63	24	2.753	4
4.80	38			4.81	3	2.04	3	5.96	13	2.657	6
4.70	53			4.62	66	2.01	5	5.57	29	2.635	5
2.79	69			4.34	86	1.964	5	4.93	6	2.593	11
				4.08	29	1.921	15				
				3.93	6	1.907	2				
				3.50	7	1.846	3				
				3.37	4	1.808	8				
				3.24	36	1.778	5				
				3.16	100	1.749	7				
				2.77	23	1.713	17				
				2.72	2	1.686	3				
				2.67	47	1.658	5				
				2.57	7	1.628	15				
				2.55	11	1.623	13				
				2.52	7	1.585	3				
				2.46	28	1.558	17				
				2.28	10	1.541	10				
				2.23	27						



**Table III. Continued**

d, A.	l	d, A.	l
<b>Zn(NH<sub>4</sub>)<sub>2</sub>H<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·2H<sub>2</sub>O</b>			
4.79	88	2.564	4
4.38	5	2.536	3
4.27	6	2.431	6
3.65	55	2.395	11
3.53	16	2.354	4
3.46	35	2.325	2
3.31	6	2.238	2
3.19	18	2.205	5
3.15	10	2.174	3
3.06	14	2.137	4
3.03	14	2.099	7
2.976	8	2.072	6
2.859	6	1.886	5
2.812	6	1.809	3
<b>Zn(NH<sub>4</sub>)<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·6H<sub>2</sub>O</b>			
9.19	10	3.28	7
8.84	21	3.22	14
8.70	100	3.16	7
7.84	83	3.11	24
6.54	47	3.05	13
6.31	10	3.00	30
6.19	41	2.93	39
5.43	9	2.78	43
5.33	38	2.70	7
4.63	6	2.59	8
4.47	7	2.29	7
4.35	34	2.28	15
4.07	7	2.19	13
4.04	11	2.18	11
3.96	13	2.17	10
3.91	10	1.959	7
3.51	53	1.931	7
3.35	24	1.814	16
3.32	52	1.610	11
<b>Zn(NH<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O</b>			
14.24	8	2.53	2
9.20	6	2.47	2
7.14	100	2.43	3
5.68	1	2.39	1
4.75	9	2.25	3
4.71	9	2.20	1
4.50	4	2.16	1
4.23	3	2.12	1
4.16	4	2.08	2
3.53	3	2.01	3
3.28	1	1.932	3
3.14	9	1.833	3
2.98	15	1.757	2
2.86	3	1.640	2
2.77	7	1.618	1
2.67	2	1.592	1
2.63	2		
<b>Zn<sub>3</sub>(NH<sub>4</sub>)<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·2H<sub>2</sub>O</b>			
9.20	100	2.244	7
6.10	10	2.222	8
5.40	23	2.137	6
4.83	23	2.039	17
4.42	21	2.009	6
4.09	2	1.961	6
4.00	6	1.937	12
3.90	12	1.894	2
3.84	28	1.870	4
3.58	6	1.843	2
3.48	41	1.826	7
3.37	23	1.794	7
3.28	44	1.773	3
3.00	48	1.700	9
2.88	6	1.679	5
2.81	33	1.663	9
2.70	6	1.642	2
2.64	16	1.579	6
2.612	17	1.548	9
2.479	12	1.537	8
2.453	15	1.521	7
2.415	6	1.504	8
2.342	4	1.465	5
2.291	30	1.440	8

ever, behaves much as the other divalent cations and precipitates over a wide pH range as Mn(NH<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O, or enters into isomorphous substitution with the divalent metal cation [Fe(II), Zn, Cu] in other precipitates.

**Iron and Aluminum Salts**

Iron and aluminum are quite soluble in merchant-grade acids (9), and these metals are never completely precipitated as sludge, even in clarified wet-process phosphoric acids. The amounts of iron and aluminum that remain form undesirable precipitates when the acids are ammoniated. Iron is also introduced into the wet-process acid before and during ammoniation by the corrosive action of the acid on processing equipment.

Upon ammoniation, the solubility of these metals in the acid solution decreases rapidly—presumably because of the decomposition of iron and aluminum phosphate complexes—and they precipitate as compounds that not only create a handling problem but also immobilize phosphorus in forms not readily available to crops.

