

COMPOSITION AND PROPERTIES OF
SUPERPHOSPHATE

IV. FREE ACIDS IN FRESH SUPERPHOSPHATE

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In a previous paper¹ dealing with free acid in superphosphate it was shown (1) that with careful attention to details of manipulation ether and acetone extractions give concordant and accurate results for free acid in mixtures of monocalcium phosphate and aqueous phosphoric acid whose free acid-water ratios fall within the range usually encountered in commercial superphosphate, and (2) that the results obtained by the two extraction methods on cured commercial superphosphate (2-3 months old) usually agree very well. The data for superphosphate show that the results by acetone extraction are usually the higher and that the difference is greatest in the freshest materials. It was also noted that whereas small quantities of free fluorine acids are present in cured superphosphates, the amounts observed in fresh superphosphate are several times greater than in the cured materials when they come on the market. These considerations and the fact that in plant control, where the free acid determination is used extensively, the analysis is usually made on superphosphate less than one month old prompted the investigation reported herein. The investigation comprises a study of the change in the quantities of free acids with the age of the superphosphate.

GENERAL CONSIDERATION OF FREE ACID

When phosphate rock is treated with sulfuric acid in the manufacture of superphosphate, the free acid in the mixture includes free acids of phosphorus, halogens, and sulfur. Some of the free acids are soon almost completely removed from the solution by precipitation or by volatilization, and others persist more or less definitely in the free condition. The number of acids present in the free condition depends largely on (1) the composition of the ingredients, (2) the process of manufacture, and (3) the age of the superphosphate. Acidulation with phosphoric acid does not greatly alter the situation.

Orthophosphoric acid is without question the predominant free acid in superphosphate. Small quantities of fluophosphoric acid, $\text{H}_2\text{PO}_3\text{F}$, may be present, particularly in fresh materials. Other phosphorus acids that should be mentioned in this connection, although lack of specific data makes an intelligent discussion of their role as free acid impossible at this time, are the phospho-acids of iron and aluminum,² for example, $\text{H}_3\text{Fe}(\text{PO}_4)_2$, and pyro- and even metaphosphoric acids in superphos-

¹ Hill and Beeson, *This Journal*, 18, 244 (1935).

² Sanfourche, *Bull. soc. chim.*, (4) 53, 1517 (1933).

phate that has been dried at relatively high temperatures. The quantities of halogens other than fluorine in superphosphate are usually negligibly small. Only the simpler fluorine acids, HF, $\text{H}_2\text{PO}_3\text{F}$, and H_2SiF_6 , are considered in this paper. Although sulfuric acid is the only acid of sulfur considered in later discussion, it should be pointed out that hydrosulfuric and sulfurous acids may be present in very fresh superphosphate—the former arising from the presence of sulfides in the natural phosphate, the latter from the reduction of sulfuric acid by organic matter and other reducing constituents of the rock.

At the time the ingredients of ordinary superphosphate are mixed the phosphoric acid (H_3PO_4) equivalent of the total free acid (A), in per cent by weight of the mixture is expressed with reasonable accuracy in the general case by the equation, (1) $A = p + (k_1f_1 + k_2f_2 + \dots) + cp_s$, in which p is the free phosphoric acid, $f_1, f_2 \dots$ represent the fluorine present as the free fluorine acids, respectively, p_s is the free sulfuric acid, and $k_1, k_2 \dots$, and c are the appropriate conversion factors. A few hours after mixing p_s becomes very small, and accordingly it need not be considered in day-old superphosphate. Whereas several free fluorine acids may exist simultaneously, it is not unreasonable to suppose that some one predominates in any given case. Then, if the quantities of the other fluorine acids are small enough to be negligible in comparison with the predominant one, the equation becomes further simplified to (2) $A = p + kF$. When the total free acid undergoes change with the elapse of time, (3) $\Delta A = \Delta p + k\Delta F$, provided the value of k is not altered as a result of a shifting of the predominant fluorine acid. The change in free acid may be accompanied by various restrictions. The condition that the free phosphoric acid does not change ($\Delta p = 0$) provides an important limiting case, which is approached more or less closely by a day-old superphosphate that contains only a very small percentage of citrate-insoluble P_2O_5 . Then, in the limiting case (4) $\Delta A = k\Delta F$.

