Figure 1. Availability coefficient index plotted against geometric surface area

Results with $CaSO_4 \cdot 2H_2O$ omitted

to dicalcium phosphate increases as geometric surface area of the fertilizer increases. Granulation of mixtures of dicalcium phosphate and soluble salts or inert materials increases plant response per unit of P presumably because the geometric surface area has been increased. Results of field experiments reported by Terman et al. (8) indicate that mechanical mixing of previously granulated dicalcium phosphate with soluble salts (components in separate granules) is much less effective than granulating mixtures (all components intimately mixed within each granule). On the basis of the results reported here, the granulation of mixtures increases the geometric surface area of the fertilizer, while mechanical mixing of previously granulated components does not influence the geometric surface area of the dicalcium phosphate, which means mechanical mixtures should be inferior to granulated mixtures.

Literature Cited

(1) Bouldin, D. R., DeMent, J. D., Sample, E. C., J. Agr. Food Chem. **8,** 470 (1960).
(2) Bouldin, D. R., Sample, E. C., Soil Sci. Soc. Am. Proc. **23,** 276 (1959).
(3) Ibid., pp. 281–5.
(4) Hill, W. L., Proc. Tech. Sessions Bone Char. **1955,** 247.
(5) Kolaian, J. H., Ohlrogge, A. J., Agron. J. **51,** 106 (1959).
(6) Moreno, E. C., Soil Sci. Soc. Am. Proc. **23,** 326 (1959).
(7) Starostka, R. W., Hill, W. L., Ibid., **19,** 193 (1955).
(8) Terman, G. L., Long, O. H., Anthony, J. L., Farm Chem. **122,** No. 1, 34 (1959).

FERTILIZER MATERIALS

Preparation and Characterization of Some Calcium Pyrophosphates

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Twenty-five calcium pyrophosphates were prepared—eight containing ammonium and 10 containing potassium. Two pairs of dimorphic hydrated calcium pyrophosphates were established, and the compositions and optical and crystallographic properties of the salts were determined. The results will be useful in identifications of pyrophosphates in fertilizers and other mixtures in which they occur.

IN WATER, vitreous calcium polyphosphate (known commercially as calcium metaphosphate) degrades hydrolytically in several stages. There is first formed a sirupy, water-immiscible polymer (coacervate). On standing, the coacervate deposits crystals of calcium pyrophosphates, and in the presence of sufficient water all the solute phosphorus eventually hydrolyzes to orthophosphate. At one stage of the degradation, however, the major phosphate ion is pyrophosphate, and two crystalline calcium pyrophosphates that are formed in the process have been described briefly (5).

Treatment of the coacervate with ammonia produces crystalline calcium ammonium pyrophosphates. Two of these have been described (6), and both have been found in experimental fertilizers prepared from ammoniated calcium polyphosphate. When greenhouse tests showed these salts to be satisfactory sources of nitrogen and phosphorus for growing plants, further studies were made of the calcium pyrophosphates. Interest in these salts was stimulated by the growing use of condensed phosphates, such as calcium metaphosphate and superphosphoric acid, as fertilizer ingredients.

Twenty-five calcium pyrophosphates have been prepared. Eight of these were calcium ammonium pyrophosphates, and 10 were calcium potassium pyrophosphates. Many of these compounds may be encountered in fertilizers prepared from condensed phosphates or their hydrolysis products. A few of these compounds have been reported previously (2, 4, 7, 10), but their descriptions are incomplete and based mainly on their chemical compositions. The chemical and crystallographic descriptions of these salts will be useful in their identification in fertilizer mixtures.

Only those products that were shown by petrographic and x-ray examination to be single-phase crystalline materials were studied further. All the products were shown by paper chromatography to be pyrophosphates. Chemical analyses were made on air-dried samples of most of the products to avoid partial dehydration, and, because of the method of drying, some of the hydrate-water contents, which were determined by difference, are slightly high. Phosphorus was determined spectrophotometrically (8), calcium gravimetrically (14), potassium flame photometrically with lithium as the internal standard, and ammonia by distillation with sodium hydroxide.

The morphological and optical properties of each product were determined with a polarizing microscope. Densities of coarsely crystalline products were determined pycnometrically, and densities of finely crystalline products were calculated from the chemical composition and refractive indices by the Gladstone-Dale relationship (11).

The x-ray diffraction spectra of the products were obtained by the powder wedge technique, with Cu $K\alpha$ radiation and a camera with a diameter of 14.32 cm. Intensities were estimated visually or read from x-ray goniometer tracings. When untwinned, sufficiently large crystals were obtained, single-crystal x-ray studies were made by rotation and Weissenberg techniques to determine the unit-cell constants.

The methods of preparation of the calcium pyrophosphates were developed empirically to yield homogeneous, single-phase, crystalline products suitable for optical and x-ray studies. Subsequent studies, the results of which are being prepared for publication, of portions of multicomponent aqueous systems in which the compounds appear as solid phases showed that the proportions of the reagents could be varied somewhat without changing the compositions of the products. Most of the methods can be scaled up to yield larger quantities of the products.

The pyrophosphate starting materials were prepared in the laboratory. $K_4P_2O_7$ was prepared by heating K_2HPO_4 at 600° C. for 1 hour. Amorphous calcium pyrophosphate was precipitated by adding $CaCl_2$ solution to a solution of $Na_4P_2O_7$, but this material was seldom used because it was contaminated with sodium and because considerable care was required to obtain a reactive amorphous precipitate rather than an unreactive crystalline product. $CaH_2P_2O_7$, which was used in the preparation of many of the other calcium pyrophosphates, was prepared by the method described below. All other chemicals were reagent grade.

Table I. Calcium Pyrophosphates

| Compound | Composition, % | | | Moles/Mole P_2O_5 | |
	CaO	P_2O_5	H_2O (diff.)	CaO	Hydrate H_2O
$Ca_2P_2O_7 \cdot 2H_2O$					
Triclinic dimorph	38.29	48.88	12.83	1.98	2.07
Monoclinic dimorph	37.16	48.15	14.69[a]	1.95	2.40
Stoichiometric	38.66	48.92	12.42	2.00	2.00
$Ca_2P_2O_7 \cdot 4H_2O$					
Orthorhombic dimorph	34.23	43.22	22.35[b]	2.00	4.07
Monoclinic dimorph	34.1	43.2	22.7[c]	2.00	4.17
Stoichiometric	34.39	43.35	22.08	2.00	4.00
$CaH_2P_2O_7$	25.88	65.56	8.56	1.00	1.03
Stoichiometric	25.96	65.70	8.34	1.00	1.00
$Ca_3H_2(P_2O_7)_2 \cdot 4H_2O$	29.53	52.92	17.55	1.41	2.02
Stoichiometric	31.03	52.36	16.61	1.50	2.00
$Ca_3H_2(P_2O_7)_2 \cdot H_2O$	34.02	57.71	8.27	1.49	1.24
Stoichiometric	34.46	58.16	7.38	1.50	1.00

[a] Coarse crystals had ignition loss of 12.2%.
[b] Contained 0.2% K_2O.
[c] Coarse crystals had ignition loss of 22.2%.

Table II. Calcium Ammonium Pyrophosphates

| Compound | Composition, % | | | | Moles/Mole P_2O_5 | | |
	CaO	$(NH_4)_2O$	P_2O_5	H_2O (diff.)	CaO	NH_4	Hydrate H_2O
$Ca(NH_4)_2P_2O_7 \cdot H_2O$	20.75	19.17	52.88	7.20	0.99	1.98	1.07
Stoichiometric	20.91	19.42	52.94	6.73	1.00	2.00	1.00
$Ca_3(NH_4)_2(P_2O_7)_2 \cdot 6H_2O$	27.26	8.41	46.38	17.95	1.49	0.99	3.05
Stoichiometric	27.48	8.51	46.36	17.65	1.50	1.00	3.00
$Ca_5(NH_4)_2(P_2O_7)_3 \cdot 6H_2O$	32.31	6.34[a]	48.67	12.68[a]	1.68	0.71	2.05
Stoichiometric	32.36	6.01	49.15	12.48	1.67	0.67	2.00
$CaNH_4HP_2O_7$	23.88	10.70	59.98	5.44	1.01	0.97	0.20
Stoichiometric	24.06	11.17	60.90	3.87	1.00	1.00	0.00
$Ca_3(NH_4)_4H_6(P_2O_7)_4 \cdot 3H_2O$	17.88	10.24	59.92	11.96	0.76	0.93	0.89
Stoichiometric	17.74	10.98	59.88	11.40	0.75	1.00	0.75
$Ca(NH_4)_2H_4(P_2O_7)_2$	13.07	12.26	65.91	8.76	0.50	1.02	0.05
Stoichiometric	13.10	12.17	66.31	8.42	0.50	1.00	0.00
$Ca_2NH_4H_3(P_2O_7)_2 \cdot 3H_2O$	23.39	5.38	56.45	14.78	1.05	0.52	1.38
Stoichiometric	22.29	5.18	56.42	16.11	1.00	0.50	1.50
$Ca_2NH_4H_3(P_2O_7)_2 \cdot H_2O$	23.76	5.50	59.94	10.80	1.01	0.50	0.68
Stoichiometric	24.01	5.57	60.78	9.64	1.00	0.50	0.50

[a] Contained 1 to 2% occluded NH_4Cl.

