

Factors Affecting Fluorine Volatilization during Acidulation of Phosphate Rock with Sulfuric and Phosphoric Acids

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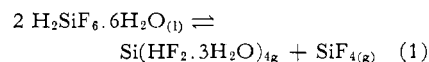
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The evolution of fluorine in the reaction of phosphate rock with sulfuric and phosphoric acids is affected by the following factors: amount and concentration of sulfuric and phosphoric acids, initial acid temperature, order and type of mixing of the reagents, the presence of water, and the acid-rock ratios. The determination of fluorine and the mechanism governing its release are also considered.

THE EVOLUTION OF FLUORINE in superphosphate manufacture has engaged the interest of this laboratory for many years and certain aspects of the subject have been discussed (5-9, 15). Several papers describing the behavior of hydrogen fluoride (3, 4) and of fluosilicic acid (10, 14, 19) in aqueous solutions have also been published. The findings of such studies with pure compounds provide a sound theoretical basis for the presentation and discussion of the heretofore unpublished results of a study of factors affecting the volatilization of fluorine during the acidulation of phosphate rock. Observations made during this investigation cast considerable doubt upon the generally accepted notions about the relationship between fluorine and silica in phosphate rock (17, 18).

Evolution of Silicon Tetrafluoride Gas from Aqueous Fluosilicic Acid

The conditions that govern the release of gaseous silicon tetrafluoride from the solution phase of phosphate rock acidulates are deducible from the known behavior of fluosilicic acid in aqueous solution. In the ternary system, hydrogen fluoride-silicon tetrafluoride-water, the composition of the invariant solution, which boils at 116.1° C., corresponds to 10% hydrogen fluoride, 36% fluosilicic acid, and 54% water (14), or 20% hydrogen fluoride, 26% silicon tetrafluoride, and 54% water. The partial pressure of silicon tetrafluoride above aqueous solutions of fluosilicic acid (1, 19) may be correlated with these data on the basis of a simple equilibrium equation,



in which the invariant solution of Munter, Aepli, and Kossatz (14) is represented by the complex compound, $\text{Si}(\text{HF}_2 \cdot 3\text{H}_2\text{O})_4$ or $\text{H}_4\text{SiF}_8 \cdot 12\text{H}_2\text{O}$.

The equation for the partial pressure of silicon tetrafluoride above aqueous solutions of fluosilicic acid is

$$\log p(\text{SiF}_4)_{75^\circ \text{C.}} = -2.934 + 0.1018 w \quad (2)$$

where w represents weight per cent of fluosilicic acid in solution. According to this equation, the partial pressure of silicon tetrafluoride in the gas phase becomes appreciable ($p = 1$ mm. of mercury, $\log p = 0$) at 28.85% fluosilicic acid (Figure 1) and reaches 1 atm. ($p = 760$ mm., $\log p = 2.8808$) at 57.13% of fluosilicic acid equivalent to 100% $\text{H}_2\text{SiF}_6 \cdot 6\text{H}_2\text{O}$ (Equation 1).

In Figure 1, the vapor pressure measurements of Whynes and Dee (19)

and the reciprocal of the $\text{H}_2\text{F}_2/\text{SiF}_4$ measurements of Baur (7) are correlated with the theoretical partial pressures of silicon tetrafluoride gas, based on Equations 1 and 2.

The formation of a series of hydrates of hydrogen fluoride, indicated by the cryoscopic data of Cady and Hildebrand (4), is confirmed by the isothermal vapor pressure measurements of Brosheer, Lenfesty, and Elmore (3) and the isobaric data of Munter, Aepli, and Kossatz (14). The cryoscopic data (4) indicate a HF-H₂O ratio of 1 to 2, while considerations of the fact that hydrofluoric acid forms bifluoride salts lead to the conclusion that $\text{H}_2\text{F}_2 \cdot 4\text{H}_2\text{O}$ is probably the correct formula for the highest

