

Urea-Monocalcium Phosphate, a Component of Mixed Fertilizers

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Urea reacts with the $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ in concentrated superphosphate to form the adduct $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$. The adduct is stable and nonhygroscopic, but the water of hydration released in the reaction forms a viscous solution

that makes the mixture wet and sticky. The region in the system $\text{CaO}-\text{P}_2\text{O}_5-\text{CO}(\text{NH}_2)_2-\text{H}_2\text{O}$ in which the adduct is stable was defined, and the crystallographic properties and x-ray pattern of the adduct were determined.

Urea is a desirable component of mixed fertilizers, but with many fertilizer salts it reacts to form compounds that are hygroscopic or cause caking. Urea reacts with the calcium sulfate in ordinary superphosphate to form hygroscopic $\text{CaSO}_4 \cdot 4\text{CO}(\text{NH}_2)_2$ (8). In mixtures that contain ammonium salts and potassium chloride, urea forms $\text{CO}(\text{NH}_2)_2 \cdot \text{NH}_4\text{Cl}$ which cakes the entire mixture severely (7). Although urea forms the adduct $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ (6), the poor physical properties of combinations of urea and nitric phosphates result from the hygroscopicity of urea and ammonium nitrate mixtures which have a critical relative humidity of 18.1% (1). In recent studies of fertilizers containing urea and concentrated superphosphate, a new adduct, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$, was identified in mixtures that deteriorated rapidly in storage. The water of hydration of monocalcium phosphate monohydrate that is released in the formation of the adduct forms a viscous saturated solution that makes the mixture wet and sticky.

Bosch (2) and Whittaker, Lundstrom, and Shimp (9) attributed the undesirable properties of mixtures of urea and superphosphate to the formation of $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$ and CaHPO_4 , based on the chemical composition and results of hygroscopicity tests of simulated product mixtures. Whittaker further concluded that the wet, sticky condition of the mixture was caused by excess urea or by the urea phosphoric acid adduct. In the mixtures studied by Whittaker [mole ratios of $\text{CO}(\text{NH}_2)_2-\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ in the range 1.0 to 4.2], the new adduct $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ is the controlling reaction product, and the poor physical condition of the mixture is due to the presence of a saturated solution of the adduct.

The new adduct was isolated and its crystallographic properties were determined; the region in the system $\text{CaO}-\text{P}_2\text{O}_5-\text{CO}(\text{NH}_2)_2-\text{H}_2\text{O}$ in which it is stable was defined.

Preparation and Characterization

A saturated aqueous solution of monocalcium phosphate (10.5% P, 4.1% Ca; 24.1% P_2O_5 , 5.7% CaO) was saturated with urea and filtered. The new adduct $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ was obtained from the filtrate by slow evaporation of water or by addition of either phosphoric acid or a soluble calcium salt. All the pre-

cipitates had the same chemical composition, optical properties, and x-ray pattern. The compositions of typical preparations are shown in Table I and the x-ray powder diffraction pattern is listed in Table II.

The adduct $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ crystallizes as colorless tabular crystals with monoclinic symmetry, class 2/m. Crystals are usually tabular on (010) with the modifying forms $\{110\}$, $\{011\}$, (111), $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}\bar{1}\bar{1})$, and $(\bar{1}\bar{1}\bar{1})$; monoclinic angle $\beta = 91^\circ$. The density calculated from the refractive indices and composition is 1.75 grams per cc. There is an excellent cleavage parallel to (010). The salt is nonhygroscopic and stable in air.

The crystals are biaxial (+) with measured and calculated optic axial angle $(2V) = 54^\circ$. The OAP is normal to (010), with $X = b$ and $Z \wedge c$ on (010) = 14° in acute β . The refractive indices are $N_x = 1.531$, $N_y = 1.535$, and $N_z = 1.551$.

