

PHOSPHATE AVAILABILITY

Fluoride-Induced Phosphate Reversion in Fertilizer Mixtures

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Fluoride-induced phosphate reversion to unavailable forms in stored mixtures of normal superphosphate with thermally defluorinated phosphate rock, as well as with other non-phosphatic basic materials, appears to be attributable to the presence of water-soluble monocalcium fluorophosphate in both normal and concentrated superphosphates. The active component of thermally defluorinated phosphate rocks reacting with the monocalcium fluorophosphate appears to be calcium orthosilicate. Similar basic materials, such as calcium carbonate, may cause phosphate reversion to an unavailable form during superphosphate manufacture at high temperature. Phosphate reversion may also occur when superphosphate is overammoniated. High temperatures favor the reactions yielding citrate-insoluble fluorophosphates, Ca_2FPO_4 and $\text{Ca}_5\text{F(PO}_4)_3$.

REVERSION of available phosphate to unavailable forms in stored mixtures of normal superphosphate, calcined phosphate rock, and ammonium sulfate was first reported by Beeson and Jacob (7) in 1938. Later, MacIntire and Hardin (11) showed that reversion did not occur in stored mixtures of fluoride-free superphosphate and calcined rock, and suggested that the reversion of phosphate in fluorine-bearing mixtures might be attributable to a reaction between calcium fluoride and tricalcium phosphate, yielding fluorapatite. They also claimed that TVA fused phosphate rock, because of its physical characteristics, was compatible with normal superphosphate (12). This led to a number of experiments designed to determine the cause of phosphate reversion to unavailable forms in various fertilizer mixtures (3, 13). Previously Jacob *et al.* (9) had investigated the nature of citrate-insoluble residues of fertilizer mixtures containing ammoniated superphosphate. In none of these studies was correlation between fluorine and phosphorus good enough to support the conclusion that the reverted phosphate was all combined as fluorapatite. The problem, however, was generally complicated by the presence of unknown quantities of undecomposed phosphate rock, so that it was not easy to differentiate between citrate-insoluble residues of the original components of fertilizer mixtures and reverted phosphate that developed after mixing.

Earlier Experiments

In an experiment designed to determine the relative reactivities of three different types of thermally defluorinated

rock phosphates, the materials listed in Table I were reduced to comparable particle sizes, mixed with a commercially produced normal superphosphate, and stored under conditions similar to those described by Beeson and Jacob (7). Finely ground quartz flour was added to the mixtures made with TVA fused rock and with calcined phosphate rock to reduce the available P_2O_5 contents of these mixtures to the levels of available P_2O_5 in the mixtures made with the Coronet sintered rock. Samples withdrawn after 28, 56, and 84 days of storage at 30° C. and 79.2% relative humidity were analyzed for total, water-soluble, and citrate-insoluble P_2O_5 . Water-soluble and available P_2O_5 , expressed as percentages of the total P_2O_5 , are listed in Table II. From these data, the development of citrate-insoluble P_2O_5 , expressed as percentages of the available P_2O_5 in the original components of the mixtures, were computed.

Mixtures containing 5 and 20% of defluorinated rocks showed considerable conversion of water-soluble to citrate-soluble phosphate, but relatively little development of citrate-insoluble phosphate. For this reason, these data have been omitted from Table II.

The results of these tests apparently

revealed nothing more than the fact that fused rock, like other types of defluorinated rock, reacted with a fluorine-bearing superphosphate to produce a form of citrate-insoluble phosphate and that, under like conditions of particle size, temperature, and relative humidity, the extent of phosphate reversion was about the same for all three types. Therefore, these results, obtained in 1945, have not heretofore been submitted for publication. Later, it was learned that the fluorine evidently was combined as fluosilicate in phosphate rock (5), and previously published data on the composition of phosphate rock have been re-examined in the light of this new postulate (6, 7). In continuation of these studies, these old data and other published data are being critically examined for any light they might throw on the chemistry of fluorine-bearing compounds in phosphate fertilizers.

As stated above, limited amounts of fused, sintered, and calcined phosphate rocks may all be admixed with normal fluorine-bearing superphosphate without causing phosphate reversion. The proportions that may be added will vary, depending upon the type of defluorinated rock notwithstanding the fact that the

Table I. Analyses of Reactant Materials

Sample No.	Reactant	P_2O_5 , %		Fluorine, %
		Total	Available	
2261	Normal superphosphate	20.8	20.7 ^a	1.46
2219	TVA fused rock	29.6	22.1	0.03
2340	Coronet sintered rock	20.4	18.3	(?)
1374	Calcined phosphate rock	35.2	31.3	0.13

^a Including 18.0% water-soluble P_2O_5 .