When acids that contain only orthophosphate are ammoniated, the most common initial precipitate above pH 3 is an amorphous gel with a variable composition of about (Al,Fe)PO<sub>4</sub>·nH<sub>2</sub>O in which small amounts of other metals may be substituted. On standing in an ammoniated solution with pH 3 to 5 for a few days, the gel reacts to form crystals of (NH<sub>4</sub>,K)<sub>3</sub>Al<sub>3</sub>H<sub>8</sub>(PO<sub>4</sub>)<sub>8</sub>·18H<sub>2</sub>O (taranakite) and NH<sub>4</sub>Fe(HPO<sub>4</sub>)<sub>2</sub> (10, 15).

On ammoniation of the acid, to near neutrality or alkalinity, both iron and aluminum precipitate immediately as gelatinous phosphates. On standing in the mother liquor, the iron phosphate remains unchanged, but the aluminum phosphate crystallizes in a few days as Al(NH<sub>4</sub>)<sub>2</sub>H(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (5) at pH 5 to 7 and as AlNH<sub>4</sub>PO<sub>4</sub>OH·2H<sub>2</sub>O at pH's above 7. In dilute solutions at pH's above 7, the crystals are mixtures of AlNH<sub>4</sub>PO<sub>4</sub>OH·3H<sub>2</sub>O and the dihydrate (5). The two hydrates can be differentiated by infrared; both contain strong OH<sup>-</sup> absorption bands in accord with the assigned formula.

Solutions of condensed ammonium phosphates, such as TVA's 10-34-0 liquid fertilizer obtained by ammoniating superphosphoric acid (33% P, 75% P<sub>2</sub>O<sub>5</sub>) (78), sequester aluminum and ferric iron. In a study of this effect, samples of the 10-34-0 solution were adjusted to pH 6 or 8, and to portions of each of these was added aluminum or ferric nitrate to provide 1.5% Al or Fe in solution. At pH 8, the solution containing aluminum yielded a precipitate of Al(NH<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·OH·2H<sub>2</sub>O after 2 weeks, but the solution containing iron yielded no precipitate in 4 years. At pH 6, the solution containing aluminum

yielded a precipitate after 6 months; this precipitate has not been identified. The solution containing iron started to precipitate in a few days, but 6 months were required to produce a significant amount of precipitate. Increasing the iron content of the solution did not increase the rate or the amount of precipitate proportionately.

The iron precipitate is unusual in that it contains both ortho- and pyrophosphate; its formula is Fe(NH<sub>4</sub>)<sub>3</sub>HPO<sub>4</sub>·P<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O. The corresponding anhydrous crystalline salt appears in solid ammonium polyphosphate prepared by ammoniating merchant grade or concentrated wet-process phosphoric acid under pressure at temperatures below 240° C. (6). Both the anhydrous salt and its monohydrate can be prepared readily from reagent grade chemicals. Their infrared spectra show P-O absorption bands for both PO<sub>4</sub><sup>-3</sup> and P<sub>2</sub>O<sub>7</sub><sup>-4</sup>; those of the pyrophosphate are more intense. Chromatographic analysis showed that the distribution of the phosphorus in the anhydrous salt was 37% ortho-, 60% pyro-, and 3% more highly condensed phosphates, and in the monohydrate was 35% ortho-, 64% pyro-, and 1% more highly condensed phosphates. Only two other mixed ortho- and pyrophosphates have been reported in the literature—K<sub>3</sub>H<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (13) and K<sub>3</sub>H<sub>2</sub>PO<sub>4</sub>·P<sub>2</sub>O<sub>7</sub> (17). Both Fe(NH<sub>4</sub>)<sub>3</sub>HPO<sub>4</sub>·P<sub>2</sub>O<sub>7</sub> and its monohydrate are soluble in dilute mineral acid and neutral ammonium citrate solution.