The powder x-ray diffraction pattern (Table II) was obtained at a scanning rate of $0.5^\circ 2\theta$ per minute. Weissenberg single-crystal x-ray studies showed the space group symmetry to be $C_{2h}^2-P2_1/n$, with $a = 5.66$ A., $b = 21.57$ A., $c = 7.40$ A., and $\beta = 90^\circ 56'$. The unit cell contains two formula weights of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ and has a calculated density of 1.732 grams per cc.

Although $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ and $\text{CaSO}_4 \cdot 4\text{CO}(\text{NH}_2)_2$ differ chemically only in the nature and number of the tetrahedral anions, the phosphate and sulfate (5) adducts have different space group symmetries, cell dimensions, and packing arrangements, and the two adducts do not appear to be structurally related.

The adduct $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ has a structure of alternating sheets of urea molecules and calcium phosphate molecules parallel to (010). This arrangement satisfies the site symmetry of the space group and accounts for the excellent cleavage parallel to (010). Within the urea sheets, pairs of urea molecules (related through centers of symmetry) must be in mutually inclined positions to normalize the contributions of the strongly polarizing $\text{C}=\text{O}$ bonds to refractive indices in the (010) plane.

The System $\text{CaO}-\text{P}_2\text{O}_5-\text{CO}(\text{NH}_2)_2-\text{H}_2\text{O}$

To determine conditions under which $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ is stable, a brief study was made of the region of the system $\text{CaO}-\text{P}_2\text{O}_5-\text{CO}(\text{NH}_2)_2-\text{H}_2\text{O}$ in which the adduct is the stable solid phase. The other solid phases in this region are urea, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$,

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Table I. Preparations of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$

	Composition, %				Moles per Mole P					
	CaO	P ₂ O ₅	CO(NH ₂) ₂	H ₂ O, diff.	Ca	P	N	Ca	CO(NH ₂) ₂	H ₂ O
Sample 1	11.9	29.8	50.6	7.7	8.5	13.0	23.6	0.508	2.01	1.02
Sample 2	11.9	30.0	50.2	7.9	8.5	13.1	23.4	0.504	1.98	1.04
Stoichiometric	11.82	29.93	50.65	7.60	8.45	13.06	23.63	0.500	2.00	1.00

Table II. X-Ray Diffraction Spectrum of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ ^a

d, A.	I	d, A.	I	d, A.	I	d, A.	I
10.72	100	3.59	97	2.53	7	1.892	5
7.00	47	3.47	27	2.50	5	1.860	4
6.09	9	3.43	56	2.45	3	1.793	4
5.37	5	3.29	7	2.43	3	1.778	3
5.15	2	3.12	3	2.33	2	1.762	3
4.53	4	3.09	3	2.28	4	1.743	5
4.44	16	3.03	11	2.24	4	1.725	4
4.34	3	2.95	3	2.19	8	1.714	5
4.11	13	2.81	27	2.15	5	1.694	2
3.97	3	2.61	6	2.14	6	1.645	3
3.83	23	2.58	3	2.10	3	1.575	3
3.79	21	2.54	5	2.01	3		
3.65	16			1.927	3		

^a Pattern obtained with Geiger counter x-ray diffractometer, CuK α radiation, $\lambda = 1.5405 \text{ \AA}$. Intensities measured as peak heights above background and expressed as per cent of strongest line.

CaHPO_4 , and $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$. The liquid phases were prepared from an aqueous solution that was saturated with monocalcium phosphate and then with urea; the compositions of portions of this solution were adjusted by additions of different components of the system to form mixtures that would define the boundaries of the regions of stability of the different solid phases. The mixtures were allowed to stand with occasional shaking at room temperature (27°C.) for 30 days, and the solid phases were identified petrographically. The compositions of solutions at phase boundaries are listed in Table III and plotted in Figures 1 and 2. Determinations of urea nitrogen and total nitrogen in several mixtures showed that there was no significant hydrolysis of urea during the equilibration period. Since the calcium contents of the saturated solutions ranged only from 1.9 to 4.3% (2.6 to 6.0% CaO), the results are plotted as a projection on the $\text{P}_2\text{O}_5\text{-CO}(\text{NH}_2)_2\text{-H}_2\text{O}$ face; the resulting slight distortion can be ignored.

