Tricalcium Phosphate and its Variation

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(Received September 24, 1957)

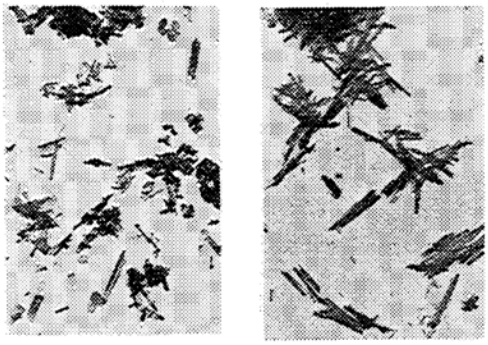
Tricalcium phosphate is important as the principal component of phosphate fertilizers. Literature on this substance is voluminous but often contradictory. For example, the inversion point from β to α modification was reported by many investigators as 1100°C[1], 1150°C[2], 1180°C[3], 1350°C[4] or 1400°C[5] and also the solubility of both modifications was reported variously. It seems that the contradiction was caused by the effects of a small amount of impurities which vary the properties of the phosphate considerably, and also by admixture of hydroxy apatite or pyrophosphate.

In the present work, the properties of tricalcium phosphate and the effect of other ingredients upon the structure and solubility of the phosphate were investigated in order to clarify the nature of fused and calcined phosphate fertilizers consisting mainly of tricalcium phosphate.

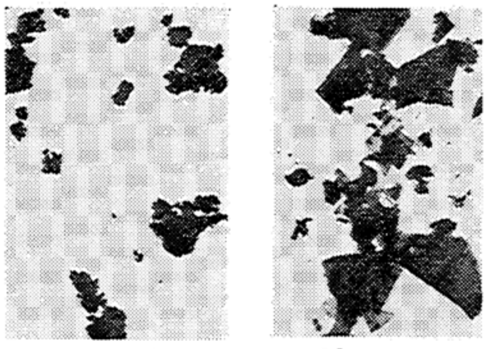
Experimental and Results

(I) Precipitated Tricalcium Phosphate —Tricalcium phosphate and hydroxy apatite were prepared in aqueous solution with sodium or ammonium phosphate and calcium nitrate or chloride under various conditions as indicated in Table I.

Some of the samples (SS-1, SA-2, etc.) were prepared by slow addition of the reagents with continuous agitation in order to obtain crystalline products, pH of the solution being adjusted by adding diluted ammonia from a capillary tube all



SS-2 (×6,000) HSA-1 (6,000)



QS-1 (×2,400) SS-3 (×2,400)

Photographs by Electron Microscope

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1) Britske, E. V. and V. K. Veselovskii, *Izvest. Akad. Nauk. S.S.S.R, Otdel. Tekh. Nauk*, No. 4, 479-88 (1937).

2) A. O. McIntosh and W. L. Jablonski, *Anal. Chem.*, **28**, 1424-27 (1956).

3) M. A. Bredig, H. H. Franck and H. Z. Fülder, *Elektro. Chem.*, **38**, 158-64 (1932).

4) W. F. Bale, J. F. Bonner, H. C. Hodge, H. Adler, A. R. Wreath and R. Bell, *Ind. Eng. Chem., Anal. Ed.*, **19**, 491-5 (1945).

5) F. Körder and G. Trömel, *Arch. Eisenhüttenw.*, **7**, 7-20 (1933).

