

Sludge-Free Wet-Process Phosphoric Acid for Use as Liquid Fertilizer

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In a study directed toward conditioning wet-process phosphoric acid for use in the preparation of liquid fertilizer, it was found that acid-soluble organic matter, fluosilicate, and aluminiferous clay phosphate are the principal reactants in the formation of sludge in wet-process acid. Sludge formation may be avoided by neutralizing the acid with phosphate rock to precipitate the fluosilicate, filtering to remove calcium fluosilicate, and removing the calcium as sulfate from the resulting aqueous calcium phosphate solution. An aqueous extract of superphosphate, a naturally occurring intermediate product in the process, may also be used as a starting solution for wet-process phosphoric acid. Water-soluble calcium salts of pentabasic phosphoric and octabasic diphosphoric acids appear to be responsible for high calcium concentrations in aqueous extracts of superphosphate.

A MAJOR PROBLEM in the production, storage, transportation, handling, and utilization of wet-process phosphoric acid is its pronounced tendency to form sludge deposits. The recent trend toward the production of liquid mixed fertilizers (3, 28) has created a demand for sludge-free acid. The solid materials that ordinarily are carried over into dry fertilizers cannot be tolerated in liquid fertilizers, where they would clog pipelines and spray nozzles.

The Tennessee Valley Authority (29, 30) and industry (37) have conducted research on methods designed to maintain the sludge in colloidal suspension and on procedures for its removal by filtration, centrifugation, or sedimentation. The U. S. Department of Agriculture has directed its studies toward a determination of the nature of sludge

deposits and the causes of their formation with the objective of developing a procedure for the production of phosphoric acid without sludge, if possible.

Sludge Formation in Wet-Process Acid

The chemical processes by which solids continue to separate from wet-process acid over long periods of time have not been clearly defined. Sludge from crude dilute (filter-press) acid appears to be composed primarily of organic matter and hydrous silica, evidently derived from acid-soluble impurities of phosphate rock. Concentration of the acid by evaporation of water causes more solids to separate, and neutralizing it, as in the production of sodium and ammonium phosphates, precipitates iron and aluminum phosphates. If the product is still further refined, as in the pro-

duction of C. P. chemicals, other impurities, such as lead and arsenic compounds, are thrown down. All of these solid materials are variously referred to as sludge. In the discussion that follows an attempt is made to clear up some of the more puzzling phenomena generally associated with sludge formation.

Organic Matter. Natural deposits of phosphate rock are formed by soluble phosphates leached from bird guano reacting with porous coral limestone (76) in which the skeletal remains of various marine animals are embedded. Vegetable matter derived from plants that sprang up after the coral reef became dry land is another source of organic materials. Accordingly many and varied forms of organic matter constitute a considerable proportion of the impurities found in phosphate rock.

Some rocks, notably those from the western deposits, have such high organic matter contents that it is a common practice to eliminate it by dry combustion prior to acidulation of the rock (78). Oil-bearing shale admixed with some of these deposits indicates that the strata in which these deposits are found could once have been swampland covered with vegetation.

Both the organic and the inorganic content of materials separated by the procedure of Fieldner, Selvig, and Taylor (5) from phosphate rocks from different sources varied widely (74, 76). Nitrogen (0.16 to 3.41%), hydrogen (2.08 to 5.26%), and carbon (22.6 to 63.3%) varied inversely with sulfur (39.1 to 7.3%) and ash (50.2 to 2.3%). The weight ratio of sulfur to ash, which consisted mostly of red iron oxide, was roughly in the proportions of two atoms of sulfur to one of iron in the form of ferric oxide. This suggests that the iron and sulfur may have been com-

Wet-Process Phosphoric Acid Symposium

The following three articles are from the Symposium on Production of Wet-Process Phosphoric Acid and Its Uses in Fertilizer Processes, which was given at the 138th Meeting of the American Chemical Society in New York, September 1960. Four other articles from this symposium appear in the September issue of Industrial and Engineering Chemistry.

A Method for Recovering Fluorine as Sodium Silicofluoride
by Sydney Atkin, Enrico Pelitti, A. P. Vila, and John Hegedus

Submerged Combustion Equipment by W. I. Weisman

Pilot-Plant Production by W. C. Scott, G. G. Patterson, and H. W. Elder

Continuous Pilot Plant for the Manufacture of Phosphoric Acid by D. W. Leyshon and W. A. Lutz

bined as pyrite, FeS_2 , in the rock. Their inverse proportionality to organic matter indicates that the isolated materials consisted mostly of mixtures of pyrite and organic residues in varying proportions.

A comparison of the results obtained with phosphate rocks from different sources indicates some correlation of the amount of calcium in excess of the requirements of $\text{Ca}_3\text{P}_2\text{O}_8$, CaSiF_6 , and CaCO_3 with the contents of organic matter and the geologic age of the phosphate rock deposit as shown in Table I. Florida soft rock and waste-pond phosphates are largely the products of reaction between soluble phosphate and clay, while the aluminum phosphate of the Connetable Islands deposits was probably formed in a like manner from bauxite. These materials, therefore, have no excess of calcium, but their organic matter contents are comparable with the others.

The more recent deposits of Curacao Island phosphate show relatively low excess calcium and low nitrogen and carbon contents compared with the much higher contents in the older continental deposits. This suggests that the organic matter probably was derived from vegetable, rather than animal, sources. This conclusion is supported by the observation of plant residues in rock samples from the Idaho and Wyoming deposits (16).

It is reasonable to assume that some of the carbonate from this excess calcium has been replaced by humic acid. It is equally logical to assume that some of it has been replaced by water-borne silicic and fluosilicic acids. It is also evident that all of these substitutionary anions, as well as the residue of carbonate ions (27), would be replaced by sulfate in the acidulation of the rock.

Waggaman and Sauchelli (34) state that the organic matter reduces sulfuric acid to sulfur dioxide (SO_2) and sometimes to hydrogen sulfide (H_2S). This means, of course, a consumption of acid, but because of the difficulty in ascertaining in just what form the organic matter occurs, the amount of acid it will consume can be predicted only by trial test. In the opinion of the writers, any hydrogen sulfide that may be evolved during the acidulation of phosphate rock would originate from pyritic materials rather than from the reduction of sulfuric acid by organic matter. The fact that organic matter may be eliminated by dry or wet combustion points the way to a possible solution to the problem of its occurrence as sludge in wet-process acid.

Hydrous Silica. All acid-insoluble residues, including quartz sand, are eliminated by filtration along with the gypsum from wet-process acid. Any hydrous silica as well as organic matter deposited as solids subsequent thereto

Table I. Relation of Calcium to Water, Nitrogen, and Organic Carbon in Phosphate Rocks^a

No. of Samples	Source and Type of Rock	Grams/Gram-Mole P_2O_5			
		Ex. CaO^b	H_2O	N	C
1	Curacao Island	2.5	8.4	0.05	0.63
2	Florida, waste-pond		42.1	0.02	2.08
1	Florida, soft rock	0.0	17.2	0.08	0.71
2	Florida, hard rock	10.0	10.6	0.05	1.54
5	Florida, land pebble	14.7	9.4	0.05	1.37
2	Tennessee, white rock	12.3	8.7	0.10	2.63
4	Tennessee, brown rock	17.0	6.0	0.05	0.80
3	Tennessee, blue rock	19.8	8.2	0.48	3.08
2	Idaho, Conda	17.9	8.5	0.42	10.20
1	Wyoming, Cokeville	17.9	7.1	0.52	12.65
2	Montana, Garrison	18.5	3.6	0.03	0.49
1	South Carolina, land rock	19.8	16.9	0.26	2.60
1	Tunis, Gafsa	22.2	15.7	0.24	4.43
1	Morocco	24.1	5.8	0.07	0.69
1	Connetable Islands	^d	4.4	0.13	0.73

^a Calculated from data by Hill, Marshall, and Jacob (14).