Many of the pyrophosphates were either quite insoluble or very slowly soluble in water. The crystals of these materials were washed thoroughly with water, rinsed with acetone, and allowed to dry in air at room temperature. Some of the pyrophosphates, however, were readily soluble in water, and the details of the washing and drying of these materials are included in the methods of their preparation.

Calcium Pyrophosphates

Six calcium pyrophosphates, including two pairs of dimorphs of hydrated calcium pyrophosphate, were prepared. The compositions of typical preparations of these materials are shown in Table I.

Calcium Pyrophosphate Dihydrate, Triclinic. The triclinic dimorph of $Ca_2P_2O_7 \cdot 2H_2O$ was prepared by allowing a solution of 1.1 grams of $CaH_2P_2O_7$ in 100 ml. of water to stand at room temperature. Coarse prismatic crystals appeared in 3 days, and the crystallization was virtually complete in 7 days.

The triclinic is the more stable of the dimorphs of $Ca_2P_2O_7 \cdot 2H_2O$, and is one of the hydrolytic degradation product of calcium polyphosphate. It dehydrate rapidly at 300° to 400° C. to oriented pseudomorphs of β-$Ca_2P_2O_7$.

Calcium Pyrophosphate Dihydrate, Monoclinic. The monoclinic dimorph of $Ca_2P_2O_7 \cdot 2H_2O$ is prepared in nearly neutral media, rather than in the acid media in which the triclinic dimorph is formed. In the preparation of the monoclinic dimorph, a saturated $CaCl_2$ solution was added to a solution of 1 gram of $K_4P_2O_7$ and 10 grams of KCl in 60 ml. of water, with care that the pH did not fall below 6. The mixture was then diluted to 100 ml. with water, and the gelatinous precipitate of amorphous calcium pyrophosphate was allowed to stand undisturbed in its mother liquor at 45°C. for 2 weeks to form crystals of monoclinic $Ca_2P_2O_7 \cdot 2H_2O$. This dimorph also is very insoluble in water.

The presence of a dilute electrolyte appears essential to the crystallization of monoclinic $Ca_2P_2O_7 \cdot 2H_2O$. In water, the monoclinic dimorph slowly alters to the triclinic dimorph. In the preparation of the monoclinic dimorph, lowering of either the pH or the temperature

tends to form $Ca_2P_2O_7.4H_2O$ instead of the dihydrate.

Calcium Pyrophosphate Tetrahydrate, Orthorhombic. The orthorhombic dimorph of $Ca_2P_2O_7.4H_2O$ is formed in a very dilute solution of an electrolyte in the pH range 3 to 5. It was prepared by adding 1.1 grams of $CaH_2P_2O_7$ to 200 ml. of $0.05M$ NH_4OH and allowing the mixture to stand at room temperature. The gelatinous precipitate crystallized to orthorhombic $Ca_2P_2O_7.4H_2O$ within 24 hours. The product is very insoluble in water.

Even slight warming of the mixture tends to form monoclinic $Ca_2P_2O_7.2H_2O$ instead of the orthorhombic tetrahydrate, and in water or dilute solutions orthorhombic $Ca_2P_2O_7.4H_2O$ alters slowly to triclinic $Ca_2P_2O_7.2H_2O$. In the preparation of orthorhombic $Ca_2P_2O_7.-4H_2O$, therefore, the product should be removed from the mother liquor as soon as possible.

Calcium Pyrophosphate Tetrahydrate, Monoclinic. The monoclinic dimorph of $Ca_2P_2O_7.4H_2O$ also is formed in the pH range 3 to 5, but in solutions of electrolytes more concentrated than those in which the orthorhombic dimorph is formed. The monoclinic dimorph was prepared by mixing 35 ml. of $2.2M$ $Ca(C_2H_3O_2)_2$ solution with a solution of 17 grams of $CaH_2P_2O_7$ in 425 ml. of water and allowing the precipitated amorphous calcium pyrophosphate to stand in the mother liquor at room temperature. Well-formed stable crystals of monoclinic $Ca_2P_2-O_7.4H_2O$ appeared in a few hours. The product is very insoluble in water. On standing in water, however, monoclinic $Ca_2P_2O_7.4H_2O$ is slowly replaced by its orthorhombic dimorph.

Calcium Acid Pyrophosphate. This compound, $CaH_2P_2O_7$, which was used in the preparation of many of the other pyrophosphates, was described by Hill and coworkers (*10*) and prepared in quantity by Bassett (*3*). In a modification of Bassett's method, 250 ml. of reagent-grade 85% H_3PO_4 in a borosilicate-glass beaker was heated rapidly to 210° C. with vigorous stirring which was continued throughout the preparation to prevent supersaturation. $Ca(H_2-PO_4)_2.H_2O$ was then added at the rate of about 1 gram per minute until the first crystals of $CaH_2P_2O_7$ appeared. Seeding or scratching the walls of the beaker with a glass rod helped to prevent supersaturation. The rate of addition of $Ca(H_2PO_4)_2.H_2O$ was then decreased to about 0.2 gram per minute, and the addition was continued until a reasonably thick suspension (about 20% solids) was obtained. The hot mixture was filtered immediately by suction on a fritted-glass filter. When cool, the crystals were washed liberally with acetone to remove residual acid and then allowed to air dry.

The usual crop of $CaH_2P_2O_7$ weighed about 50 grams. The salt is soluble to the extent of about 4 grams in 100 ml. of water, but the solution is not stable. On standing, a solution of $CaH_2P_2O_7$ in water deposits crystals of either $Ca_3H_2(P_2O_7)_2.4H_2O$ or triclinic $Ca_2-P_2O_7.2H_2O$, depending upon the concentration of the solution.

Tricalcium Dihydrogen Pyrophosphate Tetrahydrate. The tetrahydrate $Ca_3H_2(P_2O_7)_2.4H_2O$ was prepared by allowing mixtures of one part by weight of $CaH_2P_2O_7$ and no more than 19 parts of water to stand at room temperature for several hours. Higher yields and more uniform crystals were obtained with smaller proportions of water, but longer times, usually 3 or 4 days, were required. If more than 19 parts of water was used, the initially precipitated $Ca_3H_2(P_2O_7)_2.-4H_2O$ was metastable and rapidly altered to triclinic $Ca_2P_2O_7.2H_2O$. The preparation of larger crystals may be carried out at higher temperatures if the amount of water in the initial mixture is decreased to 10 parts or less. $Ca_3H_2-(P_2O_7)_2.4H_2O$ dissolves very slowly in water.

Tricalcium Dihydrogen Pyrophosphate Monohydrate. The monohydrate $Ca_3H_2(P_2O_7)_2.H_2O$ was prepared by digesting mixtures of 1 part by weight of $CaH_2P_2O_7$ and no more than 10 parts of water at 65° to 75° C. for about 24 hours. The initially precipitated $Ca_3H_2(P_2O_7)_2.4H_2O$ was metastable; it slowly redissolved as the monohydrate crystallized. If more than 10 parts of water was used, or if the temperature was much above 75° C., the monohydrate was slowly replaced by triclinic $Ca_2P_2O_7.2H_2O$. $Ca_3H_2(P_2O_7)_2.-H_2O$ dissolves very slowly in water.

Calcium Ammonium Pyrophosphates

Three neutral and five acid calcium ammonium pyrophosphates were prepared. The compositions of typical preparations of these materials are shown in Table II.

Calcium Diammonium Pyrophosphate Monohydrate. The salt $Ca-(NH_4)_2P_2O_7.H_2O$ was prepared by treating at room temperature a solution of $CaH_2P_2O_7$ with NH_4OH to form a mixture with a pH of 7 or more and in which the water was no more than 95% of the total weight of the mixture. Small crystals of the product formed immediately.

When the pH was below 7 or the water content more than 95%, the initially precipitated $Ca(NH_4)_2P_2O_7.-H_2O$ was replaced rapidly by $Ca_3(NH_4)_2-(P_2O_7)_2.6H_2O$. On the other hand, large crystals of $Ca(NH_4)_2P_2O_7.H_2O$ were prepared by allowing crystals of $Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$ to stand at room temperature in a 5 to $10M$ NH_4OH solution.

$Ca(NH_4)_2P_2O_7.H_2O$ dissolves slowly and incongruently in water. The crystals were washed rapidly with a minimum amount of water, rinsed with acetone, and air dried. The crystals tend to dehydrate at temperatures much above room temperature.

Tricalcium Diammonium Pyrophosphate Hexahydrate. Crystals of $Ca_3-(NH_4)_2(P_2O_7)_2.6H_2O$ were prepared by allowing a mixture of 1 gram of $CaH_2-P_2O_7$ and 15 ml. of $0.6M$ NH_4OH to stand at room temperature for 24 to 48 hours. The crystals were small, but well-formed plates, and they were washed and dried like other slowly soluble materials.

$Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$ is the stable phase in the region of the system $CaH_2-P_2O_7–NH_4OH–H_2O$ in which the pH is 5 to 8 and the H_2O content is 80 to 95%. Use of less soluble sources of pyrophosphate, such as $Ca_3H_2(P_2O_7)_2.-4H_2O$, $CaNH_4HP_2O_7$, or $Ca(NH_4)_2-P_2O_7.H_2O$, instead of $CaH_2P_2O_7$ in the preparation yields larger crystals of $Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$, but a longer time is required. On standing in water, $Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$ is slowly replaced by orthorhombic $Ca_2P_2O_7.4H_2O$.