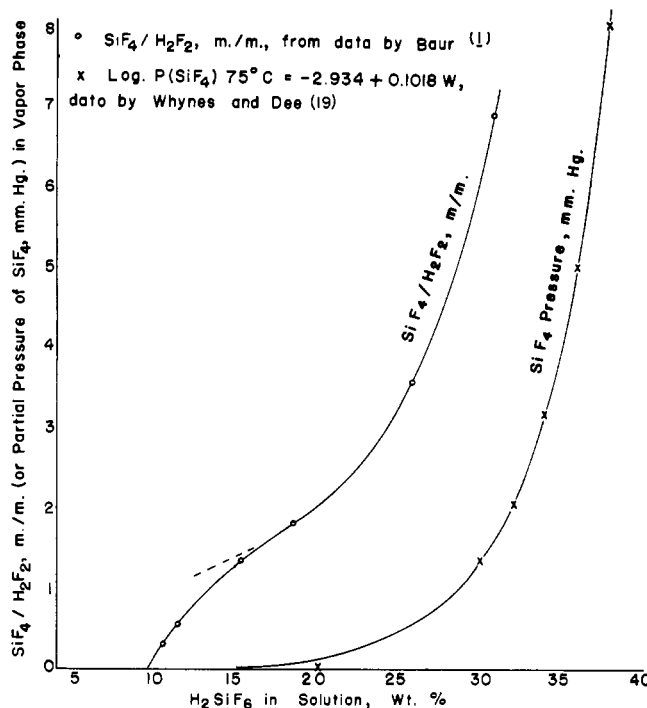


Figure 1. Correlation of silicon tetrafluoride to hydrogen fluoride mole-ratio with partial pressure of silicon tetrafluoride in the gas phase above fluosilicic acid

hydrate in the $H_2F_2-H_2O$ system. An unusually high degree of stability is indicated for these hydrates by the relatively low coefficient of activity of aqueous hydrofluoric acid solutions (2) and by the fact that no known chemical reagent will effect a separation of water from hydrogen fluoride (16). It is logical to assume that the reaction of these hydrates of hydrogen fluoride with silica will yield the fluosilicate complexes indicated in Equation 1.

Methods and Materials

Mixing Technique. A specially designed laboratory mixer was used in most of the work. It consisted of a stainless steel cup (11-cm. outside diameter, 10.2-cm. inside diameter) detachably mounted on a turntable motor driven at 320 r.p.m. Fixed stainless steel mixing blades set at about a 30° angle to the direction of movement rabbled the material from the sides toward the center of the cup in much the same manner as the mixing blades of an ice cream freezer. The mixing blades were attached to a cover plate secured by a screw clamp and grooved guide to a binding post and could be raised or lowered into position without touching the walls or bottom of the mixing cup.

Gases evolved during mixing operations were drawn off by a hydraulic aspirating pump attached to a tube passing through the cover plate.

The usual procedure was to place a weighed portion of prediluted acid in the mixing cup and then, with stirrer going, add a weighed portion of rock. Deviations from this order of mixing will be noted. Stirring was continued, until the mixture stiffened to the point where the danger of segregation due to sedimentation was past. Overmixing, which tends to produce a hard crumb, was avoided as far as possible. After the mixture had set, it was transferred from the cup to open glass beakers to cure at room temperature to constant weight. The product was turned and stirred several times while curing so as to expose fresh surfaces and promote uniform drying. After drying to constant weight, the product was ground to pass a 20-mesh screen and carefully rolled on paper to ensure uniform mixing before storing in sealed glass jars for analysis. Analyses were run in duplicate and rechecked when differences greater than about 2% on the absolute scale were observed.

Hand mixing was used in some of the earlier experiments, particularly those concerned with the determination of acid requirements.