^b CaO in excess of $\text{Ca}_3\text{P}_2\text{O}_8$, CaSiF_6 , and CaCO_3 .

^c Clay phosphate.

^d Aluminum phosphate.

Table II. Distribution of Principal Rock Constituents during Production of Wet-Process Phosphoric Acid^a

Phosphate Rock		Filter Cake, %		Dilute Acid, %		Concd. Acid, %	
Constituent	% of sample	Of sample	Of total	Of sample	Of total	Of sample	Of total
CaO	52.2	29.5	100.0
P_2O_5	34.0	1.4	7.3	21.6	92.7	49.5	92.7
F	3.72	0.97	46.2	1.24	48.6	0.78	13.3 ^b

^a Made from Florida land pebble rock.

^b Fluorine volatilized = $100.0 - 46.2 - 13.3 = 40.5\%$ of total.

Table III. Distribution of Phosphoric Oxide and Fluorine during H_3PO_4 Production from Different Types of Rock

Type of Rock	% of P_2O_5		% of Total F			% of F Volatilized		
	CaSO_4	Acid	CaSO_4	Dilute acid	Concd. acid	Digestion	Evaporation	Total
Florida land pebble	7.3	92.7	46.2	48.6	13.3	5.4	35.1	40.5
Tennessee brown	6.8	93.2	12.3	76.4	66.5	11.3	9.9	20.2
Idaho rock ^a	8.5	91.5	27.8	60.3	21.7	11.9	38.6	50.5
Montana rock	8.9	91.1	12.3	63.9	49.2	23.8	14.7	38.5
Av.	7.9	92.1	24.7	62.3	37.7	13.0	24.6	37.4

^a Calcined to destroy organic matter previous to digestion.

must be derived by hydrolytic or other processes from the acid-soluble impurities of the rock. Recent investigations (7) show that the fluorine is present as fluosilicate in phosphate rock. Hence fluosilicic acid, derived as one of the products of the primary reaction between phosphate rock and sulfuric acid, could be the source of hydrous silica.

The reagent acid requirement for wet-process acid production is equal to the moles of calcium per mole of P_2O_5 in the rock, whereas the acid requirement for superphosphate production may be calculated from the same ratio by correcting for calcium combined as fluosilicate and mono-calcium phosphate. Estimates obtained in this manner (9) are in substantial agreement with results obtained by the Shoeld-Wight-Sauchelli (27) method, based on years of actual plant experience. Thus, both laboratory and plant

experience supports the fluosilicate postulate for fluorine in phosphate rock. This means that fluosilicic acid, released by the reaction of sulfuric acid, recombines preferentially to the phosphoric acid with excess rock in superphosphate manufacture. This postulate is in line with the respective solubilities of the calcium salts of these acids.

In the acidulation process the fluosilicic acid is partly dissociated (7) into silicon tetrafluoride gas and aqueous hydrofluoric acid solution, so that some fluorine is reprecipitated as fluoride and/or fluosilicate salts, some is retained in the acid solution, and some is volatilized as gaseous silicon tetrafluoride. The estimated distribution of fluorine among the filter cake, the acid solution, and the gas phase in the manufacture of wet-process acid in a typical plant using Florida land pebble phosphate rock is shown in Table II.

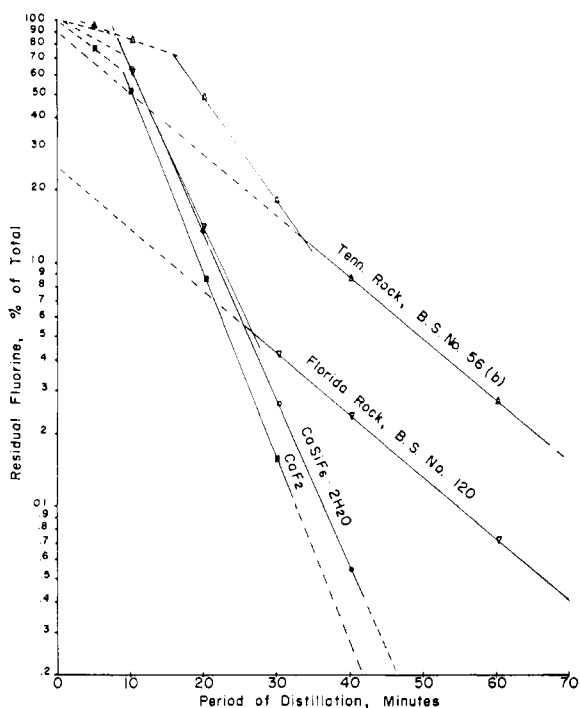


Figure 1. Steam distillation of fluorine at 125° C. from perchloric acid solutions of calcium fluoride, calcium fluosilicate, and phosphate rock

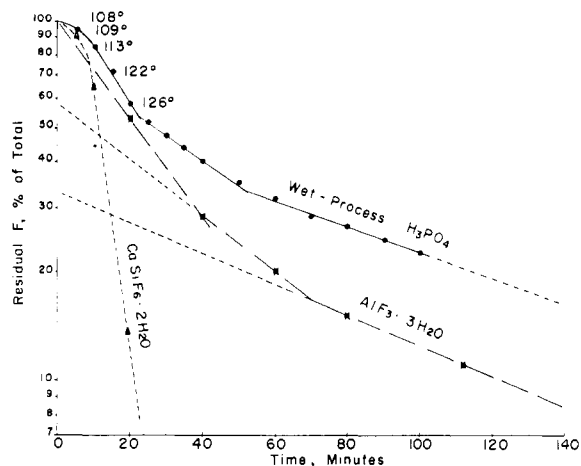


Figure 2. Steam distillations of fluorine at 125° C. from wet-process phosphoric acid

Compared with distillation from perchloric acid solutions of aluminum fluoride and calcium fluosilicate

In making these estimates it was assumed that all phosphorus, except that carried out with the waste calcium sulfate, was recovered in the dilute and concentrated acids. On the basis of this assumption, about 93% of the P_2O_5 was obtained in the acid solution. From the F/CaO ratios in the rock and in the filter cake, it appears that about 46% of the fluorine was carried out with the gypsum, and from the F/ P_2O_5 ratio in solution, about 49% of the fluorine was in the filter-press acid. The remaining 5% may have been, and probably was, volatilized as silicon tetrafluoride gas. Of the 49% fluorine in the dilute acid, only about 13% was retained in the concentrated acid. Neglecting that which may have been deposited as sludge (Tables V and VI), about 35% of the fluorine appears to have been vaporized during acid concentration by evaporation. Similar data obtained in like manner for acids made from Tennessee brown rock and phosphate rocks from Idaho and Montana (77) are compared in Table III.

Clay Phosphate. Soluble phosphates leached from bird guano also react with other components of the soil. The fixative properties of the clay component of soils for phosphorus have long been recognized. The end products of the phosphate fixation process that occurs when superphosphate is added to clay soils (25) may be the same as the clay phosphates that constitute a large part of the waste-pond materials (77, 76). Most of this clay phosphate is eliminated along with quartz sand in the flotation processes used in refining phosphate

rock, but some comes through with the final product.

The amount varies with the source and type of rock and with the efficiency of the ore-dressing process. The non-floated Tennessee brown rock contains a relatively high proportion of clay phosphate.

