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FERTILIZER MATERIALS

Vitreous Calcium Metaphosphate—Some Properties of Its Aqueous Systems

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In water, vitreous calcium metaphosphate forms a coacervate, a viscous solution of highly condensed phosphates, which hydrolyzes slowly to pyrophosphate. Incorporated silica decreases the formation of the coacervate and increases the solubility of the metaphosphate; incorporated alumina has the opposite effect. Vitreous calcium metaphosphate behaves in moist soil much as it does in water, and yields residues of calcium pyrophosphates.

THE PRODUCT of the dehydration and fusion of monocalcium phosphate monohydrate or of the reaction of phosphate rock with phosphoric oxide vapor at 1100° C. has a composition close to that of $Ca(PO_3)_2$. When cooled slowly from its melt, it crystallizes as β-calcium metaphosphate, which is quite insoluble and of little value as a fertilizer. When cooled rapidly from its melt, however, it solidifies as a glass that dissolves slowly in water and has considerable value as a fertilizer (*5*) and as an intermediate in the preparation of other fertilizers. Little is known of the condensed phosphate species of which the vitreous material is composed, but for convenience it is referred to as calcium metaphosphate.

As part of a broader study of the behavior of vitreous calcium metaphosphate in the soil and in its processing into other phosphate fertilizers, a study was made of the calcium metaphosphate–water system. In water, vitreous calcium metaphosphate forms a water-immiscible coacervate and a dilute solution; the coacervate, the solution, and their degradation products were examined chemically, chromatographically, petrographically, and by x-ray powder diffraction. A study was made also of the effect of incorporated silica and alumina on the dissolution of the metaphosphate.

Materials and Procedure

Vitreous calcium metaphosphate was prepared by heating reagent grade monocalcium phosphate monohydrate in a platinum dish to fusion at about 1100° C. and quenching the melt. The products appeared to be clear glasses, but petrographic examination showed that they sometimes contained very small amounts of crystalline β-calcium metaphosphate. The mole ratio P:Ca (P_2O_5:CaO) ranged from 1.980 to 2.044 (0.990 to 1.022), and the sum of the calcium and phosphorus contents ranged from 51.43 to 51.54% (CaO + P_2O_5, 99.83 to 100.04%).

Vitreous metaphosphates containing dissolved silica or alumina were prepared by fusing and quenching mixtures of pure vitreous calcium metaphosphate and the oxide.

The fertilizer grade metaphosphate was a product of the TVA demonstration plant in which rock phosphate is treated with phosphoric oxide vapor at 1100° C. It contained Ca 19.0, P 27.4, Al 0.6, Fe 1.0, and Si 2.9% (CaO 26.6, P_2O_5 62.8, Al_2O_3 1.1, Fe_2O_3 1.4, and SiO_2 6.2%), and its mole ratio P:Ca (P_2O_5:CaO) was 1.866 (0.933). Much of the silica in this material was present as unreacted quartz; the product usually contained 1 to 2% of β-calcium pyrophosphate.

In water, pure vitreous calcium metaphosphate yields a viscous, water-immiscible liquid (coacervate) and a dilute aqueous phase. The reaction is slow at room temperature; raising the temperature accelerates both the dissolution and the hydrolysis of the dissolved phosphate. The mole ratio P:Ca in both the coacervate and the dilute phase is the same as that in the original metaphosphate.

The coacervate may be prepared by covering crushed vitreous calcium metaphosphate with water and allowing the mixture to stand at room temperature with occasional stirring for about 3 days. The lighter aqueous phase is decanted off, and the coacervate is removed by pressure filtration. From an initial mixture of 85 grams of −60-mesh metaphosphate and 110 grams of water there was obtained 50 ml. (78 grams) of coacervate that contained 52% solute phosphate, which is defined for convenience as the sum of the calcium oxide and phosphoric oxide contents.