TABLE I

CONDITIONS OF PREPARATION AND MOLE. RATIOS OF THE PRODUCTS

Sample	Reagent	Temp. (°C)	pH	Time of Adding	CaO/P_2O_5 Added	Mole. Ratios Products
SS-1	$Na_2HPO_4+CaCl_2$	65	7.2—8.0	3.5 hr.	3.00	3.08
SS-2	〃	60	6.8—7.6	〃	〃	2.95
SS-3	〃	50	6.2—6.8	〃	〃	2.69
SS-4	〃	65	〃	〃	〃	2.84
HSS	$CaCl_2+Na_2HPO_4$	70	7.6—8.2	〃	3.33	3.22
SA-2	$(NH_4)_2HPO_4+Ca(NO_3)_2$	65	7.0—7.6	2.5 hr.	3.00	3.04
SA-3	〃	60	〃	〃	〃	2.98
SA-4	〃	〃	6.8—7.4	〃	〃	2.95
SA-6	〃	45	7.4—7.8	〃	〃	2.91
SA-7	〃	25	〃	〃	〃	2.90
HSA-1	$Ca(NO_3)_2+(NH_4)_2HPO_4$	70	8.0—8.6	〃	3.33	3.33
HSA-2	〃	65	8.0—8.4	〃	〃	3.25
QS-1	$Ca(NO_3)_2+(NH_4)_2HPO_4$	20	10	5 sec.	3.00	3.11
QA-2	〃	25	8.2	〃	〃	2.87
QA-3	〃	〃	9.0	〃	〃	2.97
PQA-1	〃	〃	8.9	〃	〃	2.95
PQA-2	〃	〃	9.2	〃	〃	2.96

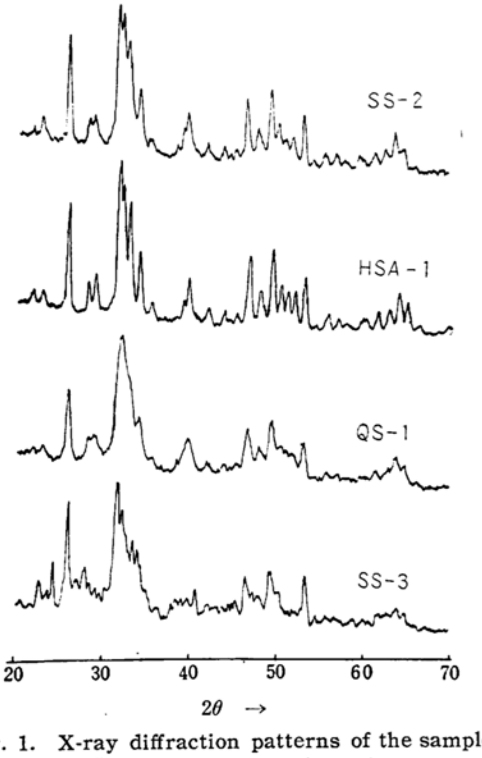

Fig. 1. X-ray diffraction patterns of the samples by Geiger-counter spectrometer. (Cu K_α, Ni Filter)

the while. Others (QS-1, QA-2 etc.) were prepared by quick addition of the reagents in order to obtain colloidal products. In this case, ammonia was added previously to the phosphate solution to adjust pH of the solution after the reaction. The amount of products, after being filtered, washed with water and then dried at 90°C, was 10—15 g., and the amount of the total solution was 1.5—2 liters for each preparation. These products were tested by electron microscope, X-ray diffraction and chemical analysis as shown in the Photographs, Fig. 1, and Table I.

Structure of both samples, SS-2 and QS-1, CaO/P_2O_5 ratio of which are 2.97 and 3.11 respectively, is the same as that of hydroxy apatite HSA-1 with the ratio 3.33, though the state of crystallization differs. Sample SS-3 with the ratio 2.69 consists of hydroxy apatite and dicalcium phosphate; the latter forms larger, thin crystals as shown in the photograph. These results confirm the modern view that tricalcium phosphate hydrate with a definite structure may not be formed but hydroxy apatite with excessive phosphoric acid may be formed.

(II) Variation by Heating—This precipitated apatite contains about 5% zeolitic water which is gradually evaporated by heating under 700°C. Then the hydroxy apatite with excessive phosphoric acid varies to form β-tricalcium phosphate between 700—800°C (Figs. 2 and 3) and solubility of the phosphate increases (Figs. 4 and 5). However, if the CaO/P_2O_5 ratio of the phosphate is slightly more than 3.0, a considerable amount of hydroxy apatite remains above 800°C, which gradually loses water of crystallization (OH) above 1100°C but scarcely ever decomposes even at 1450°C in air. Above 1500°C it is almost decomposed to form α-tricalcium phosphate