Pentacalcium Diammonium Pyrophosphate Hexahydrate. The salt $Ca_5(NH_4)_2(P_2O_7)_3.6H_2O$ was prepared by allowing 1 gram of monoclinic $Ca_2P_2O_7.4H_2O$ to stand at room temperature in 50 ml. of $5M$ NH_4Cl solution. The preparation could be accelerated by warming and stirring the mixture, but the crystals then were smaller. The product is so insoluble that it may be washed liberally with hot water.

Tricalcium Tetraammonium Acid Pyrophosphate Trihydrate. The salt $Ca_3(NH_4)_4H_6(P_2O_7)_4.3H_2O$ was prepared by allowing 1 gram of $CaH_2P_2O_7$ to stand for about 1 hour at room temperature in 50 ml. of $6.5M$ NH_4Cl solution. The product is quite soluble in water. The crystals were filtered from the mother liquor, washed repeatedly with ethyl alcohol to remove NH_4Cl, rinsed with acetone, and air dried.

$Ca_3(NH_4)_4H_6(P_2O_7)_4.3H_2O$ is metastable in its mother liquor, but it persists unchanged for several hours, after which a slow alteration to $CaNH_4HP_2O_7$ begins.

Calcium Ammonium Hydrogen Pyrophosphate. The salt $CaNH_4HP_2O_7$ was prepared by digesting 1 gram of $CaH_2P_2O_7$ in 75 ml. of $0.6M$ NH_4Cl solution at 65° to 70° C. for about 1 hour. The preparation was accelerated by stirring the mixture, but the product then was composed of spherulites of small blade crystals. $CaNH_4HP_2O_7$ is very slowly soluble in water.

$CaNH_4HP_2O_7$ is the stable phase in the region of the system $CaH_2P_2O_7–NH_4OH–H_2O$ in which the pH is

2.5 to 5 and the H₂O content

2.5 to 5 and the H_2O content is less than 95%. $CaNH_4HP_2O_7$ may be prepared also by prolonging the equilibration in the method of preparation of $Ca_3(NH_4)_4H_6(P_2O_7)_4 \cdot 3H_2O$.

Calcium Diammonium Tetrahydrogen Pyrophosphate. The salt $Ca(NH_4)_2H_4(P_2O_7)_2$ is formed in concentrated salt solutions that have a pH below 2. It was prepared by allowing 5 grams of $CaH_2P_2O_7$ to stand at room temperature in 20 ml. of a saturated solution of NH_4Cl for about 24 hours, but the time could be shortened by seeding the mixture. $Ca(NH_4)_2H_4(P_2O_7)_2$ is very soluble in water in which it rapidly alters to $Ca_2NH_4H_3(P_2O_7)_2 \cdot 3H_2O$. The crystals of $Ca(NH_4)_2H_4(P_2O_7)_2$ were filtered rapidly by suction, suspended in ethyl alcohol to remove NH_4Cl, filtered, rinsed with acetone, and air dried. The dry crystals were stable in the usual laboratory atmosphere.

Dicalcium Ammonium Trihydrogen Pyrophosphate Trihydrate. The salt $Ca_2NH_4H_3(P_2O_7)_2 \cdot 3H_2O$ was prepared by allowing 2 grams of $CaH_2P_2O_7$ to stand in 25 ml. of $1.5M$ NH_4Cl solution at room temperature for about 1 hour. The preparation could be accelerated by stirring and warming the mixture to 40° or 45° C. The product is insoluble in water.

Dicalcium Ammonium Trihydrogen Pyrophosphate Monohydrate. The salt $Ca_2NH_4H_3(P_2O_7)_2 \cdot H_2O$ was prepared by allowing 10 grams of $CaH_2P_2O_7$ to stand in 20 ml. of $4.7M$ NH_4Cl solution in a stoppered container at room temperature for 6 months. The crystals are quite insoluble in water.

$Ca_2NH_4H_3(P_2O_7)_2 \cdot H_2O$ is formed in salt solutions more concentrated than those used in the preparation of the trihydrate, but both hydrates are formed in the pH range 2.0 to 2.5. In the preparation of the monohydrate, there is first formed a mixture of $Ca_2NH_4H_3(P_2O_7)_2 \cdot 3H_2O$ and $Ca_3(NH_4)_2(P_2O_7)_2 \cdot 6H_2O$, and these phases slowly dissolve, and crystals of $Ca_2NH_4H_3(P_2O_7)_2 \cdot H_2O$ appear after several weeks.

Calcium Potassium Pyrophosphates

Four neutral and six acid calcium potassium pyrophosphates were prepared. The compositions of typical preparations of these materials are shown in Table III.

Calcium Dipotassium Pyrophosphate. Crystals of $CaK_2P_2O_7$ were prepared by placing 1 gram of $CaH_2P_2O_7$ in 20 ml. of $0.5M$ $K_4P_2O_7$ solution and allowing the mixture to stand at room temperature. Hexagonal plates of $CaK_2P_2O_7 \cdot 4H_2O$ were formed immediately, but these were unstable and were replaced by small sixling twin crystals of the desired anhydrous salt. The replacement was complete within an hour at room temperature; warming

hastened the replacement and also produced larger crystals. $CaK_2P_2O_7$ is very insoluble in water and is stable over a wide range of temperature.

In the preparation of $CaK_2P_2O_7$, the ratio of the reagents may be varied considerably if the pH is kept between 6 and 8 and the water content of the mixture is kept below 95%. At pH's above 8, the stable phase is $CaK_2P_2O_7 \cdot 4H_2O$.

Calcium Dipotassium Pyrophosphate Tetrahydrate. The tetrahydrate $CaK_2P_2O_7 \cdot 4H_2O$ was prepared by adding, slowly and with stirring, 15 ml. of $0.5M$ $Ca(C_2H_3O_2)_2$ solution to a solution of 5 grams of $K_4P_2O_7$ in 50 ml. of water at room temperature. The product crystallized rapidly, and the crystals are quite insoluble in water. The crystals dehydrate at temperatures above 100° C. to pseudomorphs of $CaK_2P_2O_7$.

$CaK_2P_2O_7 \cdot 4H_2O$ forms in solutions with pH's in the range 6 to 10.5, but it is stable only at pH's above 8. At lower pH, it is replaced by the anhydrous salt.

Tricalcium Dipotassium Pyrophosphate Dihydrate. The salt $Ca_3K_2(P_2O_7)_2 \cdot 2H_2O$ was prepared by allowing a mixture of 6.80 grams of $K_4P_2O_7$, 4.27 grams of $CaH_2P_2O_7$, and 100 ml. of water to stand at room temperature for 4 to 7 days. The finely divided crystalline product is very slowly soluble in water.

The proportions given for the preparation of $Ca_3K_2(P_2O_7)_2 \cdot 2H_2O$ place the mixture in the center of its field of stability. The salt is formed in any mixture of 10 grams of $K_4P_2O_7$, 6.8 grams of $CaH_2P_2O_7$, and 70 to 320 ml. of water that is allowed to stand at room temperature for about a week. Increasing the amount of water in the mixture increases both the time required and the size of the crystals produced. $CaKHP_2O_7$ and $Ca_5K_2(P_2O_7)_3 \cdot 6H_2O$ are first formed, but

these metastable intermediates are slowly replaced by $Ca_3K_2(P_2O_7)_2 \cdot 2H_2O$.

Pentacalcium Dipotassium Pyrophosphate Hexahydrate. The salt $Ca_5K_2(P_2O_7)_3 \cdot 6H_2O$ was prepared by adding monoclinic $Ca_2P_2O_7 \cdot 4H_2O$ or amorphous calcium pyrophosphate (prepared from $Na_4P_2O_7$ and $CaCl_2$) to a stirred $5M$ KCl solution at 70° to 75° C. The product precipitated rapidly. Larger crystals were prepared by allowing a diluted mixture of the reagents to stand at room temperature for about a week. $Ca_5K_2(P_2O_7)_3 \cdot 6H_2O$ is very insoluble; it was washed liberally with warm water to remove KCl.

Calcium Tetrapotassium Dihydrogen Pyrophosphate. The salt $CaK_4H_2(P_2O_7)_2$ was prepared by adding a mixture of 6 grams of $K_4P_2O_7$ and 4 grams of $CaH_2P_2O_7$ to 100 ml. of a saturated $(4.5M)$ KCl solution at room temperature. A gelatinous precipitate was formed initially, but this precipitate crystallized within 24 hours. Stirring hastened the crystallization but produced smaller crystals. The product is moderately soluble, but it can be washed sparingly with water.

Calcium Dipotassium Tetrahydrogen Pyrophosphate. The salt $CaK_2H_4(P_2O_7)_2$ was prepared by adding 5 grams of $CaH_2P_2O_7$ to a mixture of 20 ml. of saturated KCl solution and 10 grams of solid KCl and allowing the mixture to stand at room temperature for 12 to 24 hours. Stirring or seeding accelerated the crystallization but produced smaller crystals.

$CaK_2H_4(P_2O_7)_2$, like its ammonium isomorph, is soluble in water. The product was filtered rapidly by suction, suspended in ethyl alcohol to remove KCl, filtered, rinsed with acetone, and air dried.