Some of the properties of a highly refined sample of clay phosphate have been described by Hill, Armiger, and Gooch (77). Its composition suggests that it may have been formed by the reaction of water-soluble monocalcium phosphate with kaolin-like clay residues (9). In this discussion, its behavior during the steam distillation of fluorine from a perchloric acid solution of its acid-soluble constituents (8) is of primary interest.

Fluorine (1.25%) was extracted along with the phosphate (24.9% P_2O_5), calcium (8.9% CaO), and aluminum (29.0% Al_2O_3) in an hour's digestion in perchloric acid at 125° C., but the evolution of fluorine was greatly retarded by being complexed with aluminum and other ions in solution, which lowered the partial pressure of hydrofluoric acid in the gas phase (8). The acid-insoluble silica (17.5% SiO_2) was left as a porous residue (38).

Influence of Rock Composition on Sludge Formation

The influence of rock composition on the rates of fluorine distillation is illustrated in Figure 1, in which steam distillations at 125° C. from perchloric acid solutions of National Bureau of Standards samples of Florida land

pebble (B.S. No. 120) and Tennessee brown phosphate rock (B.S. No. 56b) are compared with those of calcium fluoride and calcium fluosilicate. In this graph, the higher aluminum content of the Tennessee rock is reflected in a greater interference with the distillation of fluorine.

In Figure 2, the steam distillation of fluorine from a commercial wet-process phosphoric acid made from Florida rock is compared with the steam distillation of fluorine from a perchloric acid solution of aluminum fluoride. Normal fluorine losses due to changing conditions of temperature and acid concentration occurred during concentration of the phosphoric acid over the range 108° to 126° C. At this point, steam distillation was started and continued under conditions of temperature and pressure comparable to those of the distillation of fluorine from the perchloric acid solutions of aluminum fluoride and calcium fluosilicate.

The evident similarity of the fluorine distillation rate curves for the wet-process phosphoric acid and the perchloric acid solution of aluminum fluoride confirms the influence of aluminum on the distribution of fluorine among the solid, liquid, and gas phases represented by the data of Tables II and III.

Hill, Marshall, and Jacob (73) give the analyses for 21 different elements found in dilute and concentrated phosphoric acid made from Florida land pebble and Tennessee brown and Idaho phosphate rocks. The changes in the weight ratio of some of the more common constituents to phosphoric acid in solution

Table IV. Relative Concentrations of Impurities in Dilute and Concentrated Wet-Process Acids Made from Different Phosphate Rocks^a

Constituent	Florida Land Pebble		Tennessee Brown Rock		Conda, Idaho Rock	
	Dilute	Concd.	Dilute	Concd.	Dilute	Concd.
C, organic	0.47	0.66	0.36	0.16	0.04	0.38
Al ₂ O ₃	2.63	2.40	6.42	5.25	2.43	2.53
Fe ₂ O ₃	2.08	1.71	5.42	3.54	1.04	1.03
CaO	0.31	0.07	0.89	0.02	0.50	0.00
K ₂ O	0.13	0.04	0.16	0.02	0.13	0.02
Na ₂ O	0.005	0.38	0.006	0.002	0.43	0.28
SO ₃	9.08	8.73	3.57	2.56	6.37	7.01
SiO ₂	2.95	0.03	0.18	0.37	1.79	0.11
F, total	5.73	0.93	6.10	3.47	3.29	0.25
F, as SiF ₆	5.58	0.07	0.36	0.70	3.40	0.21

^a Calculated from data by Hill, Marshall, and Jacob (13).

Table VI. Probable Combination of Constituents of Sludge Recovered from Commercial Wet-Process Acids

Compound	Tennessee Rock		Idaho Rock	
	Gram-moles/kg.	Wt. %	Gram-moles/kg.	Wt. %
AlPO ₃ ^a	0.600	7.3	0.066	0.8
FePO ₄ ^b	0.950	14.3	0.050	0.8
CaSO ₄ ^c	0.892	12.1	1.264	17.2
CaSiF ₆ ^d	0.281	5.1	1.055	19.2
CaF ₂ ^d	0.913	7.1	0.422	3.3
NaF ^d	0.920	3.9	4.998	21.0
KF ^d	0.482	2.8	2.760	16.0
Other ^e	...	47.4	...	21.7

^a Equivalent of Al₂O₃.

^b Equivalent of Fe₂O₃.

^c Equivalent of SO₃.

^d Fluorine distributed as fluoride and fluosilicate among cations in excess of RPO₄ and CaSO₄.

^e By difference.

Table VII. Distribution of Fluorine in Phosphoric Acids Made from Florida Pebble Phosphate Rock

	P. Rock ^a	Acid A ^b	Acid B ^c	Acid C ^d	Acid D ^e
P ₂ O ₅ , % of sample	33.6	30.4	31.3	28.8	34.6
F, % of sample	4.1	2.40	0.72	2.20	2.26
F/P ₂ O ₅ , wt. ratio	0.122	0.079	0.023	0.076	0.065
F in acid, % of total	...	64.7	18.8	62.3	53.5

^a Lot 3253.

^b SO₃/CaO in rock-acid mixture = 1.10.

^c Fresh acid A + phosphate rock.

^d Same as acid B, but made from acid A after standing several weeks and filtering to remove precipitated silica.

^e Same as acid A, except phosphate rock in excess.

on concentrating the acids are shown in Table IV. Constituents that apparently were deposited during the process of concentrating the acids include organic carbon from Tennessee brown rock acid; iron and aluminum oxides from Florida and Tennessee rock acids; calcium and potassium oxides from all three, and sodium oxide from Tennessee and Idaho rock acids; sulfate from Florida and Tennessee rock acids; and fluorine and silica (probably as fluosilicate) from all three acids.

The analyses of alcohol-washed air-dried samples of sludge recovered from concentrated wet-process acids made from Tennessee and Idaho rocks (14) are given in Table V. The amount of sludge recovered from the acid made from the Tennessee rock was 15%;

from the acid made from the preignited Idaho rock, only 1.2% of the total weight of acid. Comparison of the analyses of these sludges brings out highly significant similarities and differences (Table VI).

The fact that the combined iron and aluminum oxides are equivalent to the phosphoric oxide contents in each case suggests that these constituents are combined as iron and aluminum phosphates in both samples. Calcium sulfate equivalent to the SO₃ content is an important constituent of both samples. The fluorine is distributed as fluoride and fluosilicate salts among the cations remaining over and above RPO₄ and CaSO₄. Since the Idaho rock was ignited to burn out organic matter before it was digested with sulfuric acid, it is reason-

Table V. Analyses of Sludge Separated from Crude Concentrated Phosphoric Acid^a

Constituent	Tennessee Brown Rock		Conda Idaho Rock	
	Wt. %	G./kg.	Wt. %	G./kg.
Al ₂ O ₃	3.10	0.304	0.34	0.033
Fe ₂ O ₃	7.60	0.476	0.40	0.025
CaO	11.70	2.086	15.37	2.741
K ₂ O	2.27	0.241	13.00	1.380
Na ₂ O	2.85	0.460	15.49	2.499
P ₂ O ₅	11.00	0.775	0.85	0.060
SO ₃	7.14	0.892	10.12	1.264
F (as SiF ₆)	9.34	0.819	28.37	2.489
Other (by difference)	45.00	...	16.06	...