More conveniently, the apparatus in Figure 1 is filled with water to the level of the overflow and −20- plus 35-mesh metaphosphate is placed on a thin layer of glass wool on the perforated plate. Warm water is circulated through the jacket to maintain the temperature at 45° C., and water is dripped slowly onto the charge. The coacervate drips
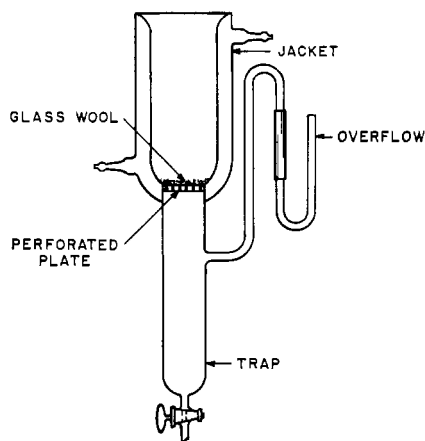
Figure 1. Apparatus for preparation of coacervate

Table I. Degradation of Coacervate

Distribution, %, of Phosphorus in Indicated Phosphate Species

Time, Days	Ortho	Pyro	Tripoly	Ring[a]	Long chains
0	2	1	2	3	92
22	15	10	12	13	50
26	17	13	12	22	36
39[b]	27	33	20	17	3
40	27	35	20	16	2
41[c]	26	36	20	13	5
42[c]	30	34	23	10	3

[a] Mostly trimetaphosphate, some tetrametaphosphate.

[b] First appearance of crystals of Ca_3H_2 $(P_2O_7)_2 \cdot 4H_2O$.

[c] Mother liquor after sample had nearly solidified.

Table II. Liquid Phases from Dissolution of Siliceous Metaphosphate

SiO₂ Content, %, of Original Glass	Distribution, %, of Phosphorus in Indicated Phosphate Species[a]		
	Ortho	Other	Condensed
AQUEOUS PHASE			
0.0	6	27	67
2.7	7	27	66
5.1	6	25	69
9.8	10	7	83
COACERVATE			
2.7	2	13	85

[a] Determined chromatographically. "Other" includes all species except orthophosphate that moved on paper, "condensed," all nonmoving species.
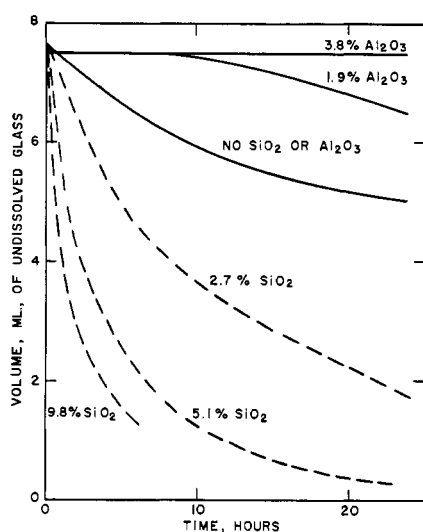

Figure 2. Effects of silica and alumina on the dissolution of vitreous calcium metaphosphate

from the perforated plate and coalesces as a separate phase in the trap from which it is withdrawn periodically; the dilute aqueous phase is removed continuously in the overflow. From a charge of 74 grams of metaphosphate there was obtained in 6 days 83 grams of coacervate that contained 52% solute phosphate.

Properties of the Coacervate

Coacervate prepared by either of these methods contains 30 to 56%, usually about 52% solute phosphate. Coacervate containing 52% solute phosphate has a refractive index of 1.430, a density of 1.56 grams per cc., a mole ratio P:Ca of 2, and a pH of about 1.

The coacervate is a mixture of condensed phosphates and appears to be similar to the hydrated magnesium polymetaphosphate described by Pfanstiel and Iler (7). A film of the coacer-

vate dries reversibly in air to a glassy product containing about 82% solute phosphate; the same product is formed by addition of acetone or ethanol to the coacervate. A similar product is obtained by treatment of the coacervate with ammonium hydroxide; this product contains a small amount of ammonia which increases as the treatment is prolonged (1).

Coacervates can be concentrated somewhat by extraction with water or by heating. Thus, 10 ml. of freshly prepared coacervate containing 52% solute phosphate was shaken with 90 ml. of water, and the aqueous phase was discarded. The extraction was repeated three times; further extraction was not made because the residual coacervate was too thick to be dispersed in water. The coacervate then had a volume of 6 ml. and a solute phosphate content of 56%. Similar results were obtained by treatment of a coacervate containing 48% solute phosphate.