Calcium Potassium Hydrogen Pyrophosphate. The salt $CaKHP_2O_7$ was

Table III. Calcium Potassium Pyrophosphates

| Compound | Composition, % | | | | Moles/Mole P₂O₅ | | |
	CaO	K₂O	P₂O₅	H₂O (diff.)	CaO	K	Hydrate H₂O
CaK₂P₂O₇	19.60	30.79	49.49	0.12	1.00	1.88	0.02
Stoichiometric	19.19	32.23	48.58	0.00	1.00	2.00	0.00
CaK₂P₂O₇.4H₂O	15.34	25.20	38.72	20.74	1.00	1.96	4.22
Stoichiometric	15.39	25.86	38.97	19.78	1.00	2.00	4.00
Ca₃K₂(P₂O₇)₂.2H₂O	28.77	15.00	48.96	7.27	1.48	0.93	1.17
Stoichiometric	28.89	16.17	48.75	6.19	1.50	1.00	1.00
Ca₅K₂(P₂O₇)₃.6H₂O	30.48	11.30	46.42	11.80	1.66	0.73	1.88
Stoichiometric	30.86	10.37	46.87	11.90	1.67	0.67	2.00
CaK₄H₂(P₂O₇)₂	10.32	32.90	51.63	5.15	0.51	1.92	0.26
Stoichiometric	10.26	34.48	51.97	3.29	0.50	2.00	0.00
CaK₂H₄(P₂O₇)₂	11.85	19.81	59.15	9.19	0.51	1.01	0.24
Stoichiometric	11.93	20.03	60.38	7.66	0.50	1.00	0.00
CaKHP₂O₇	22.30	17.77	55.86	4.07	1.01	0.96	0.06
Stoichiometric	22.07	18.53	55.86	3.54	1.00	1.00	0.00
CaKHP₂O₇.2H₂O	19.11	15.99	48.63	16.27	0.99	0.99	2.12
Stoichiometric	19.33	16.23	48.92	15.52	1.00	1.00	2.00
Ca₂KH₃(P₂O₇)₂.3H₂O	21.47	9.50	54.21	14.82	1.00	0.53	1.42
Stoichiometric	21.39	8.98	54.17	15.46	1.00	0.50	1.50
Ca₃KH(P₂O₇)₂.4H₂O	28.70	8.30	49.36	13.64	1.47	0.51	1.90
Stoichiometric	28.99	8.12	48.92	13.97	1.50	0.50	2.00

Compound	Crystal System, Class, and Habit	Refractive Indices	Optical Properties[a]
$Ca_2P_2O_7 \cdot 2H_2O$	Triclinic, 1. Parallelepipedon, elongated along a	$\alpha = 1.540$ $\beta = 1.549$ $\gamma = 1.568$	Biaxial $(+)$, $2V = (68.5°)$. OAP inclined to a with Bxa $\sim \perp$ to (001). $\beta = 103°$, d. $= 2.46$
$Ca_2P_2O_7 \cdot 2H_2O$	Monoclinic, $2/m$. Rods and tablets contg. b, elongated along a or c	$\alpha = 1.541$ $\beta = 1.554$ $\gamma = 1.556$	Biaxial $(-)$, $2V = 30\text{--}40°$ $(42°)$. OAP $= (010)$, $b = N_\beta$, N_γ on $(010) = 35°$. $\beta = \sim 90°$, d. $= 2.47$
$Ca_2P_2O_7 \cdot 4H_2O$	Orthorhombic, mmm. Thin plates and blades contg. N_β and N_γ, elongated along N_γ	$\alpha = 1.533$ $\beta = 1.548+$ $\gamma = 1.549$	Biaxial $(-)$, $2V = 15\text{--}20°$ $(28°)$. OAP and $N_\alpha \perp$ to tabular plane. d. $= 2.31$
$Ca_2P_2O_7 \cdot 4H_2O$	Monoclinic, $2/m$. (010) Tablets terminated by the set $\{011\}$; tends to elongate along c^b	$\alpha = 1.509$ $\beta = 1.518$ $\gamma = 1.529$	Biaxial $(+)$, $2V = (83°)$. OAP $\perp$ to (010), $N_\gamma = b$, $N_\beta \wedge c = 41°$ in acute β. $\beta = 109°$, d. $= 2.20$
$CaH_2P_2O_7{}^c$	Orthorhombic, mmm. Barite-type plates and tablets contg. N_α and N_γ	$\alpha = 1.510$ $\beta = 1.535$ $\gamma = 1.588$	Biaxial $(+)$, $2V > 60°$ $(71°)$. OAP in plane of tabularity. d. $= 2.57$
$Ca_3H_2(P_2O_7)_2 \cdot 4H_2O$	Triclinic, 1. Long blades contg. N_α and $N_\gamma' \cong N_\gamma$, elongated along $N_\gamma'{}^d$	$\alpha = 1.533$ $\beta = 1.540$ $\gamma = 1.560$	Biaxial $(+)$, $2V \sim 60°$ $(62°)$. OAP nearly coincides with tabular plane, N_β tilted $\sim 5°$ with $\perp$, N_γ inclined $8°$ to elongation axis. $\beta = 103.5°$, d. $= 2.41$
$Ca_3H_2(P_2O_7)_2 \cdot H_2O$	Orthorhombic, mmm. Highly beveled rectangular plates contg. N_α and N_γ, elongated along N_α	$\alpha = 1.539$ $\beta = 1.543$ $\gamma = 1.565$	Biaxial $(+)$, $2V = 45°$ $(46.7°)$. OAP in plane o tabularity. d. $= 2.58$
$Ca(NH_4)_2P_2O_7 \cdot H_2O$	Monoclinic, 2. Hemimorphic plates contg. N_γ $(= b)$ and N_β'	$\alpha = 1.520$ $\beta = 1.537$ $\gamma = 1.540$	Biaxial $(-)$, $2V \sim 40°$ $(46.5°)$. OAP $\perp$ to (010), $N_\gamma = b$, N_β inclined $23°$ on (010) in obtuse β. $\beta = \sim 110°$, d. $= 1.99$
$Ca_3(NH_4)_2(P_2O_7)_2 \cdot 6H_2O$	Monoclinic,^{e} $2/m$., (100) Tablets elongated along c	$\alpha = 1.520$ $\beta = 1.528$ $\gamma = 1.531$	Biaxial $(-)$, $2V \sim 60°$ $(61°)$. OAP $= (010)$, $N_\beta = b$, N_α inclined $27°$ to c in acute β. $\beta = 110.5°$, d. $= 2.08$
$Ca_5(NH_4)_2(P_2O_7)_3 \cdot 6H_2O^f$	Hexagonal, $6/mmm$. Hexagonal rods and needles terminated by 1st- and 2nd-order pyramids	$\epsilon = 1.588^g$ $\omega = 1.565$	Uniaxial $(+)$, d. $= 2.40$
$Ca_3(NH_4)_4H_6(P_2O_7)_4 \cdot 3H_2O$	Orthorhombic, mmm. Simple plates contg. N_β and N_γ, elongated along N_γ	$\alpha = 1.509$ $\beta = 1.510-$ $\gamma = 1.522$	Biaxial $(+)$, $2V = 10°$ ($31°$ when N_β taken as 1.510). OAP and $N_\alpha \perp$ to plane of tabularity, d. $= 2.08$
$CaNH_4HP_2O_7{}^f$	Monoclinic, $2/m$. (010) Plates modified by $\{101\}$ and $\{100\}$ sets	$\alpha = 1.534$ $\beta = 1.537$ $\gamma = 1.553$	Biaxial $(+)$, $2V = 42°$ $(46°)$. OAP $\perp$ to (010) $N_\alpha = b$, $N_\gamma \wedge c$ on (010) inclined $32°$ in obtuse β. $\beta = 92°$, d. $= 2.26$
$Ca(NH_4)_2H_4(P_2O_7)_2{}^f$	Monoclinic, $2/m$. (010) Tablets modified by $\{021\}$, $\{110\}$, and sometimes $\{103\}$	$\alpha = 1.520$ $\beta = 1.545$ $\gamma = 1.549$	Biaxial $(-)$, $2V = 38\text{--}40°$ $(42.3°)$. OAP $\perp$ to (010), $N_\gamma = b$, $N_\beta \wedge c$ on $(010) = 11°$ in acute β. $\beta = 103°$, d. $= 2.19$
$Ca_2NH_4H_3(P_2O_7)_2 \cdot 3H_2O^f$	Monoclinic, $2/m$. (010) Plates and blades elongated along $N_\gamma{}^b$	$\alpha = 1.512$ $\beta = 1.523$ $\gamma = 1.530$	Biaxial $(-)$, $2V > 60°$ $(76.7°)$. OAP $\perp$ to (010) $N_\alpha = b$, $N_\gamma \wedge$ elongation axis on $(010) = 3°$ in acute β. $\beta = 96.5°$, d. $= 2.19$
$Ca_2NH_4H_3(P_2O_7)_2 \cdot H_2O$	Triclinic, 1. Thin plates contg. N_α and $N_\gamma' \cong N_\gamma$; elongated along $N_\gamma'{}^h$	$\alpha = 1.536$ $\beta = 1.545$ $\gamma = 1.570$	Biaxial $(+)$, $2V \sim 60°$ $(63°)$. OAP nearly coincides with tabular plane, N_β tilted $7°$ with $\perp$ to tabular plane, N_γ' on tabular plane inclined $6°$ to elongation axis, d. $= 2.39$
$CaK_2P_2O_7$	Monoclinic, $2/m$. Tabular on (001), twinning common. Crystals display pronounced pseudohexagonal symmetry	$\alpha = 1.542$ $\beta = 1.547$ $\gamma = 1.549$	Biaxial $(-)$, $2V = 60\text{--}65°$ $(64°)$. OAP $= (010)$, $N_\beta = b$, N_α inclined $4°$ to c on (010) in obtuse β. $\beta = 104°$, d. $= 2.77$
$CaK_2P_2O_7 \cdot 4H_2O$	Hexagonal, $6/mmm$. Tabular to platy on (0001), frequently lamellar groups of sheetlike crystals	$\epsilon = 1.495$ $\omega = 1.489$	Uniaxial $(+)$, d. $= 2.18$
$Ca_3K_2(P_2O_7)_2 \cdot 2H_2O^j$	Symmetry not determined. Minute rhombic scalar crystals, frequently in complex aggregates	$N = 1.563$ (mean)	d. $= 2.69$
$Ca_5K_2(P_2O_7)_3 \cdot 6H_2O^f$	Hexagonal, $6/mmm$. Hexagonal rods and needles terminated by 1st- and 2nd-order pyramids	$\epsilon = 1.559^g$ $\omega = 1.545$	Uniaxial $(+)$, d. $= 2.51$
$CaK_4H_2(P_2O_7)_2$	Monoclinic, $2/m$. Tablets flattened on a or c (not detd. which), elongated along b	$\alpha = 1.510$ $\beta = 1.537$ $\gamma = 1.552$	Biaxial $(-)$, $2V > 60°$ $(73°)$. OAP $\perp$ to (010), $N_\gamma = b$, N_α inclined $42°$ on (010). $\beta = 135°$, d. $= 2.66$
$CaK_2H_4(P_2O_7)_2{}^f$	Monoclinic, $2/m$. (010) Tablets elongated along c, modified by sets $\{021\}$ and $\{110\}$	$\alpha = 1.499$ $\beta = 1.529$ $\gamma = 1.533$	Biaxial $(-)$, $2V = 37°$ $(39°)$. OAP $= (010)$, $N_\beta = b$, $N_\gamma \wedge c$ on $(010) = 11°$ in acute β. $\beta = 102°$, d. $= 2.51$
$CaKHP_2O_7{}^f$	Monoclinic, $2/m$. (010) Tablets elongated along c, modified by (101) and the set $\{110\}$	$\alpha = 1.514$ $\beta = 1.527$ $\gamma = 1.537$	Biaxial $(-)$, $2V = (81°)$. OAP $\perp$ to (010), $N_\alpha = b$, $N_\beta \wedge c$ on $(010) = 42°$ in acute β. $\beta = 92°$, d. $= 2.59$
$CaKHP_2O_7 \cdot 2H_2O$	Orthorhombic, mmm. Tabular, elongated prisms terminated by a prominent (hkl) set, probably $\{111\}$	$\alpha = 1.475$ $\beta = 1.504$ $\gamma = 1.515$	Biaxial $(-)$, $2V = 62.5°$ $(62.2°)$. OAP $=$ plane of tabularity, $N_\gamma =$ elongation axis. d. $= 2.25$
$Ca_2KH_3(P_2O_7)_2 \cdot 3H_2O^f$	Monoclinic, $2/m$. (010) Plates elongated along N_β'	$\alpha = 1.508$ $\beta = 1.520$ $\gamma = 1.524$	Biaxial $(-)$, $2V \sim 60°$ $(61.5°)$. OAP $\perp$ to (010), $N_\alpha = b$, $N_\beta \wedge$ elongation axis $= 35°$ in acute β on (010). $\beta = 96°$, d. $= 2.34$
$Ca_3KH(P_2O_7)_2 \cdot 4H_2O$	Monoclinic, $2/m$. Thin (010) rhombic blades	$\alpha = 1.539$ $\beta = 1.541$ $\gamma = 1.551$	Biaxial $(+)$, $2V = (48.5°)$. OAP $\perp$ to (010), $N_\alpha = b$, N_β inclined to elongation axis by $37°$ in obtuse β. $\beta = 124°$, d. $= 2.45$