ANALYTICAL METHODS

The determination of the quantities A , p and F in equation (2) is fraught with uncertainties arising from possible changes in the relative amounts of the free acids that may be caused by the analytical operations. However, two properly chosen methods of extracting the free acid can, as a result of a difference in the behavior of the fluorine acids with respect to the two extractants, give sets of results which, when they are correlated with the aid of equation (2), make possible certain important deductions concerning the nature and amounts of the free fluorine acids in superphosphate. Accordingly, for reasons which will become apparent from subsequent discussion, and until more satisfactory methods are developed, the result for free acid by acetone extraction will be regarded as the total free acid, A_a , the result by ether extraction (excluding the ex-

tracted fluorine prior to titration) will be taken as the free phosphoric acid, p_e , and the fluorine in the ether extract will be regarded as the fluorine equivalent of the free fluorine acids, F_e . Accordingly, for laboratory purposes equation (2) may be written thus: (5) $A_a = p_e + kF_e + r$, in which r is the resultant effect of errors of manipulation (<0.1 per cent of the sample) and of unknown, though possible, differences between the behavior with respect to the two extractants of readily decomposable complex acids and of certain minor metallic components of the superphosphate solution, such as magnesium and the alkalis.

The acetone extracts of superphosphate have been found to contain only about 20–40 per cent as much fluorine as do the ether extracts. In the case of two superphosphates that were several months old, the only materials for which data are available, the quantities of fluorine extracted by ether agreed reasonably well with those indicated by the analysis of superphosphate solutions¹ synthesized from the aforementioned superphosphates. Therefore, it appears that the difference between the quantities of fluorine found in the acetone and ether extracts results from the precipitation of fluorine acid during extraction with acetone rather than from the decomposition of fluorine-bearing solid constituents during extraction with ether. Accordingly, when the acetone method is used, a part of the free fluorine acid present in the superphosphate is precipitated during extraction; the other part goes into the extract and is subsequently titrated, in part at least, with the extracted phosphoric acid. As a result of the precipitation of a part of the fluorine acid an additional quantity of phosphoric acid appears in the acetone extract, which accounts for the experimental fact that in the case of material with relatively high percentages of free fluorine acids greater quantities of H_3PO_4 are extracted by acetone than by ether. The value of k in equation (5) is not affected by this division of the fluorine acid, provided the equivalence factor for the fraction of the fluorine precipitated during extraction is identical with that for the part subject to titration. The titration characteristics of the common fluorine acids that may be present as free acid in superphosphate are given in Table 1.

The details of the analytical methods used by the writers are as follows:

*Total free acid (acetone method).*²—To 2 grams of the superphosphate (20-mesh) in a 100 ml. volumetric flask, add exactly 100 ml. of neutral C. P. acetone; stopper the flask, and mix the contents thoroughly at intervals of 5 minutes over a period of 2 hours. Filter the solution through a paper of medium porosity (for example, Whatman No. 40 filter paper), taking care to keep the paper well-filled with liquid and the funnel covered when possible during filtration. Taking more than the usual precaution to have the temperature of the extract the same as the temperature of the acetone when it was measured out, transfer at once a 50 ml. aliquot of the clear filtrate to a 400 ml. beaker containing 200 ml. of distilled water, add 4 drops of indicator (0.2 per cent solution of sodium alizarin sulfonate in water), and titrate

¹ Hill and Beeson, *Loc. cit.*

² Schucht, *Z. angew. Chem.*, 18, 1020 (1905); Shuey, *Ind. Eng. Chem.*, 17, 269 (1925).

TABLE 1.—*Titration characteristics of fluorine acids*
(End point of sodium alizarin sulfonate, 25°–30° C.)

ACID	EQUATION OF TITRATION	k ^a	REMARKS
HF	$\text{HF} + \text{NaOH} = \text{NaF} + \text{H}_2\text{O}$	5.16	Equivalence point is not quite reached
H_2SiF_6	$\text{H}_2\text{SiF}_6 + x\text{NaOH} = y\text{Na}_2\text{SiF}_6 + z\text{NaF} + \dots$	2.6	$x=3$ approximately ^b
$\text{H}_2\text{PO}_3\text{F}^\circ$	$\text{H}_2\text{PO}_3\text{F} + \text{NaOH} = \text{NaHPO}_3\text{F} + \text{H}_2\text{O}$	0.00	$\text{H}_2\text{PO}_3\text{F}$ undergoes hydrolysis fairly rapidly, forming H_3PO_4 and HF^a
	$\text{H}_2\text{PO}_3\text{F} + 2\text{NaOH} = \text{NaH}_2\text{PO}_4 + \text{NaF} + 2\text{H}_2\text{O}$	5.16	

^a Factor for the conversion of the fluorine equivalent of the acid to H_3PO_4 .