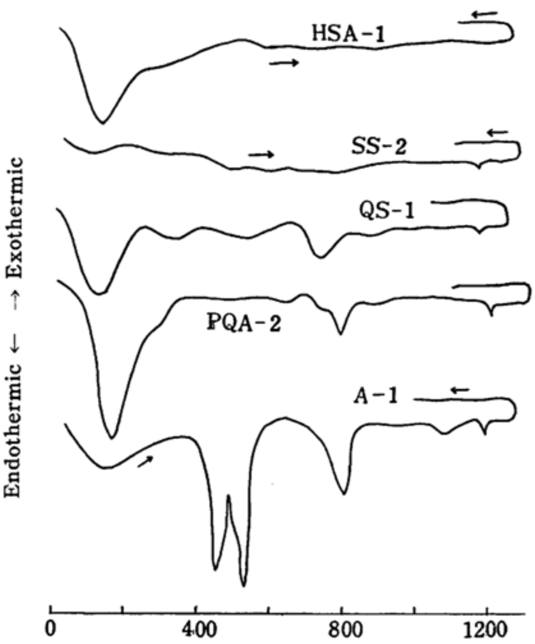

Fig. 2. Differential thermal analysis of phosphates.

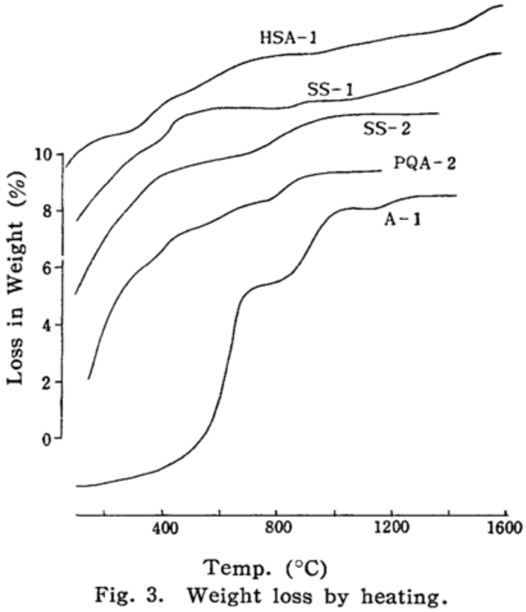

Fig. 3. Weight loss by heating.

and tetracalcium phosphate which are both soluble in citric acid. Calcined samples with CaO/P_2O_5 ratio less than 3.0 is mixed with pyrophosphate.

Sample A-1, prepared by adding phosphoric acid to refined lime by the ratio of 3 mol. CaO to 1 mol. P_2O_5, consists mainly of γ-pyrophosphate at 700°C, the ratio varies above 800°C on reaction with lime to form β-tricalcium phosphate (Figs. 2, 3, and 4). Then β-tricalcium phosphate thus formed inverts to α modification at 1180°C by endothermic reaction (Fig. 2). This inversion point coincides exactly with that described by Bredig[3]. α modification thus formed inverts to β modification slowly, by more than several hours heating at 1100°C. This α→β inversion is somewhat promoted by the presence of a slight excess of P_2O_5.

On the other hand, β-tricalcium phosphate prepared with samples of Table I inverts to α modification not exactly at 1180°C but between 1160 and 1200°C, and moreover, inverts from α to β modification easily by slow cooling. It seems that these were caused by a small amount of impurity such as Na_2O or MgO derived from the reagents.

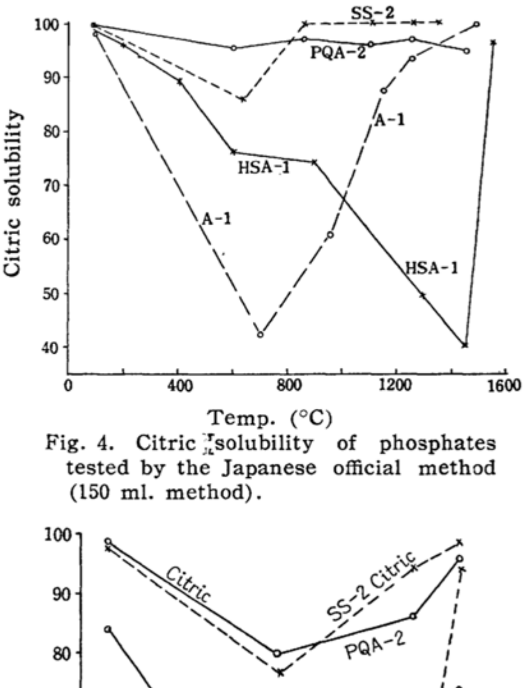

Fig. 4. Citric solubility of phosphates tested by the Japanese official method (150 ml. method).