Footnotes for Table IV at top of page 219

a Calculated values for 2V are in parentheses. All values for densities are calculated.
b Carlsbad twinning common.
c Supplements data of Hill *et al.* (*10*).
d Crystals almost always show polysynthetic twinning.
e Orientation based on x-ray, *b*-centered, unit cell.
f NH₄ and K salts are isostructural.
g Zonal variations in composition frequently reflected in variations in refractive index (hopper effect) without changes in position or intensity of x-ray spectrum.
h Albite twinning very common; morphology and x-ray diffraction spectrum very similar to those of Ca₃H₂(P₂O₇)₂.4H₂O.
i Euhedral crystals large enough for optical analysis were not obtained; even products aged in mother liquor were fine-grained crystallites.

## Table V. Powder X-Ray Diffraction Patterns of Calcium Pyrophosphates*a*

Ca₂P₂O₇.2H₂O, triclinic

d, A.	I	d, A.	I	d, A.	I
8.01	(1)vs	2.95	wm	1.54	w
6.95	(2)s	2.76	wm	1.48	w
5.48	vw	2.65	m	1.44	w
5.20	vw	2.50	w	1.40	w
4.47	vw	2.32	vw	1.38	w
3.98	w	2.23	wm	1.36	w
3.73	vw	2.09	wm	1.33	w
3.42	m	2.00	w	1.17	w
3.21	(3)ms	1.89	w	1.14	w
3.10	ms	1.73	wm		
3.04	m	1.56	wm		

Ca₂P₂O₇.2H₂O, monoclinic

d, A.	I	d, A.	I	d, A.	I
7.37	(1)s	2.77	w	1.83	w
6.08	vw	2.63	ms	1.76	w
5.27	vw	2.56	m	1.73	w
4.62	(3)s	2.41	w	1.69	w
3.74	w	2.30	m	1.60	vw
3.43	vw	2.20	vw	1.55	vw
3.22	s	2.10	w	1.53	vw
3.03	(2)s	2.00	vw	1.49	vw
2.86	vw	1.89	m	1.45	vw

Ca₂P₂O₇.4H₂O, orthorhombic

d, A.	I	d, A.	I	d, A.	I
11.4	(1)vs	3.05	wm*h*	2.04	w
5.95	wm	2.94	(2)s	1.93	w
5.37	vw	2.83	w	1.84	w
4.99	vw	2.65	w	1.78	w
4.70	vw	2.56	w	1.73	w
4.37	wm	2.41	w	1.61	vw
3.75	wm*h*	2.35	vw	1.57	w
3.52	wm*b*	2.26	vw	1.53	vw
3.37	(3)m	2.16	wm	1.39	vw
3.18	w	2.12	wm		

Ca₂P₂O₇.4H₂O, monoclinic

d, A.	I	d, A.	I	d, A.	I
6.21	(2)s	2.75	w	1.80	w
5.56	(1)s*b*	2.68	w	1.76	w
5.13	wm	2.55	m	1.70	wm
3.95	vw	2.49	vw	1.68	wm
3.62	(3)ms	2.45	vw	1.61	m
3.28	w	2.27	m	1.56	vw
3.20	ms	2.21	vw	1.49	w
3.11	ms	2.13	vw	1.42	vw
3.01	vw	2.08	m	1.41	m
2.95	vw	2.02	m	1.31	vw
2.80	ms	1.98	w		

CaH₂P₂O₇*c*

d, A.	I	d, A.	I	d, A.	I
5.40	vvw	3.18	(3)ms	1.92	w
5.03	vw	2.68	wm	1.86	vw
4.78	vw	2.50	w	1.83	w
4.42	m	2.32	w	1.76	m
4.05	vw	2.29	w	1.63	w
3.87	vw	2.18	w	1.58	w
3.73	(2)ms	2.17	w	1.57	vw
3.33	(1)s	2.05	w	1.48	w

Ca₃H₂(P₂O₇)₂.4H₂O

d, A.	I	d, A.	I	d, A.	I
10.7	(1)vs	3.14	(2)vs	1.83	vw
6.74	vw	2.78	vw	1.74	vw
6.08	vw	2.69	w	1.57	w
4.66	w	2.30	w	1.53	wm

Ca₃H₂(P₂O₇)₂.4H₂O

d, A.	I	d, A.	I	d, A.	I
3.58	m	2.03	(3)ms	1.39	vw
3.43	w	2.01	wm	1.34	vw

Ca₃H₂(P₂O₇)₂.H₂O

d, A.	I	d, A.	I	d, A.	I
6.37	0.49	2.87	0.02	2.05	0.02
4.93	0.11	2.84	0.06	2.03	0.01
4.64	0.17	2.78	0.02	2.00	0.02
4.32	0.03	2.74	0.04	1.97	0.16
4.21	0.06	2.70	0.13	1.94	0.07
4.04	0.17	2.63	0.16	1.88	0.03
3.93	0.14	2.61	0.08	1.86	0.04
3.85	0.07	2.58	0.02	1.81	0.09
3.70	0.12	2.54	0.02	1.77	0.06
3.56	0.04	2.37	0.28	1.74	0.03
3.44	0.03	2.31	0.04	1.72	0.05
3.34	0.58	2.29	0.04	1.67	0.02
3.20	1.00	2.26	0.05	1.65	0.02
3.15	0.18	2.21	0.06	1.60	0.18
3.05	0.15	2.18	0.05	1.58	0.05
3.01	0.14	2.16	0.01	1.54	0.02
2.98	0.09	2.13	0.02		