¹ Retired.

several series were all adjusted to comparable levels of available phosphate. These differences, indicative of a reactive component other than alpha tricalcium phosphate, are illustrated by the data of Table III listing constants derived for the general equation,

$$y = a + bx \quad (1)$$

where x represents the percentage of defluorinated rocks (adjusted basis), and y , the percentage of phosphate reversion in superphosphate mixtures during 84 days of storage, calculated from the data of Table II.

The values for x at $y_1 = 0$ represent the maximum proportions of defluorinated rock that may be admixed with the superphosphate without causing phosphate reversion, while the value of x at the transition point, $y_1 = y_2$, represents the proportion of defluorinated rock (adjusted basis) in mixtures yielding the maximum of phosphate reversion during 84 days of storage.

Since one of the factors limiting the reversion of phosphate to unavailable forms is a reactive form of fluorine in the superphosphate (11), and calcium fluoride in synthetic mixtures has been shown to be relatively inactive (8, 11, 13), it is logical to assume that the phosphate and fluorine are combined in some form of fluorophosphate. Accordingly, the data of Tables II and III would pertain only to a superphosphate having the composition of sample No. 2261, and to defluorinated rocks having the compositions of sample Nos. 1374, 2219, and 2340, listed in Table I.

On the other hand, the reversion of phosphate is limited by a reactive component of the defluorinated phosphate rocks. A component other than tricalcium phosphate is indicated by the fact that phosphate reversion also occurs in mixtures that do not contain any tricalcium phosphate and by differences in the relative proportions of defluorinated rock at the above transition points, notwithstanding the fact that the series containing the several types of defluorinated rock as all adjusted to comparable levels of available phosphate. The only other likely constituent common to all three types of defluorinated rock, but occurring in different proportions to tricalcium phosphate, would be calcium silicate, a basic constituent that would react with the acidic components of superphosphate. The more likely form of this component in thermally defluorinated phosphate rock would be calcium orthosilicate.

Beeson and Jacob (7) also noted that ammonia nitrogen was lost from stored mixtures containing calcined phosphate and ammonium sulfate. Similar mixtures of ammonium sulfate and ammonium nitrate with TVA fused rock and Coronet sintered rock also lost ammonia nitrogen, but in different proportions

Table II. Analyses of Normal Superphosphate-Thermally Defluorinated Phosphate Rock Mixtures Stored at 30° C. and 79.2% Relative Humidity

Defluorinated Rock % of Mixture ^a	Storage Period, Days							
	0		28		56		84	
	W.-S.	Avail.	W.-S.	Avail.	W.-S.	Avail.	W.-S.	Avail.
	TVA FUSED ROCK ^b							
40	48.5	88.6	36.2	83.2	33.2	81.3	29.3	80.2
60	31.2	83.5	13.5	72.8	10.4	70.6	8.9	68.5
80	15.1	78.8	5.4	75.9	5.6	73.7	5.5	72.4
95	3.7	75.5	2.5	78.9	2.1	78.4	1.9	76.3
	CORONET SINTERED ROCK							
40	52.4	95.6	46.7	92.4	42.5	90.9	42.4	89.6
60	35.0	93.6	26.8	82.8	22.6	81.1	20.7	79.0
80	17.6	91.6	11.2	83.5	8.5	81.7	8.3	80.0
95	4.4	90.0	3.9	88.5	3.8	86.8	4.3	84.3
	CALCINED ROCK ^c							
40	54.5	95.7	49.9	94.8	45.9	93.5	40.7	92.7
60	37.2	93.6	30.7	86.0	25.3	82.7	25.3	79.7
80	19.1	91.4	16.6	84.5	14.8	82.1	12.2	79.6
95	4.9	89.6	5.8	89.0	5.0	87.6	3.7	86.2

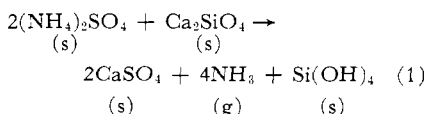
^a Adjusted weight basis. ^b Equal to 82.8% of adjusted weight. ^c Equal to 52.4% of adjusted weight.

Table III. Constants Derived for General Equation, $y = a + bx^c$ for Phosphate Reversion and Estimated Compositions at Transition Points of Normal Superphosphate-Thermally Defluorinated Phosphate Rock Mixtures Stored 84 Days at 30° C. and 79% R.H.