When ammonium polyphosphate is prepared at temperatures above 240° C., a series of acid-insoluble salts with the composition of (Fe,Al)<sub>3</sub>NH<sub>4</sub>P<sub>2</sub>O<sub>7</sub> is formed, frequently as a scalar deposit on the walls of the reaction vessel. The potassium analog, (Fe,Al)KP<sub>2</sub>O<sub>7</sub>, is formed during the production of potassium polyphosphate by heating a mixture of potassium chloride and wet-process phosphoric acid, or when potassium is added to ammonium polyphosphate; it also is insoluble in acid.

The behavior of ferrous iron in ammonium polyphosphate solutions is similar to that of zinc and divalent manganese. At pH 6, ferrous iron precipitates in two forms. The more common form is Fe(NH<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O, a gray-green precipitate that oxidizes and turns brown on exposure to the atmosphere. This salt is formed rapidly when metallic iron is attacked by the fertilizer solution. A similar salt in which potassium substituted for part of the ammonium was found as a product of the corrosion of a mild steel container in which an ammonium polyphosphate solution containing potassium had been stored.

A less common ferrous compound that is formed in the same solutions is Fe(NH<sub>4</sub>)<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·6H<sub>2</sub>O. The amount of this compound increases as the concentration of the solution is increased and

the ratio of pyro- to orthophosphate is increased much above 1.

### Discussion

Some of the metallic phosphates that appear in products of the ammoniation of merchant grade and concentrated wet-process phosphoric acids were identified and characterized. Most of the compounds are pyrophosphates of the metallic impurities that were in solution in the original acid, but some are phosphates of micronutrient metals that are added to the fertilizers. Some of the compounds have been reported previously (10, 12, 14, 15), but their descriptions were incomplete. These compounds precipitate as sludges that interfere with the handling of the fertilizer solutions, and some of the compounds immobilize phosphorus in forms that are of relatively little agronomic value.

Isomorphous substitution is common among these compounds—potassium for ammonium, aluminum for ferric iron, and Fe(II), Mn(II), Zn, and Cu for each other. These substitutions and those in series such as  $(\text{Mn,Fe})(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  and  $(\text{Zn,Mg,Fe})(\text{NH}_4)_6(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$  cause only small changes in position or intensity of the x-ray reflections. Usually there are no changes in crystal morphology or habit, but there are regular changes in the refractive indices with changes in chemical constituents.

The most common precipitates in liquid fertilizers made by ammoniating wet-process phosphoric acids are those of magnesium, iron, and aluminum. When the solutions contain only orthophosphate, struvite and gelatinous iron and aluminum phosphates form readily; when the solutions contain condensed phosphates, the dimorphs of  $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$  are usually precipitated. The impurities most commonly found in solid ammonium and potassium poly-

phosphates are  $(\text{Fe,Al})(\text{NH}_4)_3\text{HPO}_4\text{P}_2\text{O}_7$ ,  $(\text{Fe,Al})\text{NH}_4\text{P}_2\text{O}_7$ , and  $(\text{Fe,Al})\text{KP}_2\text{O}_7$ .

Two of the most common precipitates cause the most difficulty in identifying the solids. Ferrous iron precipitates as  $\text{Fe}(\text{NH}_4\text{,K})_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  in the form of poorly developed, complex blade-crystal aggregates which decompose rapidly on exposure to air because of oxidation of the ferrous iron. The crystallographic data for this salt are only approximate; its x-ray pattern was weak and diffuse. The manganous analog  $\text{Mn}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  is much like the ferrous salt. The amorphous iron and aluminum phosphates  $(\text{Fe,Al})\text{PO}_4 \cdot n\text{H}_2\text{O}$  do not have characteristic x-ray patterns; they are optically isotropic with refractive indices in the range 1.48 to 1.64. The refractive index varies widely with such factors as the amount of adsorbed water, the ratio of iron to aluminum, and the amount of foreign cations that has been coprecipitated, occluded, or adsorbed.

Micronutrient cations added to phosphate fertilizers as soluble salts usually precipitate slowly over a long time as compounds which are quite stable in the fertilizer's environment. In liquid fertilizers, these precipitations adversely alter the composition of the fertilizer and concentrate the micronutrient elements in the solid phase. When the fertilizers are applied to the soil, these compounds will control the rates at which the micronutrients are released to the plants. Further studies are being made of the agronomic value of many of these compounds and the conditions that control their formation.

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