Ca(NH₄)₂P₂O₇.H₂O

d, A.	I	d, A.	I	d, A.	I
7.23	(1)vs	2.90	m	2.11	w
5.51	wm	2.85	vw	2.06	vw
4.86	(2)s	2.75	w	1.92	w
4.23	wm	2.68	vw	1.88	wm
3.86	w	2.52	m	1.72	vw
3.56	vw	2.44	vw	1.69	vw
3.39	(3)ms	2.39	vw	1.47	wm
2.98	m	2.32	vw	1.45	wm

Ca₃(NH₄)₂(P₂O₇)₂.6H₂O

d, A.	I	d, A.	I	d, A.	I
7.27	vw	2.84	w	1.85	w
6.39	w	2.74	vw	1.80	w
5.73	(1)s	2.70	vw	1.73	vw
5.56	m	2.59	vw	1.64	vw
4.95	(3)ms	2.39	w	1.56	vw
4.20	wm	2.23	w	1.50	vw
3.27	m	2.18	vw	1.42	vw
3.19	m	2.13	vw	1.41	vw
3.11	w	2.09	w		
3.07	(2)s	1.88	vw		

Ca₅(NH₄)₂(P₂O₇)₃.6H₂O and Ca₅K₂(P₂O₇)₃.6H₂O

d, A.	I	d, A.	I	d, A.	I
10.23	(2)vs	2.70	s	1.79	m
5.85	vw	2.44	vw	1.69	m
5.03	m	2.32	vw	1.64	vw
3.84	vw	2.25	vw	1.59	w
3.74	w	2.22	vw	1.54	w
3.58	m	1.92	vw	1.49	vw
3.37	w	1.88	m	1.45	w
3.01	(1)vs	1.84	vw	1.39	w
2.82	(3)s	1.82	vw		

Ca₃(NH₄)₄H₆(P₂O₇)₄.3H₂O

d, A.	I	d, A.	I	d, A.	I
13.62	(1)vs	3.82	w	2.39	vw
6.74	m	3.60	(2)m	2.32	vw
6.36	w	3.46	vw	2.23	w
5.82	vw	3.33	wm	2.11	w
5.65	vw	3.23	m	2.02	w

Ca₃(NH₄)₄H₆(P₂O₇)₄.3H₂O

d, A.	I	d, A.	I	d, A.	I
4.97	w	3.13	vw	1.71	w
4.78	w	3.06	vw	1.64	vw
4.45	vw	2.98	vw	1.55	vw
4.19	vw	2.89	w	1.52	vw
3.99	(3)m	2.51	vw		

CaNH₄HP₂O₇ and CaKHP₂O₇

d, A.	I	d, A.	I	d, A.	I
8.80	(1)s	3.08	vw	1.95	vw
5.59	wm	2.95	w	1.89	w
5.10	wm	2.81	w	1.84	w
4.91	vw	2.70	vw	1.77	vw
4.17	(2)ms	2.56	vw	1.74	w
3.82	vw	2.44	w	1.65	vw
3.74	vw	2.37	vw	1.62	vw
3.62	vw	2.27	wm	1.58	vw
3.41	vw	2.15	vw	1.56	vw
3.34	(3)ms	2.11	vw	1.53	w
3.23	m	2.07	vw	1.42	vw
3.16	vw	2.02	wm	1.40	vw

Ca(NH₄)₂H₄(P₂O₇)₂ and CaK₂H₄(P₂O₇)₂

d, A.	I	d, A.	I	d, A.	I
6.54	ms	3.30	(3)s	1.81	vw
5.92	vw	3.09	m	1.78	w
4.99	m	2.99	m	1.76	vw
4.82	m	2.87	m	1.74	vw
4.53	(1)s	2.63	m	1.70	vw
4.37	vw	2.29	vw	1.67	vw
4.16	vw	2.23	w	1.61	vw
3.99	vw	2.18	vw	1.55	vw
3.43	(2)s	2.02	w	1.49	vw

Ca₂NH₄H₃(P₂O₇)₂.3H₂O and Ca₂KH₃(P₂O₇)₂.3H₂O

d, A.	I	d, A.	I	d, A.	I
9.7	(1)vs	3.12	wm	1.99	w
5.82	(3)m	3.07	wm	1.93	vw
5.10	vw	3.02	w	1.78*b*	vw
4.40	(2)s	2.94	vw	1.75*b*	vw
3.90	vw	2.87	m	1.62	vw
3.78	w	2.57	vw	1.58	w
3.61	w	2.36	w	1.43	w
3.46	w	2.31	w	1.38	vw
3.26	wm	2.20	wm	1.35	vw
3.18	wm	2.03	vw		

Ca₂NH₄H₃(P₂O₇)₂.H₂O

d, A.	I	d, A.	I	d, A.	I
9.7	(1)vs	2.89	vw	2.01	vw
6.08	vw	2.79	vw	1.97	vw
4.86	(3)m	2.66	vw	1.94	vw
3.91	vw	2.52	vw	1.91	vw
3.66	m	2.39	vw	1.73	vw
3.26*b*	m	2.34	vw	1.66	vw
3.13	(2)s	2.10	vw	1.57	vw
3.09	vw	2.04	vw	1.50	vw
3.00	vw				

CaK₂P₂O₇

d, A.	I	d, A.	I	d, A.	I
4.74	0.18	2.75	0.05	1.91	0.02

Table V *continued*

$CaK_2P_2O_7$

d, A.	I	d, A.	I	d, A.	I
4.35	0.28	2.64	0.02	1.88	0.02
4.21	0.03	2.50	0.02	1.84	0.02
3.64	0.02	2.37	0.12	1.82	0.03
3.40	0.18	2.26	0.09	1.77	0.03
3.27	0.03	2.18	0.35	1.73	0.05
3.14	0.25	2.10	0.05	1.69	0.10
3.00	0.85	2.06	0.14	1.67	0.12
2.83	1.00	1.99	0.02	1.64	0.10

$CaK_2P_2O_7 \cdot 4H_2O$

d, A.	I	d, A.	I	d, A.	I
10.16	0.80	2.95	0.33	2.23	0.11
6.55	0.10	2.89	1.00	2.17	0.08
5.03	0.15	2.76	0.23	2.12	0.03
4.82	0.17	2.70	0.12	2.08	0.02
4.69	0.26	2.66	0.07	2.03	0.07
4.17	0.17	2.62	0.20	2.00	0.05
4.06	0.09	2.54	0.08	1.92	0.04
3.80	0.17	2.50	0.18	1.84	0.04
3.52	0.03	2.45	0.08	1.77	0.08
3.18	0.08	2.34	0.05	1.70	0.08
3.09	0.06	2.30	0.08	1.65	0.08

$Ca_3K_2(P_2O_7)_2 \cdot 2H_2O$

d, A.	I	d, A.	I	d, A.	I
7.31	0.14	2.86	0.49	2.15	0.12
6.65	0.06	2.70	0.25	2.11	0.06
5.60	0.03	2.65	0.08	2.03	0.05
5.45	0.03	2.60	0.04	1.98	0.10
4.47	0.16	2.57	0.04	1.96	0.08
3.33	0.08	2.50	0.11	1.94	0.06
3.28	0.11	2.45	0.07	1.89	0.06
3.22	0.34	2.42	0.05	1.85	0.04
3.12	0.17	2.32	0.07	1.76	0.04
3.09	0.23	2.28	0.04	1.71	0.12
3.06	0.17	2.21	0.15	1.66	0.10
2.94	1.00				

$CaK_4H_2(P_2O_7)_2$

d, A.	I	d, A.	I	d, A.	I
9.77	w	2.98	m	1.89	w
8.56	(3)m	2.85	m	1.86	vw
5.48	vw	2.72	m	1.73	vw

$CaK_3H_2(P_2O_7)_2$

d, A.	I	d, A.	I	d, A.	I
4.54	m	2.56	m	1.69	vw
4.11	m	2.46	m	1.66	vw
3.79	w	2.35	m	1.63	vw
3.59	vw	2.30	w	1.54	vw
3.46	vw	2.25	vw	1.44	vw
3.31	vw	2.07	m	1.37	w
3.23	(2)s	1.99	vw	1.26	vw
3.10	(1)s				

$CaKHP_2O_7 \cdot 2H_2O$

d, A.	I	d, A.	I	d, A.	I
6.06	0.05	2.89	0.19	2.25	0.25
5.69	0.39	2.86	0.28	2.23	0.18
5.09	0.52	2.74	0.17	2.11	0.19
4.83	1.00	2.71	0.17	2.00	0.42
4.06	0.20	2.65	0.09	1.97	0.08
3.70	0.05	2.62	0.03	1.93	0.15
3.63	0.34	2.55	0.13	1.90	0.03
3.46	0.16	2.54	0.13	1.89	0.05
3.34	1.00	2.51	0.29	1.85	0.04
3.22	0.14	2.47	0.11	1.81	0.05
3.16	0.81	2.45	0.11	1.75	0.11
3.05	0.07	2.42	0.09	1.73	0.14
2.99	0.43	2.35	0.25	1.69	0.13
2.91	0.10	2.30	0.21		