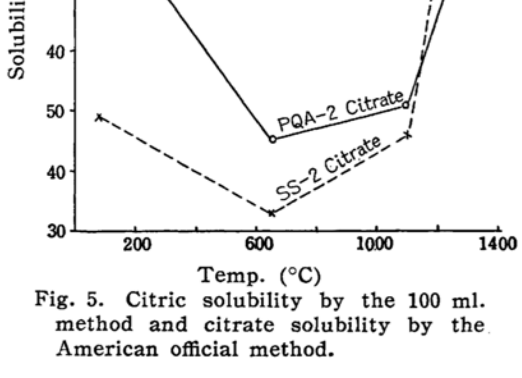

Fig. 5. Citric solubility by the 100 ml. method and citrate solubility by the American official method.

TABLE II

TYPE OF MODIFICATIONS OF TRICALCIUM PHOSPHATE COOLED QUICKLY IN AIR FROM VARIOUS TEMPERATURES (°C)

($C=CaO$, $P=P_2O_5$, $A=Al_2O_3$, $F=Fe_2O_3$, $M=MgO$, $B=BaO$, $N=Na_2O$, $S=SiO_2$)

Samples	Chemical Composition (Mol. Ratios)	Type of Modifications			
		1100	1250	1350	1450
a	3C·P	β	α	α	α
b	3C·P·0.1A	β	β	β	$\alpha+\beta$
c	3C·P·0.1F	β	β	$\alpha+\beta$	α
d	2.9C·0.1M·P	β	β	β	β
e	2.7C·0.3M·P	β	β	β	β
f	2.9C·0.1B·P	$\alpha+\beta$	α	α	α
g	2.9C·0.1N·P	β	$\beta+\alpha$	$\beta+\alpha$	$\beta+\alpha$
h	2.8C·0.2N·P·0.1A	—	β	$\alpha+\beta$	—
i	2.7C·0.2N·0.1M·P	β	β	β	—
j	2.8C·0.2B·P·0.1A	—	$\alpha+\beta$	α	—
k	2.7C·0.2B·0.1M·P	β	$\beta+\alpha$	$\alpha+\beta$	—
l	a+0.35(2C·S)	—	—	α	α
m	b+0.35(2C·S)	—	—	α	—
n	d+0.35(2C.S)	—	—	$\alpha+\beta$	—

(III) Solubility of Phosphates—Solubility was tested by the Japanese official method (150 ml. method), [150 ml. of 2% citric acid for 1 g. of sample ground to pass 100 meshes/inch sieve; shaking for 1 hour (Fig. 4)], by an other method (100 ml. method) which is being practised in other countries, [100 ml. of 2% citric acid for 1 g. of sample ; shaking for half an hour], and also by the American official method with neutral ammonium citrate (Fig. 5).

It was found that hydroxy apatite could be dissolved in 2% citric acid to an extent of 1.1 g./100 ml. ultimately at room temperature, and tricalcium phosphate could be dissolved furthermore, so that citric solubility of these compounds was a matter of velocity of dissolution which relates to the grain size, the structure and the state of crystallization of the phosphates.

Precipitated hydroxy apatite HSA-1 is almost soluble in citric acid by the 100 ml. method because of its fineness, though citrate solubility is about 50%. Other samples with less lime are more soluble than the sample HSA-1.

Solubility of these phosphates decreases gradually by heating below 700°C. By this heating zeolitic water contained in the apatite lattice is lost and the distance between the lattice planes becomes slightly smaller.

