

In a previous short-term, potassium-uptake test (3) with oats fertilized with the same fertilizers, relative availabilities of K in -6+9 mesh particles made with elemental phosphorus and KCl and with H<sub>3</sub>PO<sub>4</sub> and KCl were 46 and 41%, respectively, of potassium in KCl. Availability of potassium in the -35 mesh materials was equal to that in KCl.

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## GRANULAR FERTILIZER

# The Influence of Associated Salts on Plant Response to Dicalcium Phosphate

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The influence of granulating nonphosphatic salts or glass beads with dicalcium phosphate on plant response to phosphorus was studied in greenhouse culture. Plant response to the several fertilizers was positively correlated with the geometric surface area of the fertilizers. The results indicate that dicalcium phosphate and nonphosphatic salts should be mixed prior to granulation so that each granule contains both components.

IN PREVIOUS STUDIES (7-3), plant response to dicalcium phosphate and to other A.O.A.C. water-insoluble phosphates has been correlated with the estimated geometric surface area (4). When mixtures of monoammonium phosphate and dicalcium phosphate were studied, plant response to the dicalcium phosphate was also well correlated with the geometric surface area of granules formed from a mixture of the two phosphates (7). The objective of the experiment reported here was to study plant response to granular dicalcium phosphate fertilizers with geometric surface area varied by additions of several nonphosphatic salts or glass beads.

#### Methods and Materials

**Fertilizers.** A bulk sample of anhydrous dicalcium phosphate was prepared as follows: a 9% solution of H<sub>3</sub>PO<sub>4</sub> was saturated with reagent-grade dicalcium phosphate at room temperature. After filtering, the solution was heated with stirring to about 90° C. The anhydrous dicalcium phosphate was filtered off and washed with dilute H<sub>3</sub>PO<sub>4</sub> and acetone. The crystal size was less than 100 microns.

Dicalcium phosphate was granulated by moistening with 5% agar solution, pressing the moist mixture into pellets with a hydraulic press, and screening the

crushed pellets after drying. Mixtures of 40-micron glass beads and anhydrous dicalcium phosphate were granulated by the same procedure.

Reagent-grade salts ground to pass a 35-mesh screen were mixed with dicalcium phosphate. The mixture was moistened with water and granulated as described above.

The number of granules per gram was determined by counting weighed samples. Bulk density was determined as follows. A weighed sample of the granular fertilizers was mixed with 40-micron glass beads, and the volume of the mixture was determined after careful packing in graduated cylinders. The weight of the mixture was also determined. By using the measured bulk density of the glass beads and these data, the bulk density of the fertilizers was calculated according to Equation 1

$$D = \frac{W_F D_B}{V D_B + \frac{W_F}{W_T} - W_T} \quad (1)$$

where

- $D$  = bulk density of fertilizer
- $D_B$  = bulk density of beads
- $V$  = volume of fertilizer and bead mixture
- $W_F$  = weight of fertilizer
- $W_T$  = weight of fertilizer and bead mixture

The geometric surface area was calculated from bulk density and number of granules as follows. Granules were assumed to be spherical in shape. Using this assumption, mean radius is given by Equation 2

$$R = \left( \frac{3}{4\pi N D} \right)^{1/3} \quad (2)$$

where

- $R$  = mean radius in cm.
- $N$  = number of granules per gram of fertilizer
- $D$  = bulk density in grams per cm.<sup>3</sup>

By using the value of  $R$  given by Equation 2, the geometric surface area per gram of fertilizer is given by Equation 3

$$GSA = (4\pi N)^{1/3} \left( \frac{3}{D} \right)^{2/3} \quad (3)$$

where

- $GSA$  = geometric surface area, cm.<sup>2</sup> per gram

Characteristics of the fertilizers are listed in Table I.