Type of Defluorinated Phosphate Rock	Derived Constants				Transition Points		
	Y_1		Y_2		$Y_1 = 0$	$Y_1 = Y_2$	
	a_1	b_1	a_2	b_2	% x^b	% x	% y^c
Fused	7.5	0.425	56.7	-0.607	17.7	62.2	18.9
Sintered	-12.3	0.465	46.9	-0.427	25.9	67.4	18.1
Calcined	-20.5	0.590	61.5	-0.607	34.8	69.5	19.3

^a Where x = percentage of defluorinated rock (adjusted basis) in mixture and y = percentage of available P_2O_5 reverted to unavailable form. ^b Percentage of defluorinated rock in mixture at point of incipient reversion. ^c Maximum percentage of reverted phosphate.

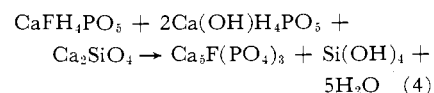
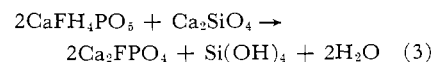
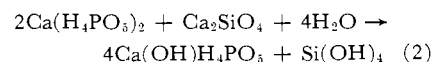
to the amounts of tricalcium phosphate present. At the end of 84 days of storage, ammonia losses amounted to 1.06 moles of NH_3 per mole of available P_2O_5 in fused rock, and to 0.60 mole of NH_3 per mole of available P_2O_5 in mixtures of sintered rock and ammonium sulfate. Losses from the ammonium nitrate mixtures were somewhat less, but in about the same relative proportions for the two defluorinated rocks. Assuming chemical reaction in these mixtures in accordance with the equation,



then the ammonia losses from these mixtures may be taken as a measure of the relative amounts of active calcium silicate to tricalcium phosphate in these two types of defluorinated rock.

The fact that not all of the water-soluble forms of phosphate were completely consumed in any of the several mixtures listed in Table II suggests that, in addition to monocalcium phosphate, there is a combination of water-soluble

phosphate and fluorine, such as monocalcium fluorophosphate, that might react with calcium silicate in accordance with the following series of reactions (6).



The complex, $CaFH_2PO_3$, is the fluorine analog of monocalcium chlorophosphate described by Fox and Clark (4). As such, it might reasonably be expected to enter into a similar series of reactions, except that the physical characteristics of the reaction products would be modified in accordance with the difference between the solubilities of calcium chloride and calcium fluoride. Since the latter is one of the least soluble salts, one would expect that its double salt with monocalcium phosphate, $CaFH_2PO_3$, would exhibit only a limited degree of solubility in aqueous solutions.

Di- and tricalcium fluorophosphates would be even less soluble.

Chlorapatite may be prepared by heating to fusion at 754° C. a stoichiometric mixture of chlorospodiosite and potassium chloride, cooling to crystallize the products, and extracting the water-soluble double salt, $\text{CaCl}_2 \cdot \text{KCl}$, leaving the crystalline apatite, $\text{Ca}_5\text{Cl}(\text{PO}_4)_3$, as the water-insoluble residue. Jacob *et al.* (10), in a study of factors affecting the determination of available phosphorus in furnace-processed phosphates, found that the citrate-insoluble residues of a nonacid phosphate, made by fusing phosphate rock with potassium sulfate, consisted of a complex having the composition of a mixture of fluorospodiosite and fluorapatite in which the spodiosite predominated as shown in Figure 1.

Among the various basic reactants that might cause phosphate reversion when mixed with superphosphate are calcium carbonate and calcium silicate—components of phosphate rock itself. This is illustrated by the data of Bridger *et al.* (2) on the influence of temperature and degree of acidulation on rock phosphate conversion, and on fluorine volatilization from concentrated superphosphate made with Tennessee brown phosphate rock (46.0% CaO , 32.7% P_2O_5 , 3.5% F) and furnace process phosphoric acid.

Figure 2 shows that fluorine losses from underacidulated mixtures made with cold acid were almost negligible, regardless of den temperature, whereas similar mixtures made with hot acid showed increasing volatilization with increasing degree of acidulation. In acidulates made with hot acid cured in a hot den, the evolution of fluorine is substantially a linear function of the degree of acidulation that may be expressed by the equation,

$$y = 1.32x - 74.1 \quad (5)$$

where x and y represent percentage degrees of rock acidulation and fluorine volatilization, respectively. By applying the limits to this equation, it was found that fluorine evolution starts at about 56% acidulation and is complete at about 131% acidulation. Fluosilicic acid released by reaction at less than 55% acidulation is neutralized by reaction with limestone before it reaches a concentration where dissociation of the acid starts (5). In overacidulated mixtures at high temperature, the fluoride ion is replaced by the less volatile phosphate ion and the reverted phosphate is reconverted to available forms as shown in Figure 2.