^a Calculated from data by Jacob *et al.* (14).

able to assume that the quantity of sludge recovered from this acid would be considerably less, while the determined constituents of the sludge would constitute a much higher percentage than in the case of the Tennessee rock acid sludge. It is probable that much of the undetermined material was composed of organic and silicate compounds, which could change the fluorine distribution considerably. In any event, it is apparent that both fluorine distribution and sludge composition are affected by the composition of the phosphate rock from which the acid is made. The factors that appear to be most significant in this variability are the fluosilicates and the acid-soluble components of clay phosphate that constitute the greater part of phosphate rock impurities. The available data seem to indicate that fluosilicic acid released in the primary reaction between phosphate rock and sulfuric acid is slowly hydrolyzed in phosphoric acid solution and deposits its silica, while the fluorine left in solution recombines with aluminum and possibly other ions to form acid-soluble complex (8) ions. This postulate was tested by acidulating phosphate rock under the following conditions.

Florida phosphate rock was digested with a slight excess of sulfuric acid in a mechanical mixer (7) under conditions designed to simulate those under which wet-process acid is produced commercially. The solution was filtered through fritted glass of medium porosity. The product was designated acid A in Table VII.

Calculations based on F/P₂O₅ ratios of the phosphate rock and the several acid samples indicate that about 65% of the total fluorine in the rock decomposed by the sulfuric acid was in acid A, compared with an average of 62.3% for the commercial acids shown in Table III, whereas only 19% of the fluorine was retained in acid B. The difference between the fluorine contents

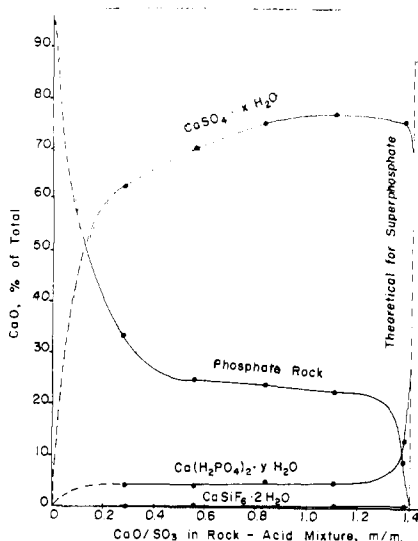


Figure 3. Estimated distribution of calcium in solid phase products

As a function of CaO/SO_3 mole ratio in phosphate rock-sulfuric acid mixtures

of acids A and B indicates that about 46% of the fluorine was precipitated from the freshly prepared acid A in its reaction with excess rock; but after depositing the hydrous silica on standing 6 to 8 weeks, the fluorine content of acid C was reduced only 2.4% in the reacton with excess phosphate rock. The fact that the fluorine did not react with the calcium carbonate in the rock to form calcium fluoride is an indication that it had already combined with the aluminum in solution (Figure 2). In the reaction of sulfuric acid with an excess of rock, the $\text{F}/\text{P}_2\text{O}_5$ ratio in solution in acid D was reduced to 0.065, or 53% of that in the original rock. These results confirm the postulated deposition of hydrous silica from fluosilicic acid released in the primary reaction between phosphate rock and sulfuric acid; and the recombination of fluorine with aluminum in solution to yield a soluble complex which interferes with the precipitation as well as the steam distillation of fluorine. Carothers and Hurka (2) describe a procedure for obtaining low-fluorine phosphates for animal-feed supplements by reacting sulfuric acid with an excess of phosphate rock and adding sodium or potassium chloride to the mixture to throw down the fluosilicate. Fluorine is recovered from the insoluble residue in a subsequent operation.

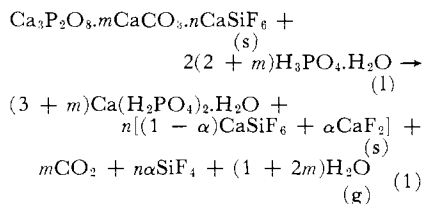
Chemistry of Wet-Process Acid Production

The postulated reaction between phosphate rock and phosphoric acid yielding soluble monocalcium phosphate in solution (35, 36), from which gypsum and phosphoric acid are subsequently formed by reaction of the monocal-

cium phosphate with sulfuric acid, is open to serious doubt, owing to the general practice of maintaining an excess of sulfuric acid in the slurry mixture at all times and the limited solubility of calcium in the presence of excess sulfate. This doubt is further accentuated by the fact that calcium fluosilicate is also less soluble than monocalcium phosphate and would be precipitated preferentially to the phosphate should the calcium ion exceed the sulfate ion in solution. Accordingly, in considering the reactions between phosphate rock and sulfuric acid the solid phase reaction products include fluorides and fluosilicates as well as the sulfate and phosphate salts.

To understand better the nature of the chemical reactions involved, consider first the products of reaction between phosphate rock and phosphoric acid and then the products of reaction between the rock and sulfuric acid.

THE REACTION OF REAGENT-GRADE (84.5%) H_3PO_4 with Florida land pebble phosphate rock (46.3% CaO , 33.2% P_2O_5 , 3.82% F) yielded monocalcium phosphate, calcium fluoride, and calcium fluosilicate in the solid phase and silicon tetrafluoride and carbon dioxide in the gas phase in accordance with the reaction equation (7),



Aqueous extracts of these products yielded 97.6% of the P_2O_5 and 96.4% of the CaO theoretically combined as monocalcium phosphate as water-soluble products. About one third of the fluorine was volatilized as silicon tetrafluoride gas during acidulation; the remainder of the fluorine was left as water-insoluble residues in the filter cake.

THE REACTION OF 49% H_2SO_4 with Curacao Island phosphate rock (51.5% CaO , 37.0% P_2O_5 , 0.62% F), mixed in the proportions of 15, 30, 45, 60, and 75 grams of ground rock to 100 grams of acid solution, yielded the results shown in Figure 3.

As soon as the initial reaction was over (as indicated by the subsidence of effervescence), the rock-acid slurries were filtered and the filter cakes were washed with acetone to remove all of the aqueous solution. After drying in air at room temperature, the solid residues were analyzed and the results computed in terms of the percentage of calcium combined as undecomposed phosphate rock (equivalent to the citrate-insoluble P_2O_5), calcium sulfate, monocalcium

phosphate (water-soluble P_2O_5), and calcium fluosilicate (F in excess of undecomposed rock). These estimated results are graphed as functions of the CaO/SO_3 mole-ratio of the rock-acid mixtures in Figure 3.

Within limits of experimental error, all of the calcium of all but one of the mixtures was found in the solid phase. The exception was the mixture containing 75 grams of rock per 100 grams of acid solution, in which case the calcium exceeded the sulfate content of the mixture and about 2.6% of the total calcium was removed with the aqueous solution.

The amount of fluorine found in the solid residues in excess of the undecomposed phosphate rock was almost negligibly small, amounting to less than 0.5% of the total calcium combined as calcium fluosilicate (1.5% of the calcium combined as calcium fluoride). The water-soluble phosphate, on the other hand, accounted for about 5% of the total calcium in the overacidulated mixtures, increasing to about 13% of the total in the underacidulated mixture.

These data suggest that superphosphate is formed as a product of the primary reaction between phosphate rock and sulfuric acid, and that this intermediate product remains almost entirely in the solid phase. The secondary reaction between excess H_2SO_4 and the superphosphate, yielding phosphoric acid in solution and solid calcium sulfate, coats the surface of phosphate rock particles with gypsum and thereby slows the rate of reaction. This would account for the need for such careful check of the concentration of excess sulfuric acid in the rock-acid slurry in order to prevent throwing the entire digestive system out of control (36).