Contrary to many other reports, it was found that β-tricalcium phosphate was fairly soluble in citric acid. Citric solubility of the phosphate with moderate grain size (mostly 120～40 μ) is 90～95% by the 150 ml. method and 80～90% by the 100 ml. method, and citrate solubility is about 40～50%. The solubility decreases when the phosphate contains a small amount of impurity as described below.

α-Tricalcium phosphate is completely soluble by the 150 ml. method and 95～100% soluble by the 100 ml. method. Though usually a small amount of insoluble residue remains in testing the citric solubility of the phosphate calcined at 1200～1500°C, the residue is not tricalcium phosphate but hydroxy apatite or pyrophosphate or β-tricalcium phosphate stabilized by a small amount of impurities.

Citrate solubility of α-tricalcium phosphate is much higher than that of β-tricalcium phosphate, but it does not reach 90% when the grains of the sample are not fine enough to pass 170 meshes/inch sieve ($-88\ \mu$).

(IV) Crystalline Solutions with other Ingredients—Phosphate rocks usually contain small amounts of silica, alumina, iron oxide, and sometimes magnesia. Moreover, in the manufacture of phosphate fertilizers, other materials are added to the phosphate rocks. So, it is thought that tricalcium phosphate in fertilizers is a crystalline solution with other ingredients. In order to clarify the effect of these ingredients upon the structure and the solubility of tricalcium phosphate, many samples with various compositions (Table 2) were prepared with calcium oxalate, phosphoric acid, hydroxides of alumina, iron and magnesium, sodium and barium carbonate and colloidal silica, all of which were refined in the laboratory. These were first mixed like a paste, dried with frequent mixing, heated at 1000°C, ground to pass 100 meshes/inch sieve, and again heated in a platinum crucible for half an hour at various temperatures as indicated in Table II. Then the products, after being cooled quickly in air, were tested by X-ray diffraction and chemical analysis. Citric and citrate solubility were tested after the products were ground to pass 100 meshes/inch sieve again. Solubility of sample (a) in Table II calcined at 1100°C (β-tricalcium phosphate) was 93.2% by the 150 ml. method, 84.2% by the 100 ml. method, and 45.1% by the citrate method.

It was found that β-tricalcium phosphate was stabilized by the addition of small amounts of alumina, ferric oxide or magnesia. β-Tricalcium phosphate with alumina hardly ever inverts to α modification at 1250°C, moreover it is less soluble in citric acid and especially in citrate. At a higher temperature, α-modification is formed to some extent and the solubility becomes higher (Table II and Fig. 6).

The effect of ferric oxide to stabilize β modification diminishes at 1450°C. The effect of magnesia which substitutes for lime is most remarkable. Containing 0.1 mol. MgO, the distance between crystal planes of the β modification becomes apparently smaller, solubility decreases, and does not invert to α modification even at 1450°C.

On the contrary, it was found that barium, the larger cation, stabilizes α modification. Tricalcium phosphate with 0.1 mol. BaO (sample f) inverts from β to α modification at 1100°C. This temperature is 80°C lower than the inversion temperature of pure tricalcium phosphate.

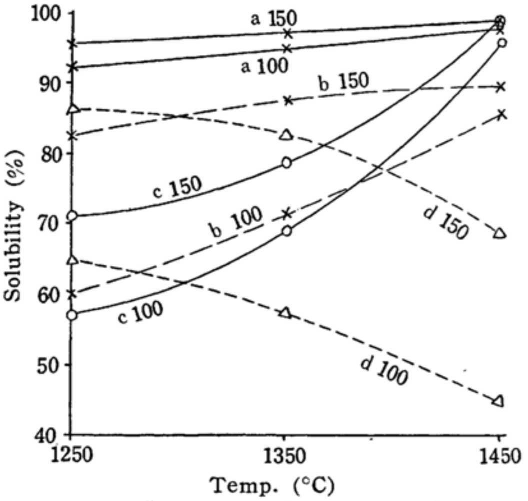

Fig. 6. Citric solubility of samples in Table II tested by 150 ml. and 100 ml. method.