The apparent phosphate conversion in acidulates made with hot acid was substantially less than in mixtures made with cold acid, regardless of den temperature. Also, underacidulated mixtures cured in hot dens showed lower

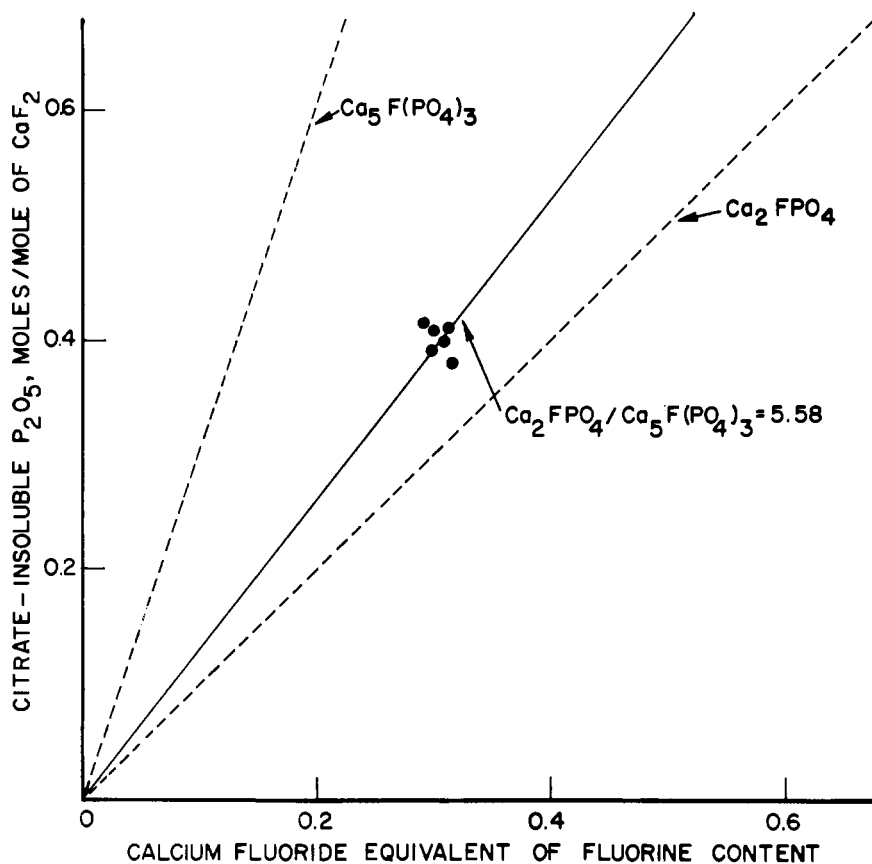
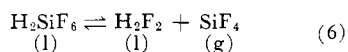


Figure 1. Correlation of the citrate-insoluble phosphate and calcium fluoride equivalent of fluorine contents of nonacid phosphate

[Data by Jacob *et al.* (9)]

conversions than similar mixtures cured in cold dens, regardless of the temperature of the reagent acid. In overacidulated mixtures, the reverse is true. Acidulates cured in hot dens yielded higher percentages of available phosphate as well as greater fluorine evolution with increasing degrees of acidulation.

The conversion of rock phosphate to available forms appeared to be less in hot- than in cold-acid mixtures. On the other hand, the extent of the reaction, as measured by the evolution of fluorine, is greater. Therefore, the apparent reduction in phosphate conversion to available forms in hot-acid mixtures may be the result of phosphate reversion to unavailable forms. This would be in line with a higher degree of dissociation of fluosilicic acid in solution in accordance with the equilibrium equation,



and the secondary reaction of the resulting hydrofluoric acid in solution (5) yielding monocalcium fluorophosphate and its subsequent reaction with calcium carbonate to form fluorospodiosite.

The rock used in this series of experiments contained 3.562 moles of CaO , and fluorine equivalent to 0.133 mole of SiF_6 per mole of P_2O_5 . At 100% acidula-

tion, fluorine loss from hot-acid, hot-den acidulates, according to Equation 5, would be equal to $1.326 \times 100 - 74.1 = 58.5\%$ equivalent to $0.133 \times 0.585/0.667 = 0.117$ gram-mole of SiF_4 per mole of P_2O_5 in the rock. Fluorine retained in the acidulate would be equal to $0.415 \times 3 \times 0.133 = 0.165$ mole of $\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{CaF}_2$ per mole of P_2O_5 in the rock. The apparent rock phosphate conversion amounts to 83.5% or the possible extent of phosphate reversion amounted to 16.5% or 0.165 mole of $\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{CaF}_2$ per mole of P_2O_5 in the rock. As the degree of acidulation increases, the reverted phosphate is again converted to available form by reaction with excess reagent acid. This reversion is also favored by high temperature.