$Ca_3KH(P_2O_7)_2 \cdot 4H_2O$

d, A.	I	d, A.	I	d, A.	I
9.82	1.00	3.12	0.41	2.27	0.04
5.94	0.12	3.05	0.06	2.20	0.05
5.82	0.18	2.97	0.46	2.13	0.07
5.12	0.24	2.91	0.13	2.10	0.10
4.87	0.06	2.87	0.15	2.05	0.12
4.39	0.27	2.85	0.26	2.02	0.13
4.07	0.16	2.82	0.16	1.94	0.23
3.90	0.15	2.74	0.13	1.89	0.12
3.80	0.08	2.71	0.13	1.87	0.06
3.67	0.72	2.61	0.25	1.84	0.05
3.57	0.19	2.58	0.24	1.81	0.10
3.32	0.35	2.46	0.19	1.77	0.10
3.26	0.55	2.40	0.10	1.73	0.06
3.16	0.56	2.34	0.23		

[a] Intensities estimated visually: vs = very strong, s = strong, ms = medium strong, m = medium, wm = weak medium, w = weak, vw = very weak; numbers 1, 2, and 3 denote 1st, 2nd, and 3rd strongest lines, respectively. Intensities reported numerically were read from x-ray goniometer tracings. [b] Double line. [c] This pattern contains more lines, but otherwise agrees with those reported by Bale *et al.* (*1*) and by Hill *et al.* (*9*).
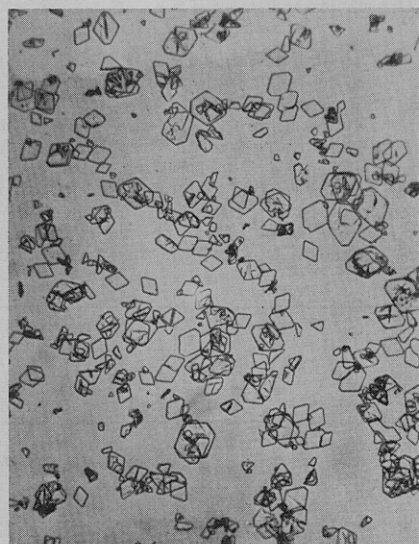
Figure 1. $CaH_2P_2O_7$
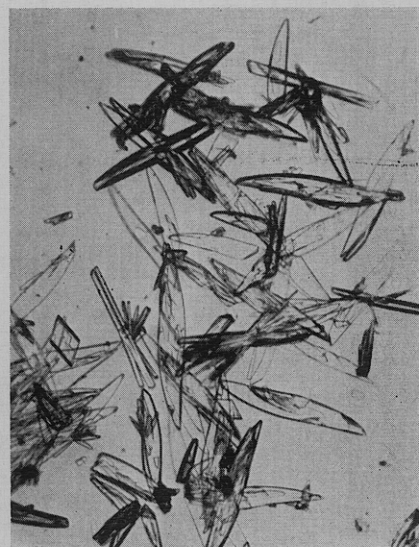
Figure 2. $Ca_3H_2(P_2O_7)_2 \cdot 4H_2O$

Figure 3. $Ca_2P_2O_7 \cdot 2H_2O$, monoclinic dimorph

prepared by adding 1 gram of $CaH_2P_2O_7$ to 100 ml. of a saturated KCl solution and allowing the mixture to stand at room temperature for 24 hours. Crystals of $Ca_2KH_3(P_2O_7)_2 \cdot 3H_2O$ were formed initially, but this metastable intermediate slowly dissolved and was replaced by $CaKHP_2O_7$. Stirring and warming hastened the transformation but produced smaller crystals. The product is relatively insoluble in water.

Calcium Potassium Hydrogen Pyrophosphate Dihydrate. The dihydrate $CaKHP_2O_7 \cdot 2H_2O$ was prepared by adding 1 gram of $CaH_2P_2O_7$ to 50 ml. of $2M$ KCl solution and adding $K_4P_2O_7$ or KOH to raise the pH to 4. The amorphous precipitate that was formed was transformed within an hour to well-formed rod crystals of $CaKHP_2O_7 \cdot 2H_2O$. The product is moderately soluble and was washed sparingly with water. The crystals lose their water of hydration slowly at room temperature, even when stored in a closed container.

Dicalcium Potassium Trihydrogen Pyrophosphate Trihydrate. The salt $Ca_2KH_3(P_2O_7)_2 \cdot 3H_2O$ was prepared by adding 1 gram of $CaH_2P_2O_7$ to 10 ml. of $2.35M$ KCl solution and allowing the mixture to stand at room temperature. Well-formed crystals of $Ca_2KH_3(P_2O_7)_2 \cdot 3H_2O$ were deposited within 1 hour. The crystals are slowly soluble in water, but they can be washed with water in the usual manner.

The composition of the mixture can be varied considerably as long as the mixture contains no more than 95% water and the pH is between 2 and 3. At pH's above 3, $CaKHP_2O_7$ is formed; at pH's below 2, $Ca_3H_2(P_2O_7)_2 \cdot 4H_2O$ is formed.

Tricalcium Potassium Hydrogen Pyrophosphate Tetrahydrate. The salt $Ca_3KH(P_2O_7)_2 \cdot 4H_2O$ was prepared from a mixture of 4.4 grams of $K_4P_2O_7$, 6.1 grams of $CaH_2P_2O_7$, and 500 ml. of water that was stirred occasionally at room temperature for about 4 days.

Table VI. Lattice Constants of Crystalline Pyrophosphates

Unit-Cell Content	Crystal System	Probable Space Group	Lattice Constants				Density (X-Ray)
			a	b	c	β	
$2[Ca_2P_2O_7 . 2H_2O]$	Triclinic	$C_i^1 - P\bar{1}$	6.70	7.38	8.31	$102°\,48'^a$	2.51
$4[Ca_2P_2O_7 . 4H_2O]$	Monoclinic	$C_{2h}^5 - P2_1/c$	6.01	25.0	6.86	$109°\,54'$	2.22
$2[Ca_3(NH_4)_2(P_2O_7)_2 . 6H_2O]$	Monoclinic	$C_{2h}^5 - P2_1/n$	7.67	11.51	11.00	$92°\,28'$	2.08
$2[Ca_5(NH_4,K)_2(P_2O_7)_3 . 6H_2O]$	Hexagonal	$D_{6h}^3, C_{6v}^3, D_{3h}^2$	11.88	...	9.83	...	2.38 (NH₄)
							2.50 (K)
$8[CaNH_4HP_2O_7]$	Monoclinic	$C_{2h}^5 - P2_1/n$	10.57	17.56	7.27	$90°\,38'$	2.28
$4[Ca(NH_4,K)_2H_4(P_2O_7)_2]$	Monoclinic	$C_{2h}^6 - C2/c$	7.17	19.99	9.33	$102°\,52'$	2.17 (NH₄)

^{a} $\alpha = 85°\,2'$; $\gamma = 107°\,23'$.
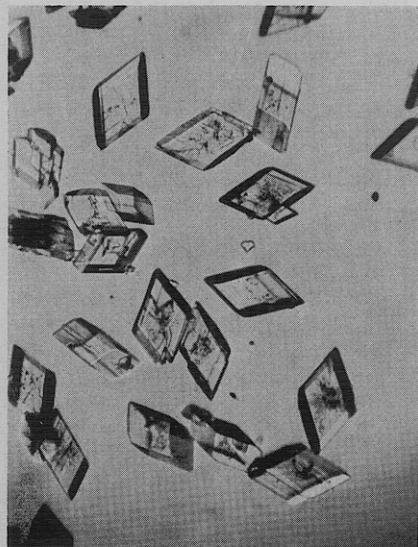
Figure 4. $Ca_2P_2O_7 . 2H_2O$, triclinic dimorph

Table VII. Typical Preparation of $Ca_3H_2(P_2O_7)_2 . 4H_2O$

Method of Preparation	Composition, %			Moles/Mole P₂O₅	
	CaO	P_2O_5	H_2O (diff.)	CaO	Hydrate H_2O
Crystallized from coacervate^a	29.38	52.98	17.74	1.404	2.042
	29.52	52.91	17.57	1.412	2.028
	29.20	53.13	17.67	1.391	2.011
	30.71	52.37	16.92	1.484	2.030
Hydrolysis of $CaH_2P_2O_7$ in water^b					
for few hours	29.94	53.08	16.98	1.428	1.948
for few hours	29.68	53.07	17.25	1.416	1.977
for 5 months	29.75	53.04	17.21	1.420	1.977
for 5 months	29.67	52.97	17.36	1.418	2.000
Hydrolysis of $CaH_2P_2O_7$ in					
$0.2M$ $CaCl_2$	29.69	52.79	17.52	1.424	2.039
$0.5M$ $CaCl_2$	29.53	52.92	17.54	1.412	2.023
$1.0M$ $CaCl_2$	29.50	52.71	17.59	1.417	2.046
Stoichiometric	31.03	52.36	16.61	1.500	2.000

^{a} Deposited from calcium polyphosphate coacervate that was allowed to stand for 2 to 11 months.
^{b} Method described in text.

Much larger crystals that were suitable for single-crystal x-ray studies were formed when 1 gram of $CaH_2P_2O_7$ was added to 100 ml. of $0.5M$ KCl solution and the mixture was allowed to stand at room temperature for a month, but the product was mixed with a small amount of $CaKHP_2O_7$. $Ca_3KH(P_2O_7)_2 . 4H_2O$ is relatively insoluble in water.