Materials. Regular acidulation grades of commercially ground Florida land pebble phosphate rock and apatite from the U.S.S.R. were used. Pertinent screen and chemical analyses and the

Table I. Composition and Acid Requirement of Test Phosphates

Lot No.	Variety of Phosphate	CaO	P ₂ O ₅	F	H ₂ SO ₄ Required, ^a G./100 G. Rock
1934 ^b	Florida land pebble	45.2	31.3	3.82	54.2
2212 ^c	Apatite from U.S.S.R. ^d	53.6	38.8	3.15	63.0

^a In accordance with Equation 3.
^b Screen analysis: -100 mesh, 78.1%; -200 mesh, 37.5%.
^c Screen analysis: -100 mesh, 88.9%; -200 mesh, 50.4%.
^d Mined on Kola Peninsula.

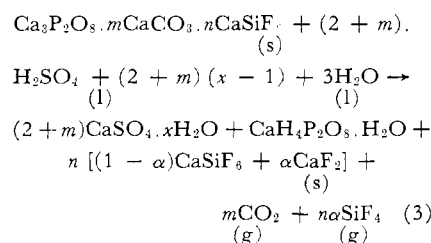
Table II. Fluorine Evolutions Calculated from Fluorine-Phosphorus Ratios and from Yield of Superphosphate

Superphosphate ^a Yield, g.	F, %	Volatilized F, G./100 G. Rock	
		Ratio method	Yield method
140.2	1.59	1.59	1.59
142.5	1.76	1.32	1.31
142.6	1.86	1.17	1.17
143.1	1.94	1.03	1.04
144.8	2.07	0.82	0.82
145.5	2.17	0.66	0.66

^a 100 grams of Florida land pebble rock with variable amounts of water acidulated with 25 ml. of 95.4% H₂SO₄.

acid requirements of these materials are given in Table I.

Acid requirement, determined from the acid consumption per unit of phosphorus pentoxide made available in underacidulated mixtures, may be computed on the basis of the calcium oxide, phosphorous pentoxide, and fluorine contents of the rock in accordance with the following equation in which the composition of the rock is expressed in terms of tricalcium phosphate, calcium carbonate, and calcium fluosilicate.



m and *n* represent the mole ratios of excess calcium considered as carbonate and fluosilicate, respectively, to tricalcium phosphate and α , the fraction of fluosilicate dissociated into hydrogen fluoride in the liquid, and silicon tetrafluoride in the gas phase. According to this reaction equation, the evolution of silicon tetrafluoride does not alter the amount of calcium bound as fluorine compounds in the superphosphate and therefore does not affect the acid requirements of the rock. Because the calcium equivalent of the fluorine considered as fluosilicate does not consume sulfuric acid, this amount of calcium

Table III. Fluorine Evolution in Replicate Acidulations^a

Replicate No.	Volatilized with Acid Concentration (% H ₂ SO ₄) of			
	60.3	70.6	80.0 ^b	90.3
	% of Total			
1	9.7	27.0	25.4	41.4
2	9.2	29.3	25.9	40.8
3	9.4	27.8	24.9	40.8
4	10.5	35.7	26.4	42.9
Mean	9.7	30.0	25.7	41.5
Deviation ^c	0.5	3.4	0.6	0.9

^a 100 grams of Florida land pebble treated with sulfuric acid corresponding to 106% of requirement (Table I).

^b 95% of acid requirement (Table I) used.

^c Root-mean-square deviation.

should be subtracted from the total for the computation of the acid-rock ratio. The acid-rock ratios for the test rocks, calculated with the aid of Equation 3, are shown in the last column of Table I.

Determination of Fluorine Volatilization. In the past the fluorine evolution was generally computed with the use of fluorine-phosphorus ratios for the rock and for the product (15). In the case of laboratory preparations, where sensibly quantitative recovery of the air-dry product can be made, the evolution can be calculated from the fluorine content of the rock and the yield and the fluorine content of the product. Because close agreement of the results by the two procedures (Table II) was found for materials of the type prepared in this work, the latter procedure was adopted.