^b Ross and Beeson, *This Journal*, 17, 238 (1934).

^c Lange, *Ber.*, 62B, 793, 1084 (1929); Lange and Stein, *Ber.*, 64B, 2772 (1931); Lange, *Z. anorg. allgem. Chem.*, 214, 44 (1933).

^d Lange, *Ber.*, 62B, 793 (1929).

with 0.1 *M* alkali until the color matches that of an equal volume of the same medium containing the same amount of indicator and an equivalent (approximately) quantity of pure monopotassium phosphate. Express the results of the titration in percentage of H_3PO_4 .

Free phosphoric acid.—Extract 2.5 grams with 100 ml. of water-free ether as described in a previous paper,¹ dilute the extract to about 250 ml. with 60 per cent ethyl alcohol, and when the solution has cooled to room temperature make up to 250 ml. Evaporate an aliquot of 100 ml. of the homogeneous solution in a 250 ml beaker on a water bath, taking care to avoid violent boiling with consequent loss of acid in the spray, until the odor of alcohol has disappeared, and then allow to stand on the bath 15–30 minutes longer to expel the fluorine. Take up the fluorine-free phosphoric acid in about 25 ml. of water and pour through a small filter; wash the beaker and filter with cold water until the volume of the filtrate is 100 ml. Titrate this solution with 2 drops of the alizarin indicator as directed under *Total free acid*.

Fluorine equivalent of the free fluorine acids.—Make an aliquot of 50 ml. of the diluted ether extract of the superphosphate alkaline to phenolphthalein with dilute sodium hydroxide and then carefully evaporate to a volume of about 3 ml. Determine the fluorine in this concentrated solution by the method of Willard and Winter.²

MATERIALS

In the selection of materials for this study one of the main objectives was to obtain superphosphates that represented a wide range in composition with special reference to the presence or virtual absence of one or more of the components of phosphate rock other than phosphorus and calcium, viz.: F, SiO_2 , R_2O_3 , MgO , and the alkalis. Whereas about 30 different samples were used, the composition range is represented by the eight ordinary superphosphates described in Table 2, comprising seven materials prepared in the laboratory by a method described previously³ and one superphosphate prepared commercially.

¹ Hill and Jacob, *This Journal*, 17, 487 (1934).

² *Ind. Eng. Chem. Anal. Ed.*, 5, 7 (1933).

³ Hill and Hendricks, *Ind. Eng. Chem.*, 28, 440 (1936).

TABLE 2.—Composition of day-old ordinary superphosphates

SAMPLE	SUPERPHOSPHATE MADE FROM—	P ₂ O ₅					MgO		Na ₂ O+K ₂ O		H ₂ O	
		TOTAL		FREE ACID ^a		F	Fe ₂ O ₃		CRYSTAL- LIZATION		FREE ^a	
		per cent	CITRATE- INSOLUBLE	per cent	per cent		per cent	per cent	per cent	per cent	per cent	per cent
ES-11	C. P. tricalcium phosphate	27.90	0.00	2.82	—	—	—	—	—	3.15	7.90	7.90
ES-5	Bone ash No. 1225	22.09	0.51	5.33	<0.03 ^b	0.2	0.10	0.60	0.51	2.31	7.47	7.47
ES-10	Bone ash No. 1225 + R ₂ O ₃ ^c	20.80	0.15	6.14	<0.03 ^b	0.2	0.44	0.55	0.46	2.58	10.03	10.03
ES-8	Nauru Island phosphate No. 450 ^a	20.74	0.28	7.77	1.34	0.1	<0.15	0.00	0.24	2.97	10.43	10.43
ES-9	Nauru Island phosphate No. 450 + SiO ₂ ^f	20.10	0.29	7.55	1.30	2.5	<0.15	0.00	0.23	2.96	9.80	9.80
ES-3	Florida land pebble No. 912 ^a	18.98	0.18	7.58	1.61	4.0	0.56	0.38	0.14	1.81	9.93	9.93
1423 ^g	Florida land pebble	18.69	3.01	6.01	1.68	^h	0.21	1.07	^h	1.63	11.59	11.59
ES-4	Tennessee brown rock No. 908 ^d	18.45	0.23	7.88	1.46	3.1	0.62	1.35	0.01	0.24	1.77	10.19