Equilibrium was attained rapidly by all mixtures in which CaHPO_4 was not added initially; the slow dissolution of CaHPO_4 delayed equilibration. To hasten equilibration of mixtures in which CaHPO_4 was a stable solid phase, CaHPO_4 was precipitated in finely divided form by addition of calcium hydroxide to mixtures containing $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ or $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ that were near the CaHPO_4 boundary.

In this system, only $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ forms a stable salt pair with each of the other solid phases. Numerous tests (not included in Table III) in the region of closest approach of the fields of $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$

and CaHPO_4 showed that the line joining points 9 and 13 in Figure 2 represents a true phase boundary. Mixtures of CaHPO_4 and $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$, as postulated by Whittaker's reaction (9), were never found together as stable solid phases. Urea and $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ also do not form a stable mixture, but react rapidly to form $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$. Although dicalcium phosphate sometimes forms as a metastable intermediate in mixtures containing $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$, the mixtures are unstable and the persistence of the dicalcium phosphate results from its low solubility and sluggish alteration to $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ or $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$.

Discussion of Results

Bosch (2) and Whittaker, Lundstrom, and Shimp (9) reported that urea reacts with the monocalcium phosphate in superphosphate to form CaHPO_4 and $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$, and they attributed the poor physical properties of the mixture to the hygroscopicity of the $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$. As shown in Figure 2, however, the two solid phases they reported are not stable together, and are not found in mixtures of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2$.

Dry mixtures of 1.2 to 4.3 moles of $\text{CO}(\text{NH}_2)_2$ with 1 mole of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ react to form $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ as the major solid phase, which is wetted by a saturated liquid phase in which the solvent is the hydrate water released from the $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. For example, a mixture of equal weights of urea and $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ —mole ratio $\text{CO}(\text{NH}_2)_2\text{-Ca}(\text{H}_2\text{PO}_4)_2 = 4.2$; 23.2% N, 12.3% P (28.2% P_2O_5)—forms a mixture of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ and a saturated solution with the composition of solution 2 in Table III and Figure 2 that amounts to 11.6% of the total mixture. This concentrated solution is viscous, and its amount is sufficient to wet the solid phase thoroughly; it is this solution, rather than the hygroscopicity of a solid phase, that causes the poor physical condition of mixtures of urea and superphosphate. Mixtures of urea and anhydrous monocalcium phosphate, however, are stable, and the adduct $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ is not formed unless moisture is present. The mixture is hygroscopic enough to absorb water from the atmosphere and form the adduct, but the final product is dry and no more hygroscopic than monocalcium phosphate monohydrate.

The formation of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ in mixtures of urea and superphosphate can be prevented by using a superphosphate that has been dried above 110°C. to convert it to anhydrous $\text{Ca}(\text{H}_2\text{PO}_4)_2$. Light ammoniation of the superphosphate also inhibits the reaction by forming protective hulls of $\text{NH}_4\text{H}_2\text{PO}_4$ and CaHPO_4 on the superphosphate particles. Alternatively, an am-

Table III. Saturated Solutions in the System $\text{CaO}-\text{P}_2\text{O}_5-\text{CO}(\text{NH}_2)_2-\text{H}_2\text{O}$