The above review of experimental data bearing on fluoride-induced phosphate reversion indicates that phosphate reversion occurs whenever a fluorine-bearing superphosphate mixed with basic materials in proportions that would yield calcium phosphate more basic than dicalcium phosphate is heated or stored at normal temperatures for long periods of time; that the reactive component responsible for the reversion appears to be a soluble form of calcium fluorophosphate; that the reverted phos-

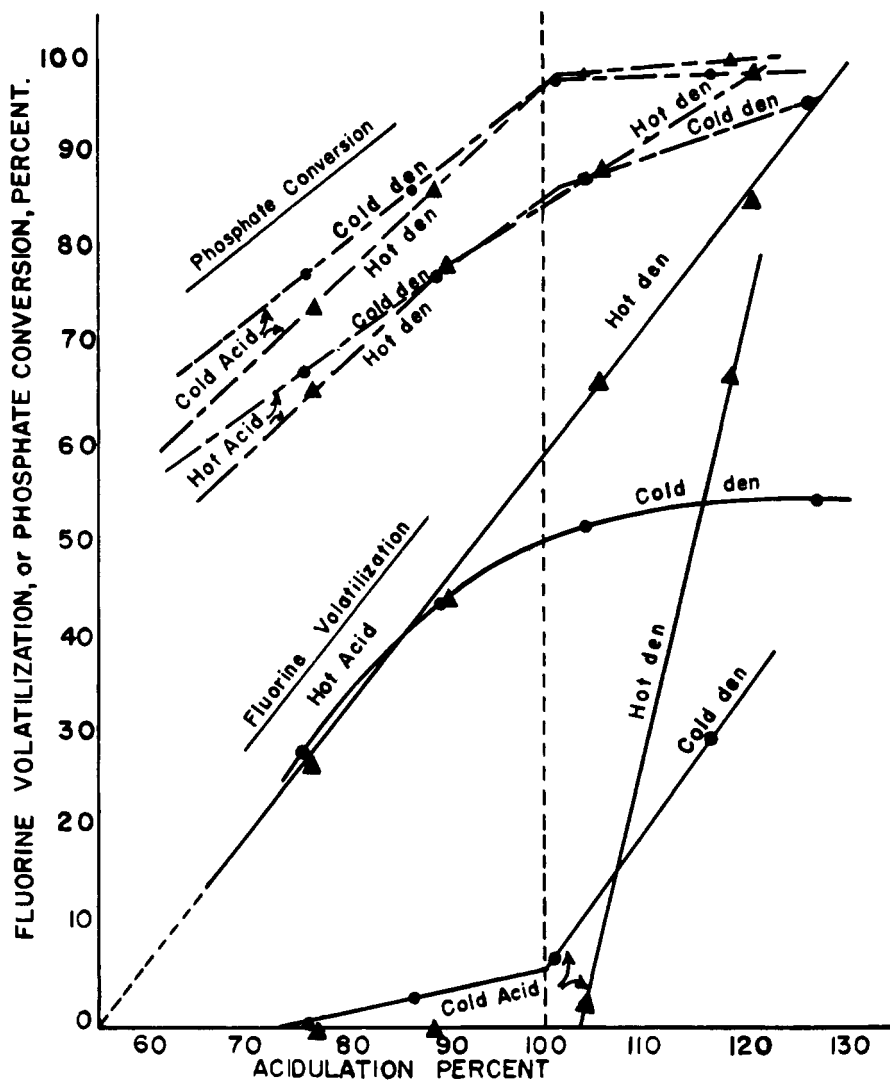


Figure 2. Influence of temperature and degree of acidulation on rock phosphate conversion and fluorine volatilization from concentrated superphosphate made with furnace process acid

[Data from Bridges *et al.*, (2)]

phosphate may be a mixture of fluorapatite and fluorspodiosite; and that the evolution of fluorine as well as the reversion of phosphate may be favored by high temperature during the acidulation of phosphate rock (2).

Recent Experimental Investigations

Several new fluorophosphate compounds postulated in the above interpretation need confirmation by additional experimentation directed toward their isolation and identification. To help meet this need, concentrated and normal superphosphates of various degrees of acidulation were prepared from Florida land pebble phosphate rock and from Kola apatite with 72% H_3PO_4 and 50% H_2SO_4 solutions, and cured at room temperature. The analyses of these products are listed in Tables IV and V.

Distribution of Fluorine Between Water-Soluble and Water-Insoluble Fractions of Superphosphate. The superphosphates made from Florida phosphate rock were leached counter-currently with water in the proportions of three 10-ml. portions of water to 5-gram samples of concentrated, and 10-gram samples of normal superphosphate on medium-fritted, glass filters. The water-insoluble residues of 10 replications were dried at 120° C., combined, and thoroughly mixed before being analyzed for fluorine. From the results of the analyses, the distribution of fluorine between the water-soluble and the water-insoluble fractions of the superphosphate were calculated as shown in Table VI. Estimates of the soluble fluorine contents ranged from 0.76% to 0.92% F in the water-soluble fractions of concentrated, and from 1.15% to 1.86% F in the soluble fraction of normal superphosphate.