^a Determined by extraction with ether; result does not include extracted fluorine.^b Calculated from the composition of the original phosphate material. Loss by volatilization disregarded.^c Natural aluminum phosphate (sample 904) equivalent to 1.25% of Al₂O₃, and sufficient C. P. Fe₂O₃ to bring the total iron (Fe₂O₃) to 2.5% of the unacidulated phosphate mixture.^d Complete analysis given by Jacob et al, U. S. Dept. Agr. Tech. Bull. 364 (1933).^e Included in figure for Al₂O₃.^f Quartz flour (100-mesh).^g Commercial material.^h Not determined.

When the laboratory materials were 1 day old they were ground to pass a 20-mesh sieve and stored in tightly stoppered bottles. The day-old commercial superphosphate was put through a 10-mesh sieve and kept in a tightly stoppered bottle. For the periodic determination of the free acid a sample representative of the entire bottle of 10-mesh material (fresh sample taken each time by quartering) was ground to pass a 20-mesh sieve. A portion of the 10-mesh commercial material was stored at a temperature of 60°–70° C. in a glass container provided with a small opening for the escape of gases; it was allowed to cool before the analytical sample was taken. The other materials were kept at 25°–30° C.

CHANGE IN FREE ACID WITH THE AGE OF SUPERPHOSPHATE

Fluorine-free superphosphate.—The materials representing this type of superphosphate are ES-11, ES-5, and ES-10, made from C P. tricalcium phosphate, bone ash, and bone ash with additions of aluminum and iron compounds, respectively. Plots showing the effect of age on the free acid (results by ether extraction method) in superphosphate prepared from tricalcium phosphate and bone ash, respectively, were given in a previous paper;¹ therefore, curves for such materials need not be reproduced here.

It is to be supposed that in day-old superphosphate that does not contain fluorine the total free acid is equal to the free phosphoric acid. Accordingly, the results for free acid obtained by ether and acetone extractions should agree within the limits of analytical error. The experimental results show almost perfect agreement (0.1 per cent or less) in the case of superphosphate prepared from tricalcium phosphate. On the other hand, the results obtained on bone-ash superphosphate differed by as much as 2 per cent; moreover acetone extraction always gave the lower figures. As an example illustrating this condition, results obtained on a superphosphate made from a mixture of bone ash with aluminum and iron compounds are given in Table 3. It may be noted in this connection

TABLE 3.—*Effect of age on the free acid in bone-ash superphosphate ES-10*
(Results expressed in percentage of day-old material)

AGE OF SUPERPHOSPHATE	FREE ACID BY EXTRACTION WITH—		DIFFERENCE
	ACETONE	ETHER	
<i>days</i>			
1	6.64	8.47	–1.83
10	5.61	7.63	–2.02
30	5.27	6.30	–1.03
90	5.64	5.81	–0.17

that with bone superphosphate that contained only small quantities of R_2O_3 (for example ES-5) the results by the two extraction methods converge somewhat more slowly than in the case for which data are given.

¹ Hill and Beeson, *Loc. cit.*

This disparity between the results by extraction with acetone and with ether was thought to be attributable to differences in the behavior of magnesium or alkali phosphates towards the extractants, but results obtained on comparable synthetic mixtures (Table 4) do not support this view. The writers have found no satisfactory explanation for the apparent irregularity of the results for the bone-ash superphosphates.

TABLE 4.—*Effect of magnesium and alkali phosphates on the determination of free acid by extraction with ether and with acetone*
(Results expressed in percentage of added H_3PO_4)

MIXTURE ^a COMPRISING 9 PARTS OF $Ca(H_2PO_4)_2 \cdot H_2O$ AND 1 PART OF—	FREE ACID BY EXTRACTION WITH—		DIFFERENCE
	ACETONE	ETHER	
$Mg(H_2PO_4)_2$	108	104	+4
NaH_2PO_4	100	98	+2
KH_2PO_4	102	97	+5
$MgHPO_4$	73	69	+4
Na_2HPO_4	70	66	+4

^a To 1 gram of the acid-free mixture was added a known quantity of 42.5% aqueous phosphoric acid sufficient to yield a synthetic sample that contained 8-9% of added H_3PO_4 .