Reproducibility of the volatilizations is illustrated by the results from repeated preparations shown in Table III.

Release of Fluorine to Solution Phase

Mixing sulfuric acid and phosphate rock gives rise to two principal reactions as regards phosphorus—a primary one, in which phosphoric acid is liberated, and a secondary one, in which the liberated phosphoric acid reacts with residual rock. According to the traditional view of the mechanism of fluorine volatilization under these conditions (17, 18), fluorine is released from the rock during the primary reaction as hydrofluoric acid, which then attacks the silica (quartz

or silicate) carried in the rock to form fluosilicic acid, and this in turn decomposes to yield silicon tetrafluoride. This long-accepted sequence of reactions is questionable, because the bulk of fluorine evolution as silicon tetrafluoride occurs on contact between the rock and acid solution, whereas reactions of moderately strong hydrofluoric acid with quartz and many silicates are usually rather slow. The prompt and rapid evolution experienced in practice seems more consistent with the direct formation of silicon tetrafluoride. The results of two rather simple tests support the latter view.

If, indeed, hydrofluoric acid be the

initial form of the released fluorine, an artificial increase in its concentration in solution should cause a proportionate increase in fluorine volatilization. Actually in laboratory acidulations of Florida land pebble with sulfuric or phosphoric acids containing up to 12% of hydrogen fluoride, increased fluorine evolution was not observed. The hydrofluoric acid reacted with the calcium phosphate component of the rock to form available phosphate rather than with the silica to enhance the volatilization of fluorine. Similarly, in an earlier experiment (6) the addition of quartz flour to a rock that was nearly silica free did not increase the fluorine volatilization, and

Table IV. Fluorine Volatilization during Acidulation^a of Florida Land Pebble with Admixed Calcium Fluosilicate

From rock	Fluorine in Acidulate		Fluorine Volatilized	
	From calcium fluo-silicate ^b	Total	Grams	% of total
3.82	0.00	3.82	1.36	35.6
	0.52	4.34	1.56	35.9
	1.04	4.86	1.72	35.4
	1.56	5.38	1.91	35.5

^a Machine mixed with sulfuric acid (70.6%) equivalent of rock and calcium fluosilicate.
^b Pure material prepared in laboratory (Lot 1350, 51.84% F).

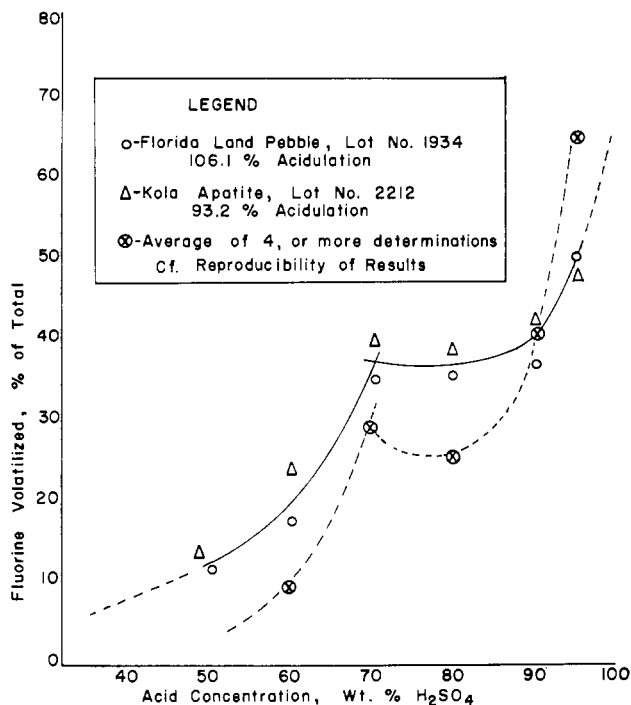


Figure 2. Influence of acid concentration on fluorine volatilization during acidulation of phosphate rock