The data of LeBaron (19) show that the reaction between sulfuric acid and phosphate rock is a surface phenomenon. Water-soluble and available phosphates increase with time and with the fineness of the rock grind. At the end of 10 days, the conversion of rock phosphate to water-soluble and available forms may be expressed by the equations

$$\text{W. S. } \text{P}_2\text{O}_5 = 50.3 + 2.5/\bar{d}, \pm 1.5\% \quad (2)$$

$$\text{Avail. } \text{P}_2\text{O}_5 = 52.0 + 2.5/\bar{d}, \pm 2.5\% \quad (3)$$

where \bar{d} represents the average diameter in microns of the screen openings over the range 35- to 325-mesh (0.417 to 0.043 mm.) and the results are expressed in percentages of the total P_2O_5 in the rock. The aggregate geometric surface of a unit weight of ground rock varies inversely with the diameter of the particles, the same as the water-soluble and the available P_2O_5 in the acidulated rock mixtures (Equations 2 and 3).

Weber and Pratt (36) state that the concentration of calcium oxide in 44%

H₃PO₄ solution (32% P₂O₅) at 70° C. varies inversely with the concentration of sulfate in solution and may be expressed by the equation

$$y = 0.45/x \quad (4)$$

where x and y represent weight per cent of H₂SO₄ and CaO, respectively, in solution. Thus, the concentration of calcium oxide in solution when the calcium and the sulfate ions are present in stoichiometric proportions ($y = 0.57x$) is equivalent to 0.51% (0.89% H₂SO₄) and continues to decrease with increasing concentration of sulfate in solution. The influence of the fluosilicate ion on these equilibria is not stated, but in view of the relative solubilities of the calcium salts it is apparent that it can only lower the concentration of calcium in solution. Thus, the probability of calcium phosphate's being present with calcium sulfate, calcium fluosilicate, or both, in solution is remote.

There are many complicating factors involved in superphosphate manufacture, which make the interpretation of all of the observed phenomena difficult. Simplifying assumptions based on incomplete, or unrelated, data have created false impressions that have become generally accepted as facts. Thus, the assumption that normal superphosphate made by acidulating phosphate rock with sulfuric acid is a physical mixture of anhydrous and hydrated forms of calcium sulfate and monocalcium phosphate has become more or less firmly fixed in the literature on the subject. The principal components of superphosphate made with 55° Be. (70%) H₂SO₄ are reported to be anhydrite and monocalcium phosphate monohydrate. To test this postulate, a physical mixture of macroscopic crystals of these two salts large enough to be readily identified by petrographic examination was moistened with water and held at room temperature. Both CaSO₄ and Ca(H₂PO₄)₂·H₂O crystals disappeared from a mixture containing the two salts in the proportions of two moles of calcium sulfate to one of monocalcium phosphate and a third solid phase of dendritic crystals characteristic of normal superphosphate appeared in their stead. The results of this test indicate that the stable solid phase in the CaO-P₂O₅-SO₃-H₂O system is a double salt of calcium sulfate and monocalcium phosphate.

The same dendritic-type crystals (35) appeared in phosphate rock-sulfuric acid mixtures whenever the concentration of phosphoric acid exceeded about 30% P₂O₅ at ordinary temperatures. Nordengren (27) and his associates (20) have determined the limits of P₂O₅ solubility in equilibrium with the several hydrates of calcium sulfate as a function of temperature and Weber (36) has also shown that the concentration

of P₂O₅ in solution in equilibrium with both gypsum and the hemihydrate of calcium sulfate decreases with increasing temperature. In other words, the transition point between gypsum and the hemihydrate shifts from high to low concentrations of phosphoric acid in solution as the temperature of the solution increases. Weber (36) also attributes citrate-soluble P₂O₅ lost with washed gypsum filter cake to the coprecipitation of dicalcium phosphate dihydrate along with the calcium sulfate, with which it appears in the form of a solid solution.

The isomorphism of dicalcium phosphate and calcium sulfate is undoubtedly a contributing factor to their simultaneous occurrence in the washed filter cake, but it is very unlikely that dicalcium phosphate would be precipitated as such in the highly acid medium generally maintained in the rock-acid slurry. It seems much more likely that it would be formed by hydrolysis of superphosphate during the filtering and washing operation. This postulate was experimentally confirmed and is supported by the well known development of a water-insoluble, citrate-soluble P₂O₅ fraction (Equations 2 and 3) during the extraction of water-soluble phosphate in routine superphosphate analysis.

The limited solubility of superphosphate, or monocalcium phosphate, in the presence of excess sulfuric acid (Equation 4) appears to be the principal reason for prescribing a preliminary reaction between phosphate rock and phosphoric acid in a procedure developed by the Tennessee Valley Authority for the production of phosphoric acid from low-grade rock (4). In this procedure, however, the acidulation of the concentrated superphosphate with the sulfuric acid before separating the reprecipitated calcium fluoride and/or fluosilicate (Equation 1) would cause fluosilicic acid to be redissolved in the phosphoric acid, whence the silica may be deposited by slow hydrolysis of the fluosilicate ion and the liberated fluorine complexed with aluminum as shown in Figure 2.

Sludge-Free Wet-Process Acid

The natural occurrence of superphosphate as an intermediate product in the production of wet-process phosphoric acid, combined with the desirability of producing a sludge-free acid, makes the aqueous extraction of ordinary superphosphate a logical starting point in the preparation of the acid (26). By mixing the rock and sulfuric acid in a simple cone mixer (32) and curing the superphosphate in open sheds, the cost of expensive corrosion-resistant digestive tanks and the cost of power consumed in keeping the rock-acid slurry in constant

circulation in conventional-type phosphoric acid plants would be eliminated. By separating the soluble calcium phosphate from the fluorine salts before precipitating the calcium from the aqueous extract, the problem of corrosion caused by the presence of hydrofluoric and fluosilicic acids would be greatly reduced, if not completely eliminated, while the efficiency of reagent acid utilization would be enhanced by the reaction of the fluosilicic acid with an equivalent amount of calcium in the rock. Also, by reacting the sulfuric acid with an excess of phosphate rock, the attack of this acid on the clay component, which is the source of most of the iron and aluminum found in wet-process acid, is minimized.

The use of phosphate rock to neutralize wet-process acid produced by conventional methods is more economical than neutralizing it with limestone (33) and the results are substantially the same in both cases. By neutralizing the solution, the fluoride and fluosilicate salts are precipitated along with the iron and aluminum phosphates, the solubilities of which are suppressed by the common ion effects of soluble calcium phosphate.

The aqueous extract of ordinary superphosphate has been recommended as a source of low-fluorine phosphorus for use as an animal feed supplement (23) and the data of Huang (15) indicate that recoveries of up to 98% the total P₂O₅ in the rock with very little fluorine are possible.

Aqueous Extracts of Superphosphate

Analyses of a series of successive extractions of water-soluble calcium phosphate from a commercial superphosphate made from Florida land pebble phosphate rock are shown in Table VIII, compared with results obtained by Patten (22) on neutralizing phosphoric acid with calcium carbonate and the equilibrium data of Bassett (7) for aqueous solutions saturated with respect to mono- and dicalcium phosphates at 25° and 50.7° C.