When heated below 90° C., the coacervate becomes cloudy with suspended droplets which redissolve on cooling. If the heating is prolonged, however, the droplets coalesce to a second phase—a more concentrated coacervate than the original—and a small amount of a dilute aqueous phase.

The coacervate is acidic, but apparently only the phosphate groups at the ends of the chains ionize. Treatment of coacervate with ammonium fluoride solution yields no calcium fluoride, indicating that the calcium is strongly complexed by the phosphate.

The coacervate hydrolyzes slowly at room temperature and, in the presence of sufficient water, eventually forms orthophosphate. At one stage of the degradation, the material is predominantly pyrophosphate and is a mass of spherulitic crystals of $Ca_3H_2(P_2O_7)_2 \cdot 4H_2O$ wetted with a concentrated solution of degradation products. With coacervate containing 52% solute phosphate, the crystals appear in about 40

days at room temperature, after which precipitation of the crystals is rapid, and the change from a liquid to a wet solid takes place within 2 days. Some coacervates, however, became transparent gels long before the appearance of crystals. In less concentrated coacervates, a second crystalline phase, Ca_2-$P_2O_7 \cdot 2H_2O$ (2) is formed before orthophosphate appears. $Ca_3H_2(P_2O_7)_2 \cdot 4H_2O$ hydrolyzes in water to $Ca_2P_2O_7 \cdot 2H_2O$ (2). Results of a chromatographic study of the degradation of the coacervate are shown in Table I.

The coacervate phosphates hydrolyze slower than the phosphates in dilute solution, and the fractions of the phosphorus as pyro- and tripolyphosphate in degraded coacervate are two or three times those in degraded dilute solution. $Ca_3H_2(P_2O_7)_2 \cdot 4H_2O$ begins to crystallize from the coacervate when about 30% of the phosphorus is present as pyrophosphate.

In a quantitative study of the degradation, 5.06 grams of coacervate containing 2.61 grams of solute phosphate was allowed to stand for 56 days at room temperature in a closed container. The precipitated $Ca_3H_2(P_2O_7)_2 \cdot 4H_2O$ weighed 1.28 grams and contained 53.8% of the calcium and 35.8% of the phosphorus in the original coacervate. The phosphorus in the liquid phase was distributed as orthophosphate 46.9, pyrophosphate 27.8, tripolyphosphate 14.7, and other species 10.5%.

In the dissolution of vitreous calcium metaphosphate, the long-chain polyphosphates tend to concentrate in the coacervate and the short-chain polyphosphates tend to concentrate in the dilute phase. Huffman and Fleming (5) showed that the average chain length of the phosphate in the aqueous phase is 23, whereas that in the coacervate is 33. Some of the solute phosphate in the aqueous phase can be coacervated by heating; the heated solution becomes cloudy, and the droplets coalesce as a coacervate. Coacervate is also

precipitated from the aqueous phase on addition of acetone.

Effect of Silica and Alumina on Calcium Metaphosphate

Preparations of vitreous calcium metaphosphate containing different amounts of silica were ground to pass a 35-mesh sieve. Ten-gram portions of each preparation were shaken mechanically at room temperature with 20 ml. of water. At intervals the mixtures were centrifuged and the apparent volume of the undissolved glass was taken as an inverse measure of the dissolution of the material. Chromatographic analyses were made of the solutions and of the one coacervate from siliceous metaphosphate that persisted at room temperature. The results are given in Table II and plotted in Figure 2.

Coacervate was formed from all the glasses, but the amount of coacervate was related inversely to the silica content of the glass, and the coacervates formed from the glasses that contained 2.4 and 4.6% Si (5.1 and 9.8% SiO_2) disappeared before the end of the run.

There is no unambiguous basis for estimation of the degree of degradation of the metaphosphate. On the basis of the formation of orthophosphate, the solute from the glass that contained 4.6% Si (9.8% SiO_2) degraded the most, but on the basis of the persistence of condensed phosphate species, this solute degraded the least. Silica did not catalyze the degradation of the solute condensed phosphate, because most of the silica precipitated very rapidly as opal during the dissolution, and silica did not affect either the time of appearance or the rate of precipitation of $Ca_3H_2(P_2O_7)_2 \cdot 4H_2O$. When viscous solutions obtained by dissolution of calcium metaphosphates containing 2.4 and 4.6% Si (5.1 and 9.8% SiO_2) were concentrated by evaporation, each solution contained Ca 14.2, P 23.9, and Si 0.14% (CaO 20.0, P_2O_5 54.7, and SiO_2 0.3%).

Two alumina-containing vitreous calcium metaphosphates, optically homogeneous and free of crystalline phases, were prepared by fusing mixtures of ignited powdered alumina and −35-mesh vitreous calcium metaphosphate. The products were ground to −35-mesh, and then 10-gram portions of each were treated with water in the same manner as the siliceous materials. The results, included in Figure 2, show that alumina markedly inhibited the dissolution of the metaphosphate. When plant metaphosphate was treated with water, it dissolved about as slowly as vitreous calcium metaphosphate but did not coacervate. Its solution contained aluminum, iron, and calcium in about the same ratio as in the metaphosphate. When the concentrated so-

lution was diluted, condensed phosphates of aluminum, iron, and calcium precipitated.

Behavior of Calcium Metaphosphate in the Soil

Small (0.3-gram) tablets of −100-mesh pure calcium metaphosphate and of plant metaphosphate were formed under a pressure of 3000 p.s.i. The tablets were placed in Hartsells (acid, pH 5.1) and in Webster (alkaline-calcareous, pH 7.2) soils in flat-walled glass containers so that one face of each tablet was against and visible through the wall of the container. The soils were moistened to their moisture equivalent, and the containers (prepared in duplicate) were sealed and allowed to stand at room temperature.

Within 2 hours, the soils surrounding the plant metaphosphate tablets showed milky patches of a colloidal precipitate that extended about 2 mm. beyond the periphery of the tablets. In 3 days, there was an apparent wet zone extending about 10 mm. into the soil. The tablets retained their original size and shape but had apparently become quite porous.

Within 2 hours, the soils surrounding the pure calcium metaphosphate tablets appeared wet for a distance of 2 to 3 mm. beyond the periphery of the tablets. The wet zone extended about 7 mm. from the tablet in 3 days, after which there was no further movement. The pellet had then become very wet and had decreased in diameter and thickness, and shrinkage of the pellet continued for 12 days.

One set of the duplicate charges was removed for examination after 50 days, the other after 120 days. The weights lost by the tablets are shown in Table III.

None of the tablet residues contained any of the original vitreous calcium metaphosphate, except that small amounts of either β-calcium pyrophosphate or β-calcium metaphosphate, present originally, remained. All the tablet sites were surrounded by a shell of

soil 2 to 3 mm. thick that was cemented by what appeared to be glassy, partially dehydrated coacervate. Chromatograms of the tablet residues and of the cemented soil shells showed that the phosphate was present primarily as pyrophosphate and condensed phosphates; the amounts of orthophosphate were very small. Apparently vitreous calcium metaphosphate releases its nutrients in the soil by dissolution and hydrolysis rather than by slow congruent dissolution.

Discussion

Finely ground vitreous calcium metaphosphate and plant metaphosphate react with water to form long-chain polyphosphates which subsequently degrade to orthophosphates. Since no coacervate is produced from plant metaphosphate, the chain lengths of the solute phosphate from this material are assumed to be shorter than those in the coacervate produced from pure calcium metaphosphate.

In this study of the reactions of calcium metaphosphate with water, the particles of the glasses were 20-mesh or smaller. The behavior of larger particles, such as 4-mesh, in water and in moist soil differed markedly from the behavior of the −20-mesh material. When the coarse glass was shaken with water, dissolution was very slow, and virtually all the solute phosphate was precipitated as a fine-grained white solid which was found to be dehydrated coacervate containing about 87% solute phosphate. Similarly, when coarse particles were placed in moist soil, dissolution apparently was negligible except for a film of dehydrated coacervate which formed on the surface. There was no visible evidence of movement of coacervate into the soil.

These apparently anomalous results can be explained by differences in rates of dissolution and degradation of the dissolved polyphosphates that comprise the coacervate. When the metaphosphate is finely ground, dissolution is much more rapid than degradation. Much

Table III. Residues from Tablets of Vitreous Calcium Metaphosphate after Contact with Moist Soil

Soil	pH	Time, Days	Weight, Mg. Tablet	Weight, Mg. Residue	Weight Loss, %
REAGENT GRADE METAPHOSPHATE					
Hartsells	5.1	50	319	24	93
		120	311	11	97
Webster	7.2	50	314	25	92
		120	310	11	97
FERTILIZER GRADE METAPHOSPHATE					
Hartsells	5.1	50	314	98	69
		120	321	90	69
Webster	7.2	50	310	136	56
		120	316	140	55

coacervate is formed, the ratio of water to coacervate is low, and the aqueous phase is saturated with short-chain polyphosphates while the coacervate is still fluid.

With coarse metaphosphate, dissolution is slow, and the small amount of coacervate that may form is in contact with a large excess of water which can extract enough of the short chains to solidify the coacervate.

MacIntire (6) explained the effect of silica on the solubility of calcium metaphosphate by assuming that the silica was present as the silicophosphate $SiO_2 \cdot P_2O_5$, which reacts with water to form silica and metaphosphoric acid, HPO_3. Metaphosphoric acid, however, was not identified in any solutions in this study, nor did it appear as a constituent of the condensed phosphates at any stage of degradation of the metaphosphate.

Du Plessis (4) recognized the influence of silica on the degree of condensation of condensed phosphates and found a definite relationship between chain length and silica content of the glass. In vitreous calcium metaphosphate with a mole ratio P:Ca of 2, the ratio of phosphorus to silicon approaches 4 as the melt becomes saturated with silica. Du Plessis then postulated a compound of the limiting composition $(Ca_2SiP_4O_{14})_x$ but there was no evidence of such a solid in the present work.

The solubility of coacervate in water increases as degradation proceeds, indicating that the solubility of condensed phosphate is an inverse function of its chain length. Silica appears to affect the chain length of the phosphate species, either within the glass or at the time of dissolution, since the amount of coacervate is related inversely to the silica content of the vitreous calcium metaphosphate. The chromatographic methods, however, did not identify individual species of chains that contained more than four phosphorus atoms.

The effect of silica indicates that change of chain length of the condensed phosphate species is an important factor in the degradation process. The breaking of long chains into chains too short to form coacervate, but too large to move from the base line, would not be detected chromatographically. It may be assumed, however, that the vitreous siliceous metaphosphate is composed of long-chain phosphates that contain some silica groups as links, and that upon dissolution the chains break at the silica links. If long-chain fragments of such chains are formed at the surface of the glass where the dissolution and initial reaction take place, silica may control the length of the chain that can leave the three-dimensional structure.

Addition of water to solutions of partially degraded coacervate reprecipitates some coacervate. As degradation of the original solution proceeds, however, less coacervate is precipitated by addition of water, and eventually the concentration of coacervate-size chains is insufficient to form a separate phase on dilution with water. When portions of the solutions of the vitreous metaphosphates were treated with water or heated to 100° C., the solution from the material that contained 4.6% Si (9.8% SiO_2) remained clear, indicating a preponderance of chains shorter than those required to form coacervate. The solutions of materials that contained less silica became cloudy, indicating the presence of chains long enough to form coacervate.

Silica does not enter or long remain in the dissolved hydrated chains. When siliceous calcium metaphosphate is placed in water, precipitated silica appears as soon as dissolution starts, and the amount of precipitated silica increases with increasing dissolution. A small amount of silica remains in the solution as either dissolved or colloidal silica. Microscopic observation of the dissolution of individual particles showed that silica is liberated at the dissolving surface, precipitates as globular particles of opal gel, and remains in this form.

Vitreous calcium metaphosphate and fertilizer grade metaphosphate in the particle sizes normally found in fertilizers undergo rapid transformations in the soil. They react with soil moisture to form viscous solutions of highly condensed phosphates which then solidify by dehydration within a few millimeters of the application site to form a shell of soil cemented with glassy condensed phosphates. Chromatographic analysis of the fertilizer residues and cemented soils after 50 days showed that most of the phosphorus was present as pyrophosphate and higher condensed phosphates, a result observed also by Donoso-Torres (3).

The relatively high water solubility of siliceous calcium metaphosphate should be advantageous in processes in which calcium metaphosphate is converted into other forms of fertilizer phosphate. Adjustment of the silica content of the initial metaphosphate would produce material containing condensed phosphates with average chain lengths that would impart the desired reactivity to the product.

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