Table IV. Analyses of Concentrated Superphosphates

Mixture	Acidulation, % ^a	CaO, %	P ₂ O ₅ , %	F, %	F in Super, % ^b
MADE WITH FLORIDA LAND PEBBLE ROCK ^c					
1	94.4	22.9	52.2	1.88	94.9
2	97.7	22.5	53.1	1.82	94.8
3	101.4	21.7	53.6	1.72	93.0
4	108.6	20.4	52.8	1.59	91.4
5	115.7	18.9	52.2	1.36	85.5
6	122.9	17.5	51.3	1.22	89.7
MADE WITH KOLA APATITE ^d					
13	99.8	22.2	53.9	0.91	63.6
14	103.6	21.6	53.8	0.90	65.2
15	107.4	20.8	53.2	0.81	60.4
16	115.0	19.6	53.2	0.77	61.1
17	122.2	18.3	56.1	0.72	61.0
18	129.9	17.3	54.1	0.68	60.7

^a Based on a $P_2O_5/(CaO-SiF_6) = 1.0$ mole/mole.

^b Percent of total fluorine in phosphate rock.

^c 49.2% CaO, 35.3% P₂O₅, 4.21% F.

^d 50.2% CaO, 38.8% P₂O₅, 3.30% F.

Table V. Analyses of Normal Superphosphate

Mixture No.	Acidulation, % ^a	CaO, %	P ₂ O ₅ , %	SO ₃ , %	F, % ^b
MADE WITH FLORIDA LAND PEBBLE ROCK ^c					
7	93.1	30.1	20.9	25.8	2.48
8	96.5	29.5	20.0	26.9	2.44
9	100.0	29.0	20.1	27.7	2.24
10	107.0	27.7	19.3	28.8	2.04
11	114.1	26.7	19.1	29.9	1.80
12	121.1	25.3	17.6	31.3	1.63
MADE WITH KOLA APATITE ^d					
19	94.1	30.1	23.1	26.4	1.41
20	102.0	28.4	22.1	27.1	1.21
21	109.6	27.3	20.7	28.6	1.18
22	117.3	25.9	19.6	30.6	0.99
23	125.3	26.9	20.3	34.4	0.98
24	132.8	23.8	19.2	36.2	0.54

^a Based on a $(P_2O_5 + SO_3)/(CaO - SiF_6) = 1.0$ mole/mole.

^b Fluorine recoveries ranged from 85.5 to 94.9% in superphosphates made with Florida rock and from 60.4 to 65.2% in superphosphates made with Kola apatite.

^c Footnote c, Table IV.

^d Footnote d, Table IV.

Table VI. Distribution of Fluorine between Water-Soluble and Water-Insoluble Fractions of Superphosphate Made with Florida Land Pebble Phosphate Rock

Mixture No.	Water-Soluble Fraction		Water-Insoluble Residue		
	% of sample	% F ^a	% of sample	% F ^b	F, % of total ^c
CONCENTRATED SUPERPHOSPHATE					
1	80.8	0.92	19.2	5.87	60.6
2	86.6	0.76	13.4	8.69	63.7
3	86.0	0.80	14.0	7.36	59.9
4	90.1	0.89	9.9	8.02	49.7
5	93.4	0.77	6.6	9.66	47.1
6	92.7	0.83	7.3	6.22	36.9
NORMAL SUPERPHOSPHATE					
7	33.7	1.27	66.3	3.10	82.7
8	33.9	1.15	66.1	3.10	84.0
9	34.9	1.86	65.1	2.44	71.0
10	40.9	1.76	59.1	2.23	64.7
11	43.8	1.80	56.2	1.80	56.1
12	41.0	1.80	59.0	1.51	54.6

^a % F in water-soluble fraction of superphosphate.
^b % F in water-insoluble residue of superphosphate.
^c % of total F in superphosphate, column 5, Table IV.