The concentration of calcium in solution in the aqueous extracts of superphosphate after only a few minutes of contact between the solid and liquid phases greatly exceeded the equilibrium values of Bassett (7), for which several months of contact were required. This called to mind the unpublished data of Patten (22), who found that the concentration of calcium in phosphoric acid neutralized with calcium carbonate also exceeded the equilibrium values. Values less than equilibrium concentrations could be explained on the grounds of incomplete saturation, while values only slightly in excess of equilibrium would ordinarily be explained as experimental error; but

Table VIII. Calcium Phosphates in Aqueous Solutions

CaO		P ₂ O ₅		H ₃ P ₂ O ₉	Ca(H ₂ P ₂ O ₇) ₂	Ca(H ₂ PO ₄) ₂
G.-mole/kg.	%	G.-mole/kg.	%	%	%	%
Aqueous Extracts of Superphosphate						
1.501	8.42	1.866	26.5		17.03	30.7
1.632	9.15	1.796	25.5		7.69	39.6
1.665	9.34	1.500	21.3	(5.71) ^a		36.0
1.566	8.78	1.493	21.2	(2.47) ^a		38.4
1.138	6.38	1.092	15.5	(1.52) ^a		28.3
0.703	3.94	0.775	11.0		3.37	17.0
H ₃ PO ₄ + CaCO ₃ (22)						
1.229	6.89	1.535	21.8		14.26	24.9
1.256	7.05	1.514	21.5		11.92	27.1
1.271	7.13	1.479	21.0		9.74	28.7
1.184	6.64	1.366	19.4		8.36	27.1
1.138	6.38	1.303	18.5		7.60	26.3
1.102	6.18	1.246	17.7		6.70	25.9
Equilibria at 25° C. (7)						
0.551	3.09	2.542	36.1	31.1	25.7	
0.876	4.91	1.993	28.3	5.23	40.8	
1.036	5.81	1.704	24.2		32.8	8.96
0.984	5.52	1.613	22.9		29.3	9.64
0.807	4.50	1.239	17.6		20.2	9.96
0.471	2.64	0.641	9.10		7.95	8.10
0.335	1.88	0.426	6.05		4.53	6.42
0.148	0.83	0.168	2.39		0.97	3.42
Equilibria at 50.7° C. (7)						
0.061	0.34	4.366	62.0	91.7	2.83	
0.114	0.64	4.091	58.1	83.5	5.32	
0.255	1.43	3.542	50.3	65.5	11.9	
0.530	2.97	2.951	41.9	40.9	24.7	
0.870	4.88	2.338	33.2	12.9	40.6	
1.022	5.73	2.084	29.6	0.89	47.6	
0.626	3.51	1.092	15.5		21.7	4.34
0.415	2.33	0.666	9.46		11.7	4.42
0.278	1.56	0.434	6.16		7.22	3.34
0.123	0.69	0.161	2.28		1.74	2.33

^a Ca(OH)H₂PO₄.

calcium concentrations almost twice equilibrium values could not be explained in this manner. A maximum of 9.34% CaO was found in solution with only 21.3% P₂O₅ in the superphosphate extract at room temperature, compared with only 5.81% CaO in solution with 24.2% P₂O₅ for aqueous solutions in equilibrium with both mono- and dicalcium phosphates in the solid phase at 25° C. and 5.73% CaO with 29.6% P₂O₅ at 50.7° C. (Table VIII).

These results show a consistent trend toward lower concentrations of calcium and higher concentrations of P₂O₅ with time and increasing temperature, which suggest soluble modifications of calcium phosphate with properties different from those of the solid phase products. This observation led to a re-examination of the fundamental data pertaining to the molecular species of phosphoric acid in solution. The results of this study can be referred to here only in brief outline.

Molecular Species of Phosphoric Acid. From theoretical consideration Graham (10), in 1883, proposed a series of acids consisting of from 1 to 5 moles of water per mole of P₂O₅. The first three members of this series are identified as the meta-, pyro-, and ortho-

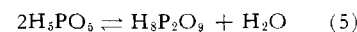
phosphoric acids. The fourth and fifth members are identified as the solid phase that separates on cooling phosphoric acid solution at its freezing point and as the ordinary 85% reagent grade phosphoric acid itself, respectively. The latter has not been generally accepted into this family of recognized compounds, since it cannot be obtained as a separate entity, the physical and chemical characteristics of which may be defined. Its existence in solution, however, may be demonstrated by graphing the cryoscopic data of Ross and Jones (24) expressed as mole fractions of H₃PO₄ and H₅P₂O₉, as shown in Figure 4.

In discussing the molecular structure of phosphoric acid, Van Wazer (37) observes that, on the basis of x-ray structure studies, the phosphate ions in 54% H₃PO₄ solution "are hydrogen bonded to the water liquid lattice, rather than to other phosphate ions."

This statement by Van Wazer confirms the conclusions drawn from the cryoscopic data of Ross and Jones (24) based on Graham's (10) postulate. Knowledge concerning the behavior of these molecules in solution is essential to a complete understanding of the physical and chemical properties of phosphate salts, as well as the technical

aspects of commercial phosphoric acid.

One would expect that phosphoric acid would be fully hydrated in dilute solution, but as the concentration of acid increases, condensation would occur in accordance with the equilibrium equation,



Starting with a dilute solution, the freezing point of water is lowered as the concentration of acid in solution increases over the range, 0 to 35.8% H₃PO₄ (N₂ = 0.08). The freezing point of the solution over this range may be expressed by the equation

$$\text{F.P., } ^\circ\text{K} = 273.1 - 134.8 N_2 \quad (6a)$$

where N₂ represents the apparent mole fraction of H₃PO₄ in solution. Above 36% H₃PO₄, condensation in accordance with equilibrium Equation 5 occurs and the introduction of the new component, H₈P₂O₉, causes a still further lowering of the freezing point of the solution along solid line *b*, Figure 4. This continues with shifting equilibrium until all of the pentabasic acid is exhausted and only H₈P₂O₉ and H₂O remain in solution at the eutectic point, corresponding to 68.2% H₈P₂O₉ (62.5% H₃PO₄). The molecular lowering of the freezing point of water over this range of acid concentration may be expressed by the equation

$$\text{F.P., } ^\circ\text{K} = 288.5 - 327.7 N_2 \quad (6b)$$

Above 68.2% H₈P₂O₉, the polymerized octabasic diphosphoric acid, otherwise known as the "hemihydrate of orthophosphoric acid," is the stable solid phase in equilibrium with the solution. The separation of this compound as the solid phase leaves a solution enriched with H₃PO₄ and equilibrium shifts from right to left as the freezing point of the solution increases. The reasons for such a shift must be found in the strong affinity of P₂O₅ for water and the low ionization of the concentrated acid. In any event, the freezing point over the range of concentration represented by solid line *c* may be represented by the equation

$$\text{F.P., } ^\circ\text{K} = 79.7 + 353.9 N_2 \quad (6c)$$

Segment *d* of the freezing point curve probably represents the molecular lowering of the freezing point of H₃PO₄ by a higher acid polymer than the dimer, while segment *e* represents the lowering of the freezing point of H₃PO₄ by H₂O. Equations for segments *d* and *e* are

$$\text{F.P., } ^\circ\text{K} = 161.1 + 171.4 N_2 \quad (6d)$$

$$\text{F.P., } ^\circ\text{K} = 228.6 + 65.4 N_2 \quad (6e)$$

The pentabasic acid has an incongruent melting point of 294° K (20.9° C.) compared with the true melting point

of 302.4° K (29.3° C.) for the octabasic (hemihydrate) acid. There is no eutectic between H_5PO_5 and $H_8P_2O_9$ (Figure 4). The probable explanation is that water released by the condensation of two molecules of H_5PO_5 escaped into the gas phase and therefore caused no freezing (or melting) point lowering, while the freezing point continued to rise as the acid solution lost water vapor.

