Iron and Aluminum Compounds in Commercial Superphosphates

A. WILLIAM FRAZIER AND JAMES R. LEHR

Concentrated superphosphates prepared from wet-process phosphoric acid high in iron and aluminum contain residual amounts of the complex iron and aluminum phosphates that were present as sludge phases in the acid, and a new salt, $Ca(Al,Fe)H(PO_4)_2.4H_2O$, which replaces a significant fraction of the $Ca(H_2PO_4)_2.H_2O$, the major constituent of concentrated super- phosphates. The new salt is citrate-soluble but water-insoluble and decreases markedly the capacity of the superphosphate for ammonia. The crystallographic properties of the new salt are described, and its x-ray powder diffraction pattern and infrared absorption spectrum are presented.

Commercial concentrated superphosphates produced in recent years show a marked increase in iron and aluminum content and a corresponding decrease in monocalcium phosphate monohydrate content. Petrographic and x-ray examinations of these superphosphates showed that the iron and aluminum are present as three crystalline phases, two of which, $(Fe,Al)_3$-$(K,H)H_8(PO_4)_6.6H_2O$ *(3, 6, 8)* and $(Fe,Al)_3KH_{14}(PO_4)_8.$-$4H_2O$ *(4)*, are described in the literature. The third phase is a new compound, $Ca(Al,Fe)H(PO_4)_2.4H_2O$. All three compounds are citrate-soluble but water-insoluble, and their presence, particularly that of the new compound, adversely affects the ammoniation characteristics of the superphosphate *(1)*.

The increase in the iron and aluminum content of superphosphate results from the use of lower grade (higher R_2O_3) phosphate rock and of unclarified wet-process phosphoric acid, or even sludge acid, in the manufacture of the superphosphate. The two compounds that contain potassium have been shown to be constituents of the sludge in wet-process acid *(4)*; the $(Fe,Al)_3KH_{14}(PO_4)_8.4H_2O$ in superphosphate is present as remnants of coarse crystals that have been severely eroded by dissolution, and the $(Fe,Al)_3(K,H)H_8(PO_4)_6.$-$6H_2O$ is present as very small grainy crystals. The $Ca(Fe,Al)H(PO_4)_2.4H_2O$ apparently is a product of the reaction of the sludge compounds with the acidic calcium phosphate solution that is formed in the acidulation of the phosphate rock. Although this compound has been recognized for several years as a minor constituent of superphosphates prepared with wet-process phosphoric acid, it is only recently that its concentration in commercial superphosphates has increased to such an extent that it interferes markedly with the water solubility and ammoniation characteristics of the superphosphates. In some superphosphates the new compound is a significant phosphate constituent and amounts to as much as 25% of the superphosphate. Commercial concentrated superphosphates now being produced usually contain 15 to 20% of the complex iron and aluminum phosphates *(1)*.

Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, Ala.

Crystallography

Homogeneous crystalline concentrates of $Ca(Al,Fe)$-$H(PO_4)_2.4H_2O$ were obtained by washing the water-insoluble residues of commercial concentrated superphosphates rapidly with 19% hydrochloric acid on a coarse fritted-glass filter with suction. Although the acid was in contact with the sample for less than 5 seconds, the potassium-containing complex phosphates were dissolved; the residue, after repeated washing with water and air-drying, consisted of $Ca(Al,Fe)H(PO_4)_2.$-$4H_2O$ and a small amount of quartz from the parent phosphate rock. A typical preparation contained (quartz-free basis) 11.18% Ca, 5.73% Al, 3.3% Fe, 17.71% P (15.65% CaO, 10.82% Al_2O_3, 4.82% Fe_2O_3, 40.59% P_2O_5), and, by difference, 28.1% H_2O, which corresponds to the empirical formula $Ca(Al_{0.78}Fe_{0.22})H$-$(PO_4)_2.4H_2O$. Although the analysis indicates that the salt is the pentahydrate, the loss on heating and the symmetry of the crystals indicate that the salt is the tetrahydrate.

The compound $Ca(Al,Fe)H(PO_4)_2.4H_2O$ crystallizes as (010) rhombic tablets with monoclinic, class $2/m$ (holohedral) symmetry. The crystals usually occur in lamellar aggregates or sheaves of thin plates united on (010) much like the habit of gypsum. Optically, the crystals are biaxial $(+)$, with OAP $=$ (010) and $Y = b$; $Z \wedge c = 28°$ on (010). The optical angle $2V$ was measured as 30° to 35° and calculated to be 37°. The density calculated from refractive indices and composition is 2.31 grams per cc. The refractive indices for the salt with mole ratio Al:Fe $= 3.5$ are $\alpha = 1.540$, $\beta = 1.545$, and $\gamma = 1.585$. These refractive indices change with change in relative proportions of aluminum and iron and often vary among crystals in a single preparation and among crystals recovered from different superphosphates. In a number of samples of crystals, the value of α ranged from 1.525 to 1.550, and that of γ from 1.575 to 1.600.