Interference of Silica with the Aqueous Extraction of Superphosphate. The deposition of hydrous silica resulting from the hydrolysis of fluosilicate salts interfered with the filtration process to such an extent that the superphosphates made with Kola apatite could not be extracted with water and filtered in the same manner as those made with the Florida phosphate rock. Successive extractions made by pulping equal parts of water and superphosphate and centrifuging the mixture at high speed yielded solutions containing soluble components as shown in Table VII. These data all show the presence of soluble fluorophosphates in both concentrated and normal superphosphates. The deposition of hydrous silica as a concomitant phenomenon with fluorine extraction demonstrates that much of the fluoride in solution results from hydrolysis of the fluosilicate ion in accordance with the equilibrium equation,

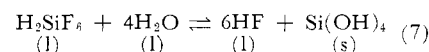


Table VII. Concentrations of Water-Soluble Components in Aqueous Extracts of Superphosphate Made with Kola Apatite

Mixture No.	First Extraction ^a				Second Extraction ^b			
	CaO, %	P ₂ O ₅ , %	F, %	SO ₃ , %	CaO, %	P ₂ O ₅ , %	F, %	SO ₃ , %
CONCENTRATED SUPERPHOSPHATE								
13	7.02	20.9	0.69	...	3.97	10.0	0.13	...
14	6.84	20.2	0.82	...	4.81	13.0	0.16	...
15	7.07	20.8	0.19	...	4.84	14.4	0.03	...
16	6.89	21.6	0.28	...	4.43	14.0	0.03	...
NORMAL SUPERPHOSPHATE								
19	5.08	18.6	0.67	0.28	1.25	4.25	0.09	0.18
20	3.74	14.3	0.60	0.18	1.23	4.00	0.10	0.18
21	2.53	11.3	0.59	0.17	1.14	4.66	0.22	0.16
22	2.35	15.1	0.68	0.77	0.24	0.95	0.09	0.06
23	1.77	13.4	0.17	0.92	0.32	1.82	0.06	0.14

^a Equal parts by weight of water and superphosphate. ^b Water-insoluble residue from first extraction plus water equal to weight of that used in first extraction.

These observations are in line with the conclusions previously reached that the fluorine is combined as fluosilicate in phosphate rock (5) and that the Kola apatite is an end product of the metamorphic process by which coral limestone is transformed into a crystalline phosphate (7).

Thermal Effects on Fluorine Distribution. Samples of superphosphate made from Florida rock were preheated 1 hour at 125° C. and analyzed for fluorine. A similar series was preheated and then extracted with water as previously described. The effects of this heat treatment on the distribution of fluorine between the volatile, the soluble, and the water-insoluble fractions of superphosphates made with Florida rock are shown by the data of Table VIII.

Table VIII. Effect of Heating Superphosphate 1 Hour at 125° C. on Fluorine Distribution

Mixture No.	Volatile Fraction		Soluble Fraction		Insoluble Fraction	
	Weight, %	Fluorine, % ^a	Weight, %	Fluorine, % ^a	Weight, %	Fluorine, % ^a
CONCENTRATED SUPERPHOSPHATE						
1	6.7	37.8	64.1	15.9	29.2	46.3
2	6.7	37.9	67.3	22.0	26.0	40.1
3	7.2	38.4	68.7	21.5	24.1	40.1
4	8.7	47.2	73.0	22.0	18.3	30.8
5	10.0	54.4	84.3	16.2	5.7	29.4
6	12.5	68.0	85.2	16.4	2.3	15.6
NORMAL SUPERPHOSPHATE						
7	8.8	19.4	27.9	30.3	63.3	50.3
8	9.9	20.5	27.6	34.9	62.5	44.6
9	10.6	22.9	26.7	31.3	62.7	45.8
10	12.1	35.3	24.2	27.0	63.7	37.7
11	13.9	55.3	24.9	17.4	61.2	27.3
12	14.9	67.0	28.8	13.0	56.3	20.0

^a Percent of fluorine in the superphosphate.

Fluorine losses during the heat treatment ranged from about 38 to 68% of the fluorine in concentrated superphosphates and from about 19 to 67% of the fluorine in normal superphosphates made from Florida rock. Fluorine volatilizations increased with increasing degrees of acidulation in both types of superphosphate (5). The fluorine contents of the water-soluble and water-insoluble fractions were correspondingly reduced. These observations indicate that the fluosilicate ion retained in the unheated superphosphate (Figure 2) is thermally (5) dissociated in accordance with equilibrium Equation 6.