Effect of Acid Condensation on Boiling Point of Solution. The boiling point of a binary mixture should be linear between the lower and the higher boiling points of its components, as represented by the dotted line in the boiling point curve of Figure 4. The fact that the observed boiling points are not linear with the apparent mole-fraction of H_5PO_5 indicates that the system is not a simple binary mixture of water and H_5PO_5 . In the range, $N_2 = 0$ to 0.3, where condensation of the pentabasic acid to form the octabasic diphosphoric acid and water occurs (Equation 5), the water formed by the reaction lowers the boiling point of the solution below that calculated for a binary mixture, but in the range $N_2 = 0.3$ to 1.0, where water is taken up by the rehydration of $H_5P_2O_9$ to H_5PO_5 , the removal of water from the mixture raises the boiling point above that calculated for a binary mixture. These effects are in line with expectations based on a shifting equilibrium in accordance with Equation 5.

Other tests, such as variations in the isothermal vapor pressure and the latent heat of vaporization of water, which cannot be included in this discussion, confirmed the postulated existence of pentabasic and octabasic diphosphoric acid molecules in aqueous solution. Having established the probable existence of such molecules in solution, consideration will be given to the chemistry of phosphates in aqueous extracts of normal superphosphate.

Reactions in $CaO-P_2O_5-SO_3-H_2O$ System

The reaction of sulfuric acid with phosphate rock to yield normal superphosphate has already been considered and evidence adduced to show that the principal phosphatic constituent of this product is a double salt of calcium sulfate and monocalcium phosphate. In making an aqueous extract of superphosphate, the calcium sulfate and the calcium salts of hydrofluoric and fluosilicic acids are left as insoluble constituents, while the calcium phosphate is brought into solution. In so doing, the process does not consist of redissolving a salt that has already been formed and crystallized as monocalcium phosphate, but consists of reacting the double salt with water, whereby the phosphatic component is dissolved, and the sulfate is left in the solid phase.

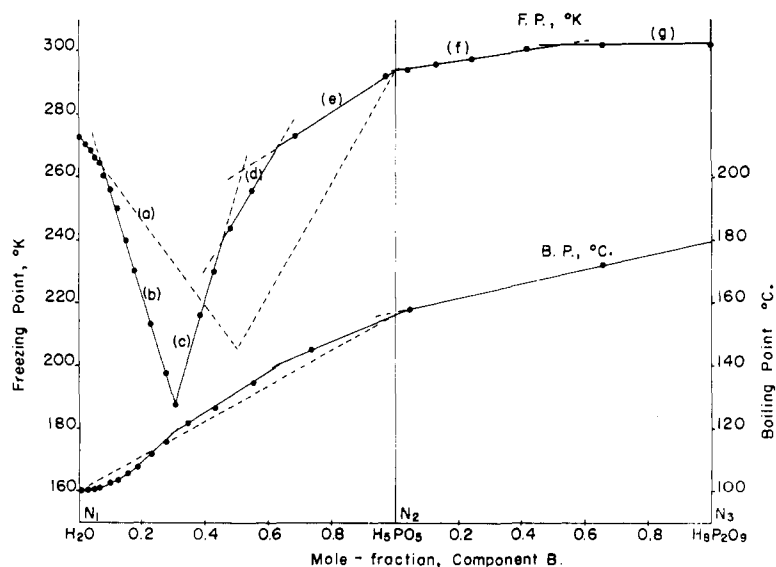


Figure 4. Freezing and boiling points of $H_5P_2O_9-H_2O$ system

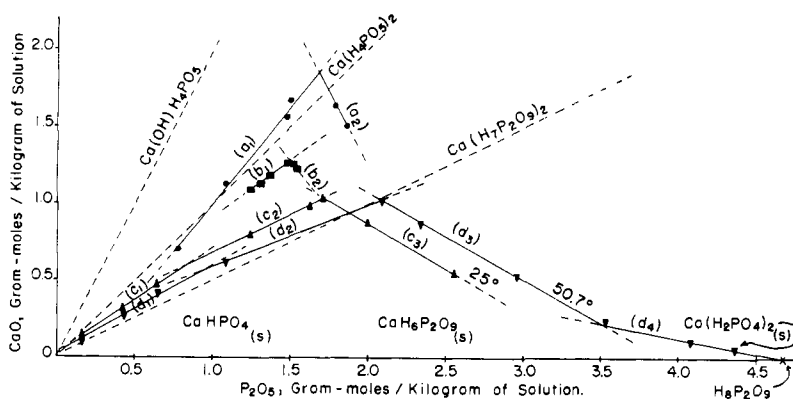
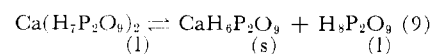
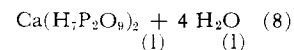
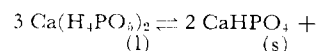
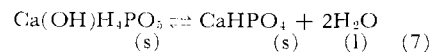


Figure 5. Solubility of calcium phosphate in aqueous solutions

- Aqueous extracts of ordinary superphosphate
- Phosphoric acid neutralized with limestone (22)
- ▲ ▼ Equilibrium at 25° and 50.7° C., respectively (1)

Concerning the calcium salts of pentabasic and octabasic diphosphoric acids, it is reasonable to assume such compounds as $Ca(OH)H_4PO_5$, $Ca(H_4PO_5)_2$, $Ca(H_7P_2O_9)_2$, and $CaH_8P_2O_9$ as definite possibilities in the $CaO-P_2O_5-H_2O$ system. The hydroxyphosphate, ordinarily referred to as the "dihydrate of dicalcium phosphate," is unstable and undergoes slow transformation into the anhydrous form and water at ordinary temperatures (72). The hydroxyl ion may be readily replaced with chloride by treating the solid with hydrogen chloride gas (6).

The normal salt, $Ca(H_4PO_5)_2$, in solution would possess properties unlike those of the anhydrous or hydrated solid monocalcium phosphate. The acid salt, $Ca(H_7P_2O_9)_2$, also in solution, would likewise possess properties unlike those of the solid phase products with which it is associated. The following reaction equations illustrate the differences referred to in this discussion:



The phase relationships of these several compounds are illustrated in Figure 5, which shows the observed mole concentrations of calcium oxide as a function of P_2O_5 in solution. The theoretical CaO/P_2O_5 mole ratios for $Ca(OH)H_4PO_5$, $Ca(K_4PO_5)_2$, and $Ca(H_7P_2O_9)_2$ in solution are shown by dotted lines; the observed data are joined by solid straight lines, for which equations of the general form,

$$y = a + bx \quad (10)$$

may be derived. Mixtures represented by observed points that lie between the theoretical for any two pairs of com-

pounds may be considered as being made up of these compounds in aqueous solution. Thus, the aqueous extracts of superphosphate appear to be composed mostly of the water-soluble form of monocalcium phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, while the equilibrium values of Bassett (7) appear to be mostly the acid salt, $\text{Ca}(\text{H}_2\text{P}_2\text{O}_7)_2$. Patten's (22) data on phosphoric acid neutralized with calcium carbonate being intermediate between the two.

The composition of the solution may be calculated in terms of the several water-soluble compounds by letting a , b , c , and d represent gram-moles of $\text{Ca}(\text{OH})\text{H}_2\text{PO}_4$, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, $\text{Ca}(\text{H}_2\text{P}_2\text{O}_7)_2$, and $\text{H}_3\text{P}_2\text{O}_7$, respectively, per kilogram of solution. Then, for mixtures of the hydroxyphosphate and soluble monocalcium phosphate,

$$a = 2(y - x) \text{ and } b = 2x - y$$

for mixtures of the soluble monocalcium phosphate and the acid salt, $\text{Ca}(\text{H}_2\text{P}_2\text{O}_7)_2$,

$$b = 2y - x \text{ and } c = x - y$$

and for the acid salt and free phosphoric acid mixtures,

$$c = y \text{ and } d = x - 2y$$

Multiplying the derived values for a , b , c , and d by one tenth of the molecular weights of the compounds they represent will convert the results into weight per cent of these salts and acid in solution, as shown in Table VIII.