**Experimental Procedure.** Samples of the fertilizers to supply 30 and 60 mg. of P were mixed with 3 kg. of Hartsells fine sandy loam (pH 5.2), and the mixture was placed in No. 10 tin cans lined with plastic bags. In addition, treatments containing 90 and 120 mg. of P as -28+35 mesh anhydrous dicalcium phosphate, and a no-phosphorus check were included to establish a response curve. Three replications of each treatment were prepared. Nitrogen and potassium levels were equalized at 200 mg. per culture using solutions of Ca(NO<sub>3</sub>)<sub>2</sub> and Mg(NO<sub>3</sub>)<sub>2</sub> and K<sub>2</sub>SO<sub>4</sub>. Oats were seeded and the cultures grown for 8 weeks in the greenhouse. One hundred milligrams of nitrogen as a

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solution of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Mg}(\text{NO}_3)_2$  were added at weekly intervals, beginning 2 weeks after seeding. Above-ground dry matter yields were determined and ground samples were analyzed for P. Availability coefficient indexes were calculated from the dry matter data using the procedure described previously (2).

### Results and Discussion

In this experiment, N, K, and S additions were judged to be adequate so that these elements did not limit plant growth. Furthermore, the levels of these elements added in supplemental treatments were somewhat higher than the levels of these elements added in conjunction with the phosphate treatments. Hence, the plant response obtained was judged to be a function primarily of the phosphate availability. The differences in availability coefficient indexes listed in Table II are judged to be the result of differences in availability of phosphate and not differences in plant response to N, K, or S added with the phosphate, except to the extent that these elements influenced the chemistry of the phosphate reactions with the soil. This conclusion was substantiated by the observation that dry matter yields were highly correlated with yields of P with all fertilizers.

By considering the data with dicalcium phosphate alone and mixed with glass beads, large increases in plant response per unit of P were obtained by mixing glass beads with the dicalcium phosphate. On a per granule basis, some decreases in plant response were obtained with the -9+14 mesh granules when glass beads were added, but the decrease in plant response was not nearly as large as would be expected on the basis of the difference in percentage P in the granules. On a per granule basis, plant response was much the same with the -28+35 mesh granules regardless of the quantity of glass beads.

These results can be explained on the following basis. Presumably, the glass beads are relatively inert and do not appreciably influence the solution composition within the granule. Furthermore, the glass beads are small and rates of diffusion of ions in solution are rapid so that, regardless of how many glass beads were added, the solution at the granule surface is essentially saturated with respect to dicalcium phosphate. Hence, the addition of glass beads would not be expected to alter greatly the concentration of phosphorus within the granule or at the granule-soil interface.

Results with the several salts were similar to those with glass beads. Here the salts (except  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) would be expected to dissolve in a few hours, leaving a porous granule of dicalcium phosphate. Again, rates of solution and diffusion would be expected to maintain surface concentrations constant, and

**Table I. Characteristics of Fertilizers Used in Greenhouse Experiment**

Components	Granule Size (Tyler Mesh)	P, %	N, %	K, %	Bulk Density, Grams/Cm. <sup>3</sup>	Number of Granules/Mg. of P	Geometric Surface Area, Cm. <sup>2</sup> /Gram of P
DCPA <sup>a</sup>	-9+14	22.7	...	...	1.97	0.923	80.2
	-28+35	22.6	...	...	1.99	25.7	244
75% DCPA + 25% beads	-9+14	17.0	...	...	1.88	1.33	114
	-28+35	17.1	...	...	1.86	34.2	336
50% DCPA + 50% beads	-9+14	11.3	...	...	1.73	2.18	186
	-28+35	11.6	...	...	1.76	58.3	539
25% DCPA + 75% beads	-9+14	5.85	...	...	1.57	4.55	395
	-28+35	6.13	...	...	1.58	121.8	1140
DCPA + KCl	-9+14	12.5	...	23.9	1.96	1.79	157
	-28+35	12.0	...	23.0	1.89	59.2	509
DCPA + $\text{NH}_4\text{Cl}$	-9+14	7.66	17.6	...	1.55	3.83	313
	-28+35	7.49	17.2	...	1.50	101.7	971
DCPA + $\text{KNO}_3$	-9+14	10.8	7.4	20.7	2.04	1.99	166
	-28+35	10.4	7.1	19.9	1.94	59.5	549
DCPA + $\text{NH}_4\text{NO}_3$	-9+14	9.46	21.7	...	1.82	2.52	211
	-28+35	9.49	21.7	...	1.77	71.2	656
DCPA + $\text{K}_2\text{SO}_4$	-9+14	11.5	...	22.0	2.19	1.78	148
	-28+35	11.4	...	21.8	2.11	53.0	468
DCPA + $(\text{NH}_4)_2\text{SO}_4$	-9+14	6.67	15.3	...	1.70	3.73	319
	-28+35	6.44	14.8	...	1.63	132.1	1099
50% DCPA + 50% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-9+14	11.4	...	...	1.99	1.86	160
	-28+35	11.0	...	...	1.87	59.6	542

<sup>a</sup> Anhydrous dicalcium phosphate.