This conclusion is supported by the analyses of air-dry insoluble residues of hot aqueous extractions of concentrated superphosphate. These residues could not be filtered and washed in the normal way because of the interference of precipitated hydrous silica that completely choked the pores of the filter

Table IX. Analyses of Air-Dried Residues of Hot Aqueous Extractions of Superphosphate

Fraction	CaO, %	P ₂ O ₅ , %	F, %	Total %
Coarse sand	38.1	34.9	3.13	76.1
Medium sand	39.7	35.5	2.91	78.1
Fine sand	39.8	42.9	1.94	84.6
Silt	40.0	39.9	2.61	82.5
Clay	39.4	36.7	2.50	78.7

Table X. Probable Combination of Constituents of Air-Dried Residues of Superphosphate^a

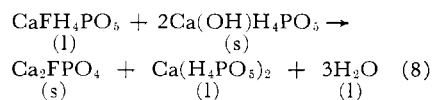
Fraction	CaHPO ₄ , %	Ca ₂ FPO ₄ , %	Ca ₅ F(PO ₄) ₃ , %	Total %
Coarse sand	38.2	27.5	11.6	77.3
Medium sand	32.3	19.2	27.6	79.1
Fine sand	67.4	19.2	1.7	88.3
Silt	54.0	24.0	7.0	85.0
Clay	37.7	15.0	27.3	80.0

^a Based on the assumption that the fluorine is combined as a mixture of fluorspodiosite and fluorapatite.

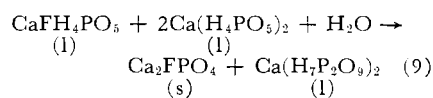
medium. Accordingly, the superphosphate was digested in hot aqueous solution, and the water-insoluble residue was separated by sedimentation and decantation. This yielded a series of residues of different particle sizes depending on the rate of sedimentation. The fractions are designated as coarse, medium, and fine sand, silt, and clay in order of diminishing particle size, as shown in Tables IX and X. The analyses of these fractions are listed in Table IX and the probable combination of the constituents in Table X.

On cooling, the clarified mother-liquor yielded a colloidal precipitate that was separated by centrifuging, washed with acetone, and air-dried at room temperature. It contained 27.6% CaO, 25.6% P₂O₅, and 13.8% F, equivalent to a mixture consisting of 50.5% CaFH₄PO₅, 13.7% Ca₂FPO₄, and 13.3% CaSiF₆·2H₂O. These products were all obtained by aqueous extraction of concentrated superphosphate, mixture No. 2, which was only 97.7% acidulated (Table IV). It is reasonable, therefore, to expect that the insoluble residues would contain some undecomposed phosphate rock. The analyses of the insoluble residues, however, indicate that all of the rock was decomposed on heating the aqueous superphosphate mixture, and the insoluble residues consisted of mixtures of dicalcium phosphate, fluorspodiosite, fluorapatite, and undetermined amounts

of hydrous silica. The precipitation of dicalcium phosphate results from heating a saturated aqueous solution of monocalcium phosphate, and the precipitation of fluorspodiosite, Ca₂FPO₄, results from a reaction between monocalcium fluorophosphate and calcium hydroxyphosphate (6) in accordance with the reaction equation,



or an analogous reaction between monocalcium fluorophosphate and monocalcium phosphate (6), as follows:



Fluorapatite was probably formed as indicated by reaction Equation 4. In any event, the shift in equilibrium caused by raising the temperature from ordinary room temperature to the boiling point of the solution was responsible for the precipitation of the dicalcium phosphate, fluorspodiosite, and fluorapatite. Monocalcium fluorophosphate is indicated as the probable source of the latter by the composition of the solid phase that separated on cooling the mother-liquor.

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Literature Cited

- (1) Beeson, K. C., Jacob, K. D., *Ind. Eng. Chem.* **30**, 304 (1938).
- (2) Bridger, G. L., Burt, R. B., Cerf, W. W., *Ibid.*, **37**, 829 (1945).
- (3) Datin, R. C., Worthington, E. A., Poudrier, G. L., *Ibid.*, **44**, 903 (1952).
- (4) Fox, E. J., Clark, K. G., *Ibid.*, **30**, 701 (1938).
- (5) Fox, E. J., Hill, W. L., *J. Agr. Food Chem.* **7**, 478 (1959).
- (6) Fox, E. J., Jackson, W. A., *Ibid.*, **9**, 334 (1961).
- (7) Fox, E. J., Jackson, W. A., *Farm. Chem.* **122**, No. 11, 60-6 (1959).
- (8) Hardesty, J. O., Ross, W. H., Adams, J. R., *J. Assoc. Offic. Agr. Chemist* **26**, 203 (1943).
- (9) Jacob, K. D., Rader, L. F., Marshall, H. L., Beeson, K. C., *Ind. Eng. Chem. Anal. Ed.* **4**, 25 (1932).
- (10) Jacob, K. D., Rader, L. F., Tremearne, L. H., *J. Assoc. Offic. Agr. Chemists* **29**, 449 (1936).
- (11) MacIntire, W. H., Hardin, L. J., *Ind. Eng. Chem.* **32**, 88 (1940).
- (12) *Ibid.*, p. 547.
- (13) MacIntire, W. H., Hardin, L. J., Oldham, F. D., Hammond, J. W., *Ibid.*, **29**, 758 (1937).

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