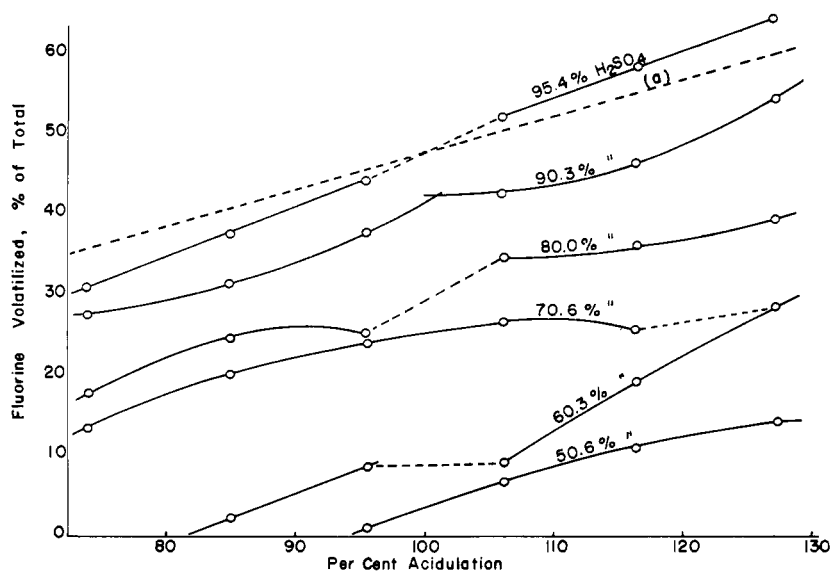


Figure 3. Influence of degree of acidulation with different concentrations of sulfuric acid on fluorine volatilization from Florida rock, lot 1934

this ineffectiveness of added silica was confirmed in plant-scale tests by a superphosphate producer using hydrous silica. On the other hand, artificial increase in the initial fluosilicate concentration by incorporating calcium fluosilicate with the rock resulted in a proportionate increase in fluorine evolution (Table IV). These findings teach that the fluorine released from phosphate rock in superphosphate manufacture behaves not like hydrofluoric acid, but as fluosilicic acid.

Influence of Water Content on Fluorine Evolution

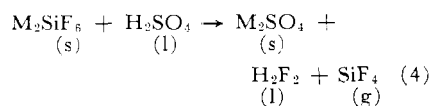
The influence of water on fluorine evolution from phosphate rock acidulates was determined, along with other factors, in a series of hand-mixed preparations in which water was the only controlled variable. The rock was 80% acidulated and the results were computed on the basis of the fluorine content of rock equivalent to the acid used, it being assumed that the excess of rock remained unaffected by the acid treatment. The results indicate that 3.78 grams of fluorine per 100 grams of water were retained in the superphosphates.

In the range, 50 to 70% sulfuric acid, there is a transition in the form of calcium sulfate from gypsum to the hemihydrate and anhydrous forms (73), due to the competition of the other products of reaction for water in the system. The influence of these products of reaction on the evolution of fluorine is shown in Figures 2 and 3.

Figure 2 shows the percentage of fluorine volatilized from superphosphates made with Florida land pebble rock 1934 and with Kola apatite, 2212. The curves represent results obtained at different seasons of the year and reflect the influence of different ambient conditions not controlled in the tests. The coincidence of the break in these curves with the calculated concentration of acid to yield phosphoric and fluosilicic acid as primary products, and calcium phosphate and calcium fluosilicate as secondary products of reaction together with calcium sulfate in the form of gypsum

indicate that the fluorine in the rock is combined as fluosilicate. As the concentration of reagent acid increases, the concentration of fluosilicic acid in the resulting solution increases, until it reaches the point of dissociation into the invariant complex, $H_4SiF_8 \cdot 12H_2O$, and silicon tetrafluoride, according to Equation 1. The transition of higher to lower hydrates of the several products of reaction prevents further increase in fluorine volatilization until substantially all water has been eliminated from the system.