Sodium oxide affects variously according to the ratio of substitution for lime. The inversion of tricalcium phosphate from α to β is so much quickened by replacing a small amount of Na_2O for CaO that α modification almost inverts to β modification even when quenched from a high temperature (Sample g). When more than 0.2 mol. of Na_2O to 1 mol. P_2O_5 is introduced into phosphate α-rhenanite type crystalline solution is formed.

By addition of small amounts of alumina, ferric oxide, magnesia, or silica, inversion of tricalcium phosphate from α to β is somewhat quickened.

Addition of 0.2 mol. Na_2O or BaO or 0.35 mol. $2CaO \cdot SiO_2$ to the tricalcium phosphate with alumina favors the formation of α modification (Samples h, j and m). Citric solubility of samples h, j and m calcined at 1350°C and air-quenched was 99.1%, 92.7%, and 98.5% respectively, by 150 ml. method showing considerable increase compared with the solubility of the sample b. The effect of magnesia to stabilize β modification is so intense that solubility of the phosphate with magnesia is hardly ever raised by adding these materials (Samples i, k and n).

Discussion

As is illustrated by the above results, magnesia reacts most remarkably to stabilize β modification of tricalcium phosphate and to depress the solubility. This explains why satisfactory results could not be obtained in the manufacture of calcined phosphate with a Swedish phosphate rock (with about 5% MgO)[6], and also why addition of serpentine to raw materials of calcined phosphate was unfavorable[7].

Alumina and iron oxide usually contained in phosphate rocks also react to prevent the formation of α-tricalcium phosphate. In calcined phosphate produced by calcining phosphate rock with silica in steam, the effect of alumina and iron oxide is not manifested very much, because excessive lime and silica react with

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[6] J. A. Hedvall, H. O. Gernandt and Y. Akesson, *Transactions of Chalmers Univ. of Tech.* Göteborg, Sweden, Nr. 100 (1950).

[7] S. Nagai and J. Ando, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **57**, 707 (1954).

these oxides to depress the effect. However, in calcined phosphate, produced by calcining phosphate rock with a small amount of phosphoric acid to promote defluorination, alumina and iron oxide affect remarkably to stabilize β modification, because excess of lime is combined with phosphoric acid to form tricalcium phosphate[8]. The phosphate obtained by such a method consists of β-tricalcium phosphate even when cooled quickly from 1350°C. The addition of a small amount of barium to the phosphate causes partial formation of α modification at 1300°C, but solubility of the phosphate is not easily raised because evaporation of fluorine in the phosphate is interrupted to some extent. Addition of 0.1 mol. Na_2O to 1 mol. P_2O_5 of the phosphate is unfavorable but more than 0.2 mol. of Na_2O favors the formation of soluble phosphate[8].

It is often said that tricalcium phosphate hydrate is formed in reverting superphosphate by adding ammonia or serpentine or by using other basic materials. However, as is illustrated by the above results, hydroxy apatite or fluor apatite must be formed instead of tricalcium phosphate. Under such conditions as in the reversion of superphosphate, the state of apatite thus formed is colloidal or crystalline. Such hydroxy apatite is almost entirely soluble in 2% citric acid and even fluor apatite can be dissolved in 2% citric acid to the extent of 0.5 g./100 cc.

Summary

Properties of tricalcium phosphate and effects of many other ingredients upon the structure and solubility of the phosphate were investigated. By the reaction of calcium salts with phosphates in aqueous solution, tricalcium phosphate hydrate with a definite structure is not formed but hydroxy apatite with an excess of phosphoric acid is formed, which varies to β-tricalcium phosphate by heating between 700—800°C. Contrary to many other reports, it was found that β-tricalcium phosphate was fairly soluble in citric acid. The solubility is reduced remarkably by a small amount of admixtures, especially of magnesia. Magnesia stabilizes the β modification and prevents β→α inversion of the phosphate. The effect of alumina and ferric oxide is similar but not so intense as magnesia. On the contrary, barium oxide stabilizes the α modification. Sodium oxide affects variously according to the ratio of substitution for lime. Constitution and solubility of phosphate fertilizers were discussed in relation to these results.

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[8] J. Ando, ibid., **60**, 542 (1957).