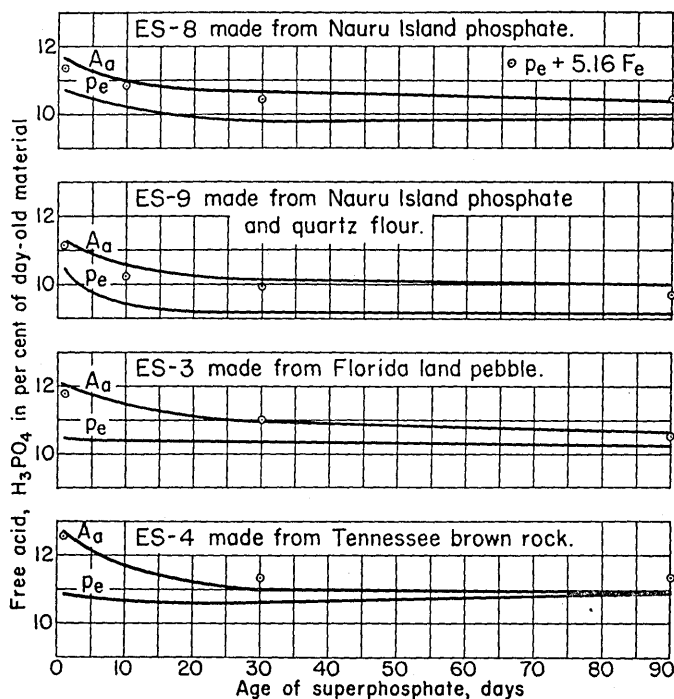


FIG. 1.—EFFECT OF AGE ON THE AMOUNTS OF TOTAL FREE ACID (A_a) AND FREE PHOSPHORIC ACID (p_e) IN ORDINARY SUPERPHOSPHATE PREPARED IN THE LABORATORY AND STORED AT 25°-30° C.

Fluorine-bearing superphosphate.—The effect of age on the quantities of total free acid and free phosphoric acid in the superphosphates prepared in the laboratory and stored at 25°–30° C. is shown in Fig. 1 with the aid of curves obtained by drawing a smooth line through the points (not shown in the plot) representing the percentage of free acid when the superphosphate was 1, 10, 30, and 90 days old, respectively. Similar curves are given in Fig. 2 for the commercial superphosphate.

It will be noted (Table 2) that the laboratory-prepared materials were initially very low in citrate-insoluble phosphorus (0.3 per cent of P_2O_5 or less), whereas the commercial superphosphate contained 3.01 per cent. Accordingly, the latter material would be expected to show the greater change in free acid with age. Furthermore, the citrate-insoluble phosphorus in ES-8 and ES-9 dropped in 30 days to 0.07 and 0.03 per cent, respectively, whereas it was sensibly constant in ES-3 and ES-4 over the 90-day period. When allowance is made for initial differences in citrate-insoluble phosphorus, a marked similarity is recognized in all pairs of curves. The curve for total free acid always lies above and with increase in age approaches that for free phosphoric acid. The total free acid always decreases, even in those cases where the amount of free phosphoric