Fluorine volatilization from the virtually anhydrous mixtures made with 90 and 95% sulfuric acid increased in accordance with the reaction equation representing complete disintegration of fluosilicate salts when treated with concentrated sulfuric acid (10),



Influence of Variable Acid-Rock Ratios

Variations in the evolution of fluorine as a function of variable acid-rock ratios with different acid concentrations are shown in Figure 3. In all cases, fluorine volatilization increased with the degree of acidulation. Fluctuations in the volatilization curves are attributable to the influence of variations in water of crystallization in the reaction products. The greatest increase in fluorine evolution occurred between 60 and 70% acids in underacidulated mixtures. In overacidulated preparations the volatilization curve of the 60% acid showed a much higher rate of increase than the other acid strengths. This concentration of acid is close to the critical value indicated for the transition from gypsum to the hemihydrate and anhydrous forms of calcium sulfate in superphosphate (13).

The degree of acidulation referred to in Figure 3 pertains to the acid requirement of the rock for superphosphate production according to Equation 3. The reaction between the rock and sulfuric acid for the production of phosphoric acid requires $3.655/2.503 = 1.46$, or 146% of the superphosphate acid requirement. Thus, the 127% acidulation on the superphosphate scale is only 87% acidulation on the phosphoric acid scale. Consequently, there was sufficient rock in all of these mixtures to consume all of the sulfuric acid, but there was not sufficient excess rock in the overacidulated mixtures to react with all of the phosphoric and fluosilicic acids in secondary reactions. As calcium fluoride and/or fluosilicate are less soluble than monocalcium phosphate, there is a tendency for these salts to be preferentially precipitated. Under these circumstances excess phosphate rock would tend to reduce fluorine volatiliza-

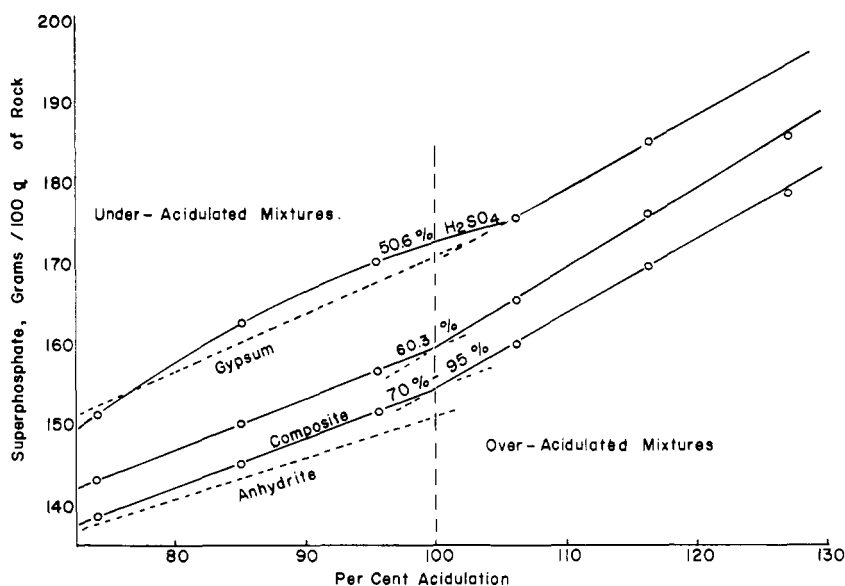


Figure 4. Influence of degree of acidulation with different concentrations of sulfuric acid on air-dry weight of superphosphate made with Florida rock, lot 1934

tion. On the other hand, hydrofluoric acid is a more volatile acid than phosphoric acid. Accordingly, in the curing and drying process, the latter would tend to displace the hydrofluoric acid from overacidulated mixtures. The resultant of these factors would tend to cause a rotation of the fluorine volatilization curve in a counterclockwise direction about the neutral point. This is represented in Figure 3 by the deviation of the volatilization curve for 95% acid from dotted line *a*, representing the proportionate volatilization observed at 100% acidulation. A similar rotation (not shown) is also indicated for the volatilization curves of some of the other acid concentrations.