The x-ray powder diffraction pattern of $Ca(Al_{0.78}$-$Fe_{0.22})H(PO_4)_2.4H_2O$ is shown in Table I, and the infrared absorption spectrum, obtained by the KBr pellet technique, is shown in Figure 1.

d, A.	I	d, A.	I	d, A.	I
6.29	100	3.06	7	2.10	18
5.69	4	2.96	37	2.05	5
4.74	7	2.88	13	2.04	14
4.57	30	2.80	3	1.999	9
3.97	17	2.67	8	1.900	8
3.62	36	2.57	12	1.801	7
3.25	10	2.37	8	1.776	11
3.16	26	2.29	4	1.743	4
3.14	23	2.26	6	1.689	5

[a] Patterns obtained with Geiger counter x-ray diffractometer, $CuK\alpha$ radiation, λ = 1.5405 A. Intensities measured as peak heights above background and expressed as per cent of strongest line.
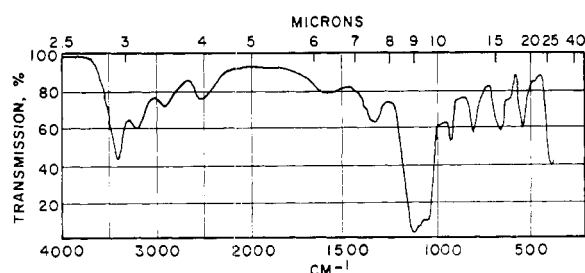

Figure 1. Infrared absorption spectrum of $Ca(Al_{0.78}Fe_{0.22})H(PO_4)_2.4H_2O$

Discussion

The compound $Ca(Al,Fe)H(PO_4)_2.4H_2O$ is the most abundant and most insoluble of the three complex iron and aluminum phosphates usually found in commercial concentrated superphosphates. All three compounds are water-insoluble but citrate-soluble, but the calcium salt is much less soluble in acids and is practically inert during ammoniation of the superphosphate (1). The rate of solution in mineral acids of the calcium salt increases with increasing substitution of aluminum for iron.

Attempts to synthesize the new tetrahydrate from reagent chemicals at temperatures in the range encountered in the production of concentrated superphosphate were unsuccessful. A similar compound, $CaAlH(PO_4)_2.6H_2O$, has been prepared at 25° to 35° C. from aluminum salts and highly acidic calcium phosphate solutions (5, 7). At temperatures of 25° to 105° C., the products of similar preparations with iron

salts were $CaFe_2H_4(PO_4)_4.5H_2O$ (2), the hydronium analog $Fe_3(H_3O)H_8(PO_4)_6.6H_2O$ (8) which is isotypic with $Fe_3(NH_4,K)H_8(PO_4)_6.6H_2O$ (6), and a new compound, apparently with the composition of $Ca_2FeH_2(PO_4)_3.H_2O$, which forms as orthorhombic, biaxial (−) crystals with α = 1.649, β = 1.670, and γ = 1.690. The tetrahydrate was never formed, even as a secondary phase.

Although the composition of the solution from which $Ca(Al,Fe)H(PO_4)_2.4H_2O$ precipitates has not been determined, it is apparent that this salt precipitates from the solution that is formed when phosphate rock dissolves in wet-process phosphoric acid. The crystals of $Ca(Al,Fe)H(PO_4)_2.4H_2O$ are always present as relatively coarse, well developed blades that could only have grown from solution. All the crystals of $(Al,Fe)KH_{14}(PO_4)_8.4H_2O$ observed in superphosphates were remnants of the largest crystals introduced in the acid sludge; the smaller crystals had been dissolved, and the larger crystals had been severely eroded by dissolution.

The complex iron and aluminum phosphates are not particularly deleterious if the concentrated superphosphates are to be used as fertilizers without further processing; the complex phosphates lower the water solubility, but not the citrate solubility, of the P_2O_5. Superphosphates containing significant amounts of these compounds—particularly $Ca(Al,Fe)H(PO_4)_2.4H_2O$—however, are not well suited for ammoniation. The complex phosphates have much less capacity for ammonia than monocalcium phosphate (1), and they react only sluggishly with ammonia. It is apparent that the use of sludge acids, settled sludges, or phosphate ores high in R_2O_3 is to be avoided in the preparation of concentrated superphosphates that are intended to be ammoniated

Literature Cited

(1) Ando, J., Lehr, J. R., "Ammoniation Reactions of Superphosphate," Division of Fertilizer Chemistry, 152nd Meeting, ACS, New York, September 1966.
(2) Cate, W. E., Huffman, E. O., Deming, M. E., *Soil Sci.* **88**, 130 (1959).
(3) Haseman, J. F., Lehr, J. R., Smith, J. P., *Soil Sci. Soc. Am. Proc.* **15**, 76 (1951).
(4) Lehr, J. R., Frazier, A. W., Smith, J. P., J. AGR. FOOD CHEM. **14**, 27 (1966).
(5) Lehr, J. R., Frazier, A. W., Smith, J. P., *Soil Sci. Soc. Am. Proc.* **28**, 38 (1964).
(6) Smith, J. P., Brown, W. E., *Am. Mineralogist* **44**, 138 (1959).
(7) Taylor, A. W., Gurney, E. L., *Soil Sci. Soc. Am. Proc.* **28**, 63 (1964).
(8) d'Yvoire, Ferdinand, *Bull. Soc. Chim. France* **1961**, p. 2283.