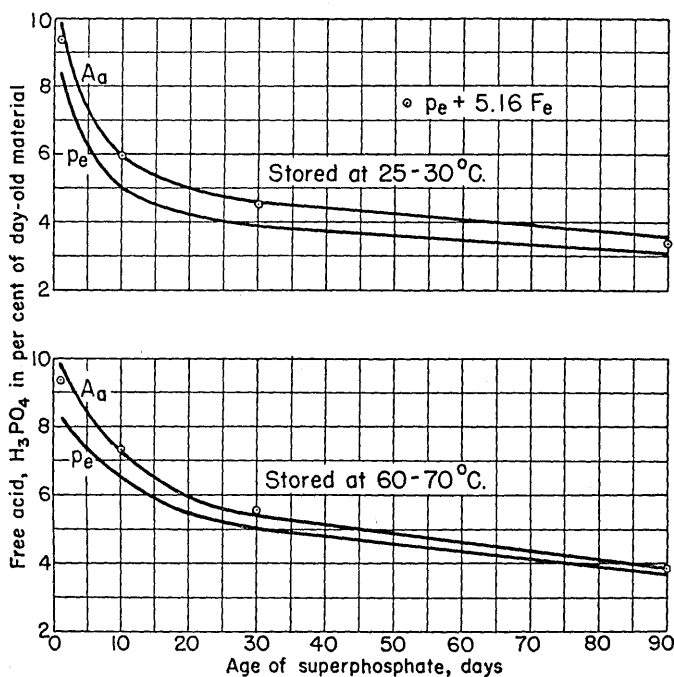


FIG. 2.—EFFECT OF AGE ON THE AMOUNTS OF TOTAL FREE ACID (A_a) AND FREE PHOSPHORIC ACID (P_e) IN ORDINARY SUPERPHOSPHATE PREPARED COMMERCIALY.

acid remains practically constant or shows a slight increase (see equation 4). Important differences between the pairs of curves are to be noted in the spacing and the rate at which the lines converge.

The change in the total amount of free fluorine acids with the age of the superphosphate (Fig. 3) in most cases shows the same trend as the change in total free acid (Figs. 1 and 2). With the exception of the R_2O_3 -free (nearly) superphosphates (ES-8 and 9) prepared from Nauru Island phosphate, the curves show a regular decrease in the quantity of fluorine

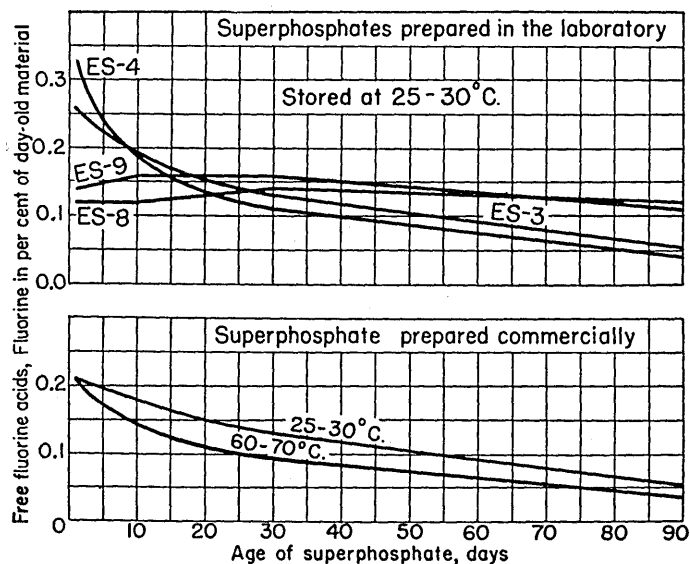


FIG. 3.—EFFECT OF AGE ON THE TOTAL AMOUNT (FLUORINE EQUIVALENT, F_e) OF FREE FLUORINE ACIDS IN ORDINARY SUPERPHOSPHATE

acids. Since observable changes in the total amount of fluorine did not occur in any of the materials, the decrease in the quantity of fluorine acid cannot be attributed to loss of fluorine by volatilization. It will also be observed that in conformity with equation (3) the rate of decrease of the free fluorine acids bears some relation to the rate of convergence of the curves for total free acid and free phosphoric acid.

FREE FLUORINE ACID IN SUPERPHOSPHATE.

In accordance with equation (5) the distance between the curves for total free acid and free phosphoric acid (Figs. 1 and 2) at a given age represents the magnitude of the sum $kF_e + r$. Since the values of F_e are now known (Fig. 3), it is possible to choose a fluorine acid (Table 1) whose k -value will yield the best agreement between the calculated values of kF_e and the differences between the determined percentages of total free

acid and free phosphoric acid. The relationship can be more conveniently observed on the plots by comparing the calculated value of the total free acid, $p_e + kF_e$, with the observed value, A_a . Accordingly, the fluorine acid with the highest k value, HF, was selected, and the values of the sum, $p_e + 5.16 F_e$, are indicated by encircled points in Figs. 1 and 2.