Discussion

The chemical compositions of typical preparations of each of the pyrophosphates are shown in Tables I, II, and III. The morphological and optical properties are listed in Table IV, the powder x-ray diffraction data are shown in Table V, and the lattice constants obtained from single-crystal x-ray studies of some of the salts are given in Table VI. The x-ray data in Table V served to establish the isotypism between certain pairs of ammonium and potassium salts that was indicated by the chemical compositions and morphological properties of those salts. The single-crystal x-ray data in Table VI not only established definitely the crystal species under examination, but also gave the unit-cell contents and so confirmed the empirical formula assigned to the compound. Photomicrographs of four calcium pyrophosphates are shown in Figures 1 to 4.

Several hydrated calcium pyrophosphates have been reported previously (2, 7, 10) but the descriptions of the products are limited mainly to their chemical compositions. There is little information on the crystallographic properties and x-ray patterns of the products.

Dubost (7) suspected, but did not demonstrate, the dimorphism of $Ca_2P_2O_7 . 2H_2O$. Dimorphs of both di- and tetrahydrated calcium pyrophosphate were prepared and characterized.

Many of the calcium pyrophosphates described in the literature were prepared from $Na_4P_2O_7$ and $CaCl_2$. In attempts to repeat the preparations, mixtures rather than single-phase precipitates were often obtained. This may explain the reported existence of a trihydrate of calcium pyrophosphate (4), for precipitates were obtained that were mixtures of $Ca_2P_2O_7 . 2H_2O$ and $Ca_2P_2O_7 . 4H_2O$, but there was no evidence of a trihydrate. In some preparations, crystals were obtained of $CaNa_2P_2O_7 . 4H_2O$, which has apparent analogs in both the ammonium and potassium systems. The sodium system apparently behaves much like the ammonium and potassium systems, and published methods for the preparation of calcium pyrophosphates are not sufficiently detailed to ensure preparation of single-phase precipitates.

In the development of methods for the preparation of calcium ammonium and calcium potassium pyrophosphates, formation of metastable compounds and subsequent transformation of those into stable compounds showed that time of contact of a precipitate with its mother liquor was often an important factor in the identity and purity of the product.

The chemical compositions of the salt designated as $Ca_3H_2(P_2O_7)_2 . 4H_2O$ consistently had mole ratios $CaO:P_2O_5$ significantly less than 1.5, even when the preparations were made in the presence of relatively large amounts of calcium ions. As shown in Table VII, different methods of preparation yielded the same crystalline compound.

Pahl (12) assigned the formula $Ca_7H_6(P_2O_7)_5 . 10H_2O$ to a product he obtained from a solution of calcium pyrophosphate (prepared from $Na_4P_2O_7$ and $CaCl_2$) in hydrochloric acid. His method of preparation yielded the compound designated $Ca_3H_2(P_2O_7)_2 . 4H_2O$. Pahl's for-

mula is a quintupling, whereas the designated formula is a doubling, of the average of the compositions of many preparations, $Ca_{1.4}H_{1.2}P_2O_7.2H_2O$, but structural considerations indicate that a compound with Pahl's formula would have either an unusually large unit cell or an inordinately high density. Van Wazer (13) has suggested that the variations in the reported compositions of this compound indicate that the material is a solid solution, but results of x-ray examinations rule out this possibility.

Boullé and Dubost (4) describe as "calcium pyrophosphate-α" a preparation with the empirical formula $Ca_{2.74}$-$H_{2.52}(P_2O_7)_2.2H_2O$ and with an x-ray pattern very similar to that of the compound designated $Ca_3H_2(P_2O_7)_2.4H_2O$. Boullé and Dubost concluded that their product was a double salt with the composition $2CaH_2P_2O_7.Ca_2P_2O_7.3H_2O$ or $Ca_4H_4(P_2O_7)_3.3H_2O$.

All the preparations listed in Table VII are essentially identical optically, morphologically, and in x-ray pattern. These preparations then must represent a single crystallographic species that is unaltered structurally by small changes in composition. The assigned formula is based on the supposition that a small deficiency in calcium can be compensated by substitution of hydrogen in a lattice in which the packing is dominated by phosphorus-oxygen tetrahedra.

Weissenberg single-crystal studies were made to establish the correct empirical formula. The study was complicated by the lamellar twinning that the crystals invariably displayed—the polysynthetic twinning occurs on the tabular (100) plane, which is also the composition plane, and the crystals frequently have such a hyperfine structure that the twinning is very difficult to detect optically. Because of the twinning, the x-ray results yielded two possible sets of cell constants. The volumes of the two mirror-image unit cells are identical, however, and each cell accommodates precisely one formula weight of the composition $Ca_3H_2(P_2O_7)_2.4H_2O$. The computed cell density is 2.46, which agrees reasonably well with the density, 2.41, calculated from the refractive indices and chemical composition. The tentative results of the Weissenberg study support the empirical formula $Ca_3H_2(P_2O_7)_2.4H_2O$.

In the region of composition in which $Ca_3H_2(P_2O_7)_2.4H_2O$ appears at room temperature, a lower hydrate with otherwise the same composition, Ca_3H_2-$(P_2O_7)_2.H_2O$, appears at 50° to 75° C. The monohydrate has higher crystal symmetry than the tetrahydrate and crystallizes in well-formed, untwinned units. The mole ratio $CaO:P_2O_5$ in the monohydrate is consistently close to 1.50. The lower mole ratios $CaO:P_2O_5$ in the tetrahydrate probably result from lattice defects caused by hyperfine polysynthetic twinning that is shown by nearly all the preparations of the tetrahydrate.

Literature Cited

(1) Bale, W. F., Bonner, J. F., Hodge, H. C., Adler, H., Wreath, A. R., Bell, R., Ind. Eng. Chem. Anal. Ed. 17, 491 (1945).
(2) Bartholomew, R. P., Jacob, K. D., J. Assoc. Offic. Agr. Chemists 16, 598 (1933).
(3) Bassett, H., J. Chem. Soc. 1958, 2949.
(4) Boullé, A., Dubost, M. P., Compt. rend. 247, 1864 (1958).
(5) Brown, E. H., Lehr, J. R., Smith, J. P., Brown, W. E., Frazier, A. W., J. Phys. Chem. 61, 1669 (1957).
(6) Ibid., 62, 366 (1958).
(7) Dubost, M. P., Bull. Soc. Chim. France 1959, 810.
(8) Gee, A., Deitz, V. R., Anal. Chem. 25, 1320 (1953).
(9) Hill, W. L., Hendricks, S. B., Fox, E. J., Cady, J. G., Ind. Eng. Chem. 39, 1667 (1947).
(10) Hill, W. L., Reynolds, D. S., Hendricks, S. B., Jacob, K. D., J. Assoc. Offic. Agr. Chemists 28, 105 (1945).
(11) Larsen, E. S., Berman, H., U. S. Geol. Surv. Bull. 848 (1943).
(12) Pahl, C. N., Kgl. Sven. Vetenskaps.:ad. Akad. Handl. Övers. 58, No. 2, 166 (1901).
(13) Van Wazer, J. R., "Phosphorus and Its Compounds," p. 630, Interscience, New York, 1958.
(14) Willard, H. H., Boldyreff, A. W., J. Am. Chem. Soc. 52, 1888 (1920).

DEFOLIANT METABOLISM

The Fate of Cyanamide in Cotton

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CYANAMIDE is a colorless, crystalline solid which melts at 41° to 42° C. and is soluble in water, alcohol, and ether. It polymerizes at temperatures above its melting point and will react with weak acids to form salts and with strong acids to form urea.

Calcium cyanamide was patented in 1910 for use as a fertilizer (9) and was used in Germany before 1913 to kill mustard weeds in oats. Calcium cyanamide was first noted to induce cotton defoliation by Hall and Harrell in 1938 (4), and has since been used widely as a defoliant for cotton, soybeans, and for nursery stock (7).

Previous studies of the metabolism of cyanamide include the work of Hofmann et al. (7) who reported the enzymatic decomposition of cyanamide by an enzyme termed cyanamidase which was extracted from soybeans. He also noted that barley and corn plants cultured with cyanamide-C^{14} expired part of their carbon dioxide as $C^{14}O_2$.

Later, Hofmann et al. (6) stated that oats, barley, wheat, and rye converted cyanamide to dicyandiamide which could be detected after 2 to 3 days. Alanine, tryptophan, lysine, leucine, phenylalanine, and valine were present in higher concentrations in cyanamide-fed plants than in plants fed calcium nitrate as nitrogen source. Both alanine and aspartic acid had C^{14} activity when plants were fed barium cyanamide-C^{14}. Alanine displayed the greatest activity.

Latzko (8), in a review article, stated that Rathsack found dicyandiamide, guanidine, and guanyl compounds as intermediary decomposition products of cyanamide. In a previous report of limited distribution (5), the authors have summarized the results of studies conducted with mature, field-grown Deltapine 15 cotton. These plants were sprayed at rates equivalent to 2 and 4 gallons of 25% concentrate per acre of cyanamide-C^{14}. Carbon-14, which was originally contained in the cyanamide, was translocated from the sprayed leaves to the seed of developing bolls. Paper chromatographic procedures established that this seed did not contain cyanamide, but the character of the carbon-14 containing products was not established.

This study was initiated to discover