No.	Composition of Liquid Phase, %				Ca	P	N		Solid Phase ^a
	CaO	P ₂ O ₅	CO(NH ₂) ₂	H ₂ O, diff.			Urea	Total	
1	2.6	20.1	51.7	25.6	1.9	8.8	24.2	24.1	U, UPA, UMC
2	3.5	13.3	51.4	31.8	2.5	5.8	24.0	23.8	U, DC, UMC
3	3.7	15.0	51.0	30.3	2.6	6.6	23.8	23.8	U, UMC
4	2.8	10.4	51.3	35.5	2.0	4.5	23.9	24.0	U, DC
5	2.7	20.8	51.8	24.7	1.9	9.1	24.2	24.2	U, UPA
6	3.7	22.9	43.7	29.7	2.6	10.0	20.4	20.4	UPA, UMC
7	4.3	23.7	41.8	30.2	3.1	10.4	19.5	19.2	UPA, UMC
8	4.5	23.9	39.9	31.7	3.2	10.4	18.6	18.7	UPA, UMC
9	5.8	24.1	38.6	31.5	4.2	10.5	18.0	17.6	UPA, UMC, MC
10	5.2	24.7	34.3	35.8	3.7	10.8	16.0	15.9	UPA, MC
11	0.02	43.4	6.7	49.9	0.01	19.0	3.2	3.0	UPA, MC
12	5.2	22.9	18.5	53.4	3.7	10.0	8.7	8.8	DC, MC
13	6.0	23.6	38.5	31.9	4.3	10.3	18.0	17.9	DC, MC, UMC
14	5.0	18.8	43.5	32.7	3.6	8.2	20.3	20.1	DC, UMC

^a U = $\text{CO}(\text{NH}_2)_2$, UPA = $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$, UMC = $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$, DC = CaHPO_4 , MC = $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

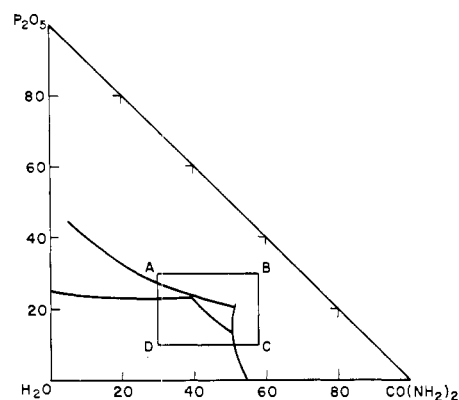


Figure 1. The system $\text{CaO}-\text{P}_2\text{O}_5-\text{CO}(\text{NH}_2)_2-\text{H}_2\text{O}$ projected on the $\text{P}_2\text{O}_5-\text{CO}(\text{NH}_2)_2-\text{H}_2\text{O}$ face

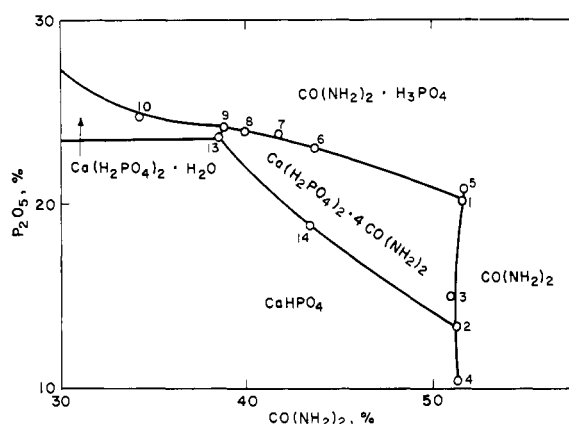


Figure 2. Section *ABCD* of Figure 1
Numbers on points are those in Table III

monium salt may be incorporated in the mixture. In the presence of a soluble source of ammonia, dissolution of monocalcium phosphate results in precipitation of water-insoluble calcium ammonium orthophosphates (3) at calcium concentrations well below those required for the precipitation of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$. These effects apparently are the basis for the claims in a recent patent (10) that mixtures of urea and superphosphate are stabilized by addition of ammonia to neutralize the free acid. Superphosphate ammoniated beyond 2 pounds of NH_3 per unit of P_2O_5 no longer contains any $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ to react with urea. Ammonia added as ammonium polyphosphates (4) also is effective in preventing formation of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$, and mixtures of superphosphate and granular urea ammonium phosphate (a mixture of urea and diammonium orthophosphate) do not form the adduct.

The adduct $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ is a dry crystalline solid that is stable and nonhygroscopic at relative humidities below about 60%. Mixtures of superphosphate and urea in which the adduct has formed probably could be dried in conventional drying equipment to form stable solid products with good physical and

agronomic properties, since the adduct contains 23.63% N and 13.06% P (29.93% P_2O_5).

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