The influences of time and temperature, as well as of the presence of one solute on the solubility of another, are clearly evident in these data. The first two aqueous extracts of superphosphate were richer in P_2O_5 , but contained less of calcium than the third, while the next three taken in succession contained a slightly higher $\text{CaO}/\text{P}_2\text{O}_5$ mole-ratio than monocalcium phosphate. This suggests hydrolysis of the double salt, yielding a solution richer in P_2O_5 than the material being dissolved and leaving a solid residue richer in calcium. As the solid phase changes from mono- to dibasic phosphate, marked by the intercept of solid lines a_1 and a_2 , the solubility of the hydroxyphosphate in the monocalcium phosphate solution starts to decline and passes back into the zone of mixtures of the soluble mono- and acid calcium phosphates. If the superphosphate consisted of a physical mixture of anhydrous calcium sulfate and monocalcium phosphate monohydrate, there would be no apparent reason for such a high degree of supersaturation.

In the case of phosphoric acid neutralized with limestone, the carbonate salt is even less soluble than the sulfate, and presumably the carbonate ion had an effect on the solubility of the

calcium, which caused a slight shift in the transition point to lower concentrations of both CaO and P_2O_5 in solution, but still not as low in CaO as in the equilibrated solution. Increasing the temperature of the solution causes a shift in the transition point from lower to higher concentrations of P_2O_5 with only very slight decrease in concentrations of CaO in solution. The precipitation of dicalcium phosphate in accordance with reaction Equation 8 would account for this shift in equilibrium values.

For solutions at equilibrium with monocalcium phosphate in the solid phase, increasing the P_2O_5 content causes a decrease in the concentration of CaO in solution. The deposition of $\text{CaH}_6\text{P}_2\text{O}_9$ [or $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$] by dissociation of the acid salt, $\text{Ca}(\text{H}_2\text{P}_2\text{O}_7)_2$, as shown in Equation 9, would account for the change in composition over the range, 2.1 to 3.5 gram-moles of P_2O_5 in solution (Figure 5). Above 3.5 moles of P_2O_5 per kilogram of solution the solid phase shifts to the anhydrous salt as the solution composition approaches that of $\text{H}_3\text{P}_2\text{O}_7$.

Removal of Calcium from Aqueous Extracts

Anions other than phosphate, such as sulfate and fluosilicate, were present in these aqueous extracts in only very small amounts. The acid solution was pale aqua in color and sparkling clear after the calcium had been removed as sulfate. The concentration of P_2O_5 attainable in solution is of the same order of magnitude as in conventional procedures. Acids obtained in this manner showed only a very light deposit of sediment after standing for months. There was no appreciable amount of sludge resulting from the hydrolysis of fluosilicic acid, nor discoloration due to organic matter.

The solid phase gypsum formed by the precipitation of calcium from the solution was readily filterable and contained no appreciable amount of coprecipitated calcium phosphate. The purity of this material after washing was such that it should find ready acceptance for building material purposes or other industrial use.

Relative Economies of Proposed Procedure

The suggested use of aqueous extracts of superphosphate in the production of sludge-free wet-process phosphoric acid introduces no new and untried innovations to the industry. The practice of neutralizing crude wet-process acid with limestone in the process of refining it for food purposes requires substantially the same type of operations as is suggested here, except that the use of phosphate rock for this purpose is

more economical. Fluorine evolution during the acidulation of phosphate rock may be avoided by the use of 50% sulfuric acid (7). By concentrating the fluorine as fluosilicate in the filter cake, a more complete recovery of it in a subsequent operation (2) would be facilitated.

The introduction of an extra extraction and filtration step entails some additional costs, which should be more than offset by the economies realized in structural materials, lower power consumption, and reduced reagent acid requirements. By producing superphosphate as an intermediate product in the process, greater flexibility in operation with considerable reduction in manpower should be possible, due to elimination of the necessity for full time around-the-clock operation. Storage facilities for materials in process should be greatly simplified with corresponding reduction in structural material costs. Enhanced corrosion problems attributable to the presence of hydrofluoric and/or fluosilicic acid in phosphoric acid solution would be avoided in both acid production and acid concentration by evaporation. The elimination of sludge should greatly reduce shutdown for cleaning operations.

The procedure may be applied to the production of sludge-free acid from crude wet-process acid produced by conventional procedures with obvious benefits, and phosphoric acid refined in this manner should find ready acceptance in the production of liquid mixed fertilizers.

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FERTILIZER TECHNOLOGY

Liquid Fertilizers from Wet-Process Phosphoric Acid. Suspension of Impurities

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Wet-process phosphoric acid has not been used extensively in liquid fertilizers because it contains impurities that precipitate during ammoniation; the precipitated impurities settle and thicken during storage. Moreover, crystals of magnesium ammonium phosphate (struvite) grow in the ammoniated products of some acids to a size large enough to plug spray nozzles. In tests of the production of liquid fertilizers from wet-process acid, a stable, nonsettling suspension was produced by adding 1 to 2% by weight of a swelling-type clay or by ammoniating at pH 7 or higher and adjusting the product to normal pH (6.7) for storage. Growth of struvite crystals was inhibited by quick cooling to room temperature or by ammoniating to a low pH (6.0); however, by the latter method, the settling rate was increased appreciably. Best results were obtained by a combination of processes involving ammoniation at a high pH and adjusting to a low pH for storage; the products were slow settling, highly fluid, and free of large crystals.

THE LIQUID mixed fertilizer industry in the United States had its beginning in California some 30 years ago. However, it was not until 1954 that the first bulk plant was built east of the Rockies. It is estimated that there are now over 350 plants producing about 200,000 tons per year of plant food as liquid mixed fertilizers. This is about 5% of the total applied as mixed goods.

The basic operation for the production of liquid mixed fertilizers is the neutralization of phosphoric acid with ammonia or ammoniacal solutions. Supplemental nitrogen may be supplied as urea, ammonium nitrate, or urea-ammonium nitrate solutions. Potash usually is supplied as potassium chloride. Most

producers use electric-furnace phosphoric acid as the source of phosphate. However, the lower cost of wet-process phosphoric acid in most areas has led to a major effort in finding ways of using it. The main difficulty is that the wet-process acid contains impurities that precipitate when the acid is ammoniated, and the resulting sludge may settle and cause handling problems. The precipitated impurities can be removed from the product or a sequestering agent can be used to keep them in solution. Another, and perhaps simpler, method is to suspend them in such a way as to give satisfactory handling and application properties; these properties are high fluidity, low degree of settling, and absence of par-

ticles large enough to clog spray nozzles.

Experience has shown that there are no serious problems, if liquid fertilizers produced by ammoniation of wet-process acid are applied to the field immediately after production. This is the basis on which several producers now use wet acid. However, difficulties may occur if the product is to be stored for more than a few days. The precipitated impurities settle and may require redispersion. Also, with some acids, struvite ($MgNH_4PO_4 \cdot 6H_2O$) crystals form and grow to a size large enough to clog spray nozzles.

This paper covers work at the Tennessee Valley Authority (TVA) aimed toward development of techniques and