Influence of Hydrate Formation on Superphosphate Yields

Water taken up in the formation of hydrated products is a factor affecting the volatilization of fluorine (Figures 1 to 3). Hydration of the products must also affect the air-dry weight of superphosphate to which attention is directed in Figure 4. The calculated yields of products containing calcium sulfate in the form of gypsum and anhydrite are indicated by dotted lines. Hemihydrate, a product undoubtedly obtained with 60% acid, would have yielded superphosphates intermediate between those containing anhydrite and gypsum. Thus, mixtures of anhydrite and hemihydrate in varying proportions depending on the degree of acidulation plausibly explain the deviation of the composite weights of 70 to 95% acid products from the calculated weights for anhydrite.

In overacidulated mixtures, the excess of phosphoric acid retained water in greater proportion to phosphorus pent-

oxide than those in which all of the phosphoric acid reacted to form calcium phosphate. The increase in the ratio of water to phosphorus pentoxide in these overacidulated products caused an increase in the slope of the curves representing yields of superphosphate. The occurrence of the break in these curves at 100% acidulation demonstrates the validity of Equation 3 on which the calculations of the degrees of acidulation are based.

Influence of Order of Mixing

Volatilizations obtained from machine-mixed preparations usually were considerably less than from previous hand-mixed preparations. This difference in otherwise comparable conditions appeared to be due to the order of mixing the several ingredients. To test this postulate a series of preparations in which the hand-mixed order of adding the concentrated acid to phosphate rock and water was compared with the usual order of adding the rock to prediluted acid (Figure 5). In this series, however, all preparations were machine-mixed and only the order of adding the reactants was varied. The greater volatilizations indicated for the order of hand-mixed preparations are attributable to higher temperatures produced by the heat of reaction between water and sulfuric acid—a factor of considerable influence at the critical 70% acid concentration.

Influence of Initial Acid Temperature

The influence of the reagent acid temperature on fluorine volatilization varied with the concentration of the acid. Increasing the initial acid temperature of 50% acid from 7° to 65° C.

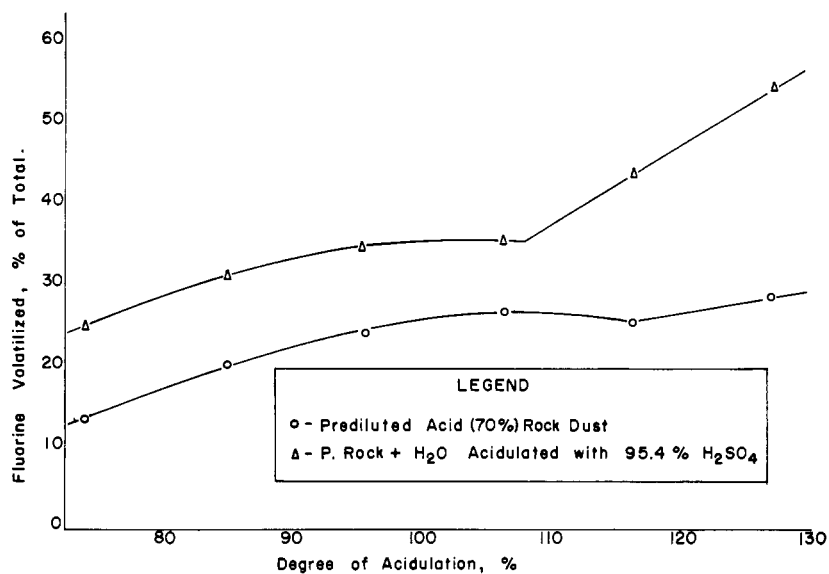


Figure 5. Influence of order of mixing phosphate rock, sulfuric acid, and water on fluorine volatilization from Florida rock, lot 1934