In most cases the agreement between the calculated and observed percentages for the phosphoric equivalent of the total free acid is close. The inference appears to be that hydrofluoric acid is the predominant free fluorine acid in superphosphate. Moreover, this view is supported by the fact that in the case of the superphosphates prepared from Nauru Island phosphate the silica-rich material showed about the same amounts of free fluorine acid as the one which was practically silica-free. The negligible effect of the presence of silica observed in this instance seems to indicate that no more than a small fraction of the free-acid fluorine in superphosphate exists as free hydrofluosilicic acid. Furthermore, on the basis of equilibrium measurements¹ for the reaction, $H_3PO_4 + HF = H_2PO_3F + H_2O$, only small quantities of free fluophosphoric acid would be expected.

EFFECT OF TEMPERATURE ON THE CHANGE IN FREE ACID WITH AGE

In the early stages of the writers' work on superphosphate the observation was made that commercial materials, as they come on the market carry smaller quantities of free fluorine acids than do materials of approximately the same age that had been prepared and cured in the laboratory. In commercial practice, where the superphosphate is usually cured in large piles, the temperature within the pile remains relatively high over a considerable period of time, whereas the laboratory-prepared materials were cooled to room temperature at the end of the first day. On this basis the smaller quantities of free fluorine acid in the commercial materials was attributed to the higher temperature that in all probability prevailed during curing, and in order to test the validity of this conclusion comparable data at two temperatures were obtained on a Florida pebble superphosphate. Losses of fluorine by volatilization during the experiments were not detectable by analyses of the material under test. The results (Fig. 3) show that the higher temperature does favor the disappearance of free fluorine acid. On the other hand, the quantities of free phosphoric acid, and also of total free acid (Fig. 4) were greater in the material that was kept at the higher temperature.

SUMMARY

Previous work on free acid in superphosphate has been extended to include fresh material.

¹ Lange, *Ber.*, 62B, 1084 (1929).

The acids that do, or may, occur in the free condition in superphosphate are discussed, and a simple equation is formulated to express the relationship between the total free acid on the one hand and the free phosphoric acid and the predominant free fluorine acid on the other.

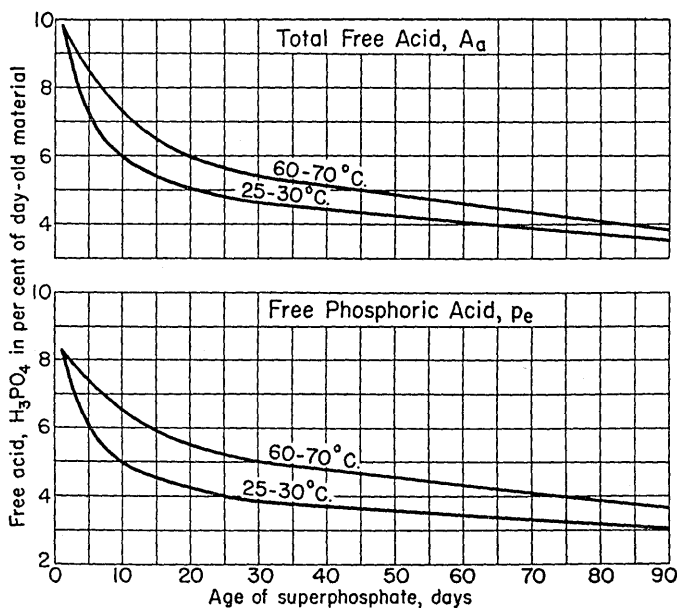


FIG. 4.—EFFECT OF TEMPERATURE OF CURING ON THE AMOUNT OF FREE ACID IN COMMERCIAL FLORIDA LAND-PEBBLE SUPERPHOSPHATE

Methods for determining the quantities entering the equation are discussed, and results are given to show the effect of (1) age of the material and (2) temperature of curing on the amounts of free acids in superphosphates.

Correlation of the data leaves the inference that hydrofluoric acid is the predominant free fluorine acid in fresh superphosphate.

SOME OBSERVATIONS RELATIVE TO DETECTING THE ADULTERATION OF HONEY WITH COMMERCIAL INVERT SUGAR*

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Present methods of detecting the adulteration of honey with commercial invert sugar are not always satisfactory. Both of these products

* Presented at the Annual Meeting of the Association of Official Agricultural Chemists held at Washington, November, 1935.