**Table II. Availability Coefficient Index per 30 Mg. of P and Per Granule Based on Yields of Dry Matter**

Fertilizer	Availability Coefficient Index ( $\times 10^4$ )			
	-9+14 Mesh		-28+35 Mesh	
	Per 30 mg. of P	Per granule	Per 30 mg. of P	Per granule
DCPA <sup>a</sup>	109	3.94	499	0.647
75% DCPA + 25% beads	153	3.84	588	0.573
50% DCPA + 50% beads	193	2.95	1140	0.652
25% DCPA + 75% beads	428	3.15	1940	0.530
DCPA + KCl	189	3.52	932	0.525
DCPA + $\text{NH}_4\text{Cl}$	363	3.16	1560	0.511
DCPA + $\text{KNO}_3$	174	2.91	937	0.525
DCPA + $\text{NH}_4\text{NO}_3$	264	3.49	1460	0.684
DCPA + $\text{K}_2\text{SO}_4$	224	4.19	865	0.544
DCPA + $(\text{NH}_4)_2\text{SO}_4$	477	4.26	1900	0.479
DCPA + $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	111	1.99	669	0.374

<sup>a</sup> Anhydrous dicalcium phosphate.

on a per granule basis, the net effect of the soluble salts would not be very great.

The addition of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  decreased the plant response on a per granule basis, but per 30 mg. of P, the plant response was comparable to that with dicalcium phosphate. Apparently, the increase in geometric surface area counterbalanced the decrease in response per granule.

In Figure 1, the availability coefficient indexes per 30 mg. of P are plotted against the geometric surface areas. These results indicate 96% of the variation in the availability coefficient indexes can be explained on the basis of geometric surface area measurements. These results are also consistent with the probability hypothesis proposed by Moreno (6).

With the exception of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , the various salts had little or no influence on response which was not explained

(statistically) on the basis of geometric surface area. Starostka and Hill (7) reported the influence of saturated solutions of several salts on the solubility of dicalcium phosphate. The nitrogen and potassium salts considered here dissolve readily in the soil to form saturated solutions (5). The length of time required to dissolve a granule of salt will depend on the quantity of salt per granule. In considering the influence of soluble salts on the dissolution of admixed dicalcium phosphate, the time required for dissolution of the salt is an important variable. Hence, as granule size is increased, the effect of added salts will become greater. This discussion suggests that with very large granules, the influence of the individual salts on the plant response to dicalcium phosphate on a per granule basis would be more apparent.

The results indicate that plant response

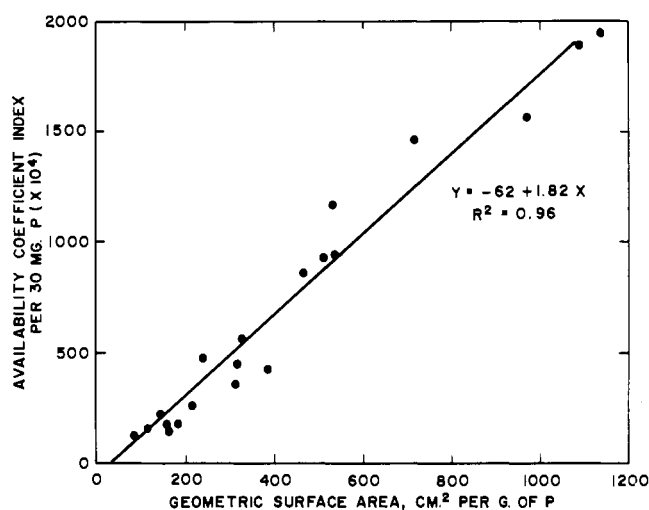


Figure 1. Availability coefficient index plotted against geometric surface area

Results with  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  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.

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## 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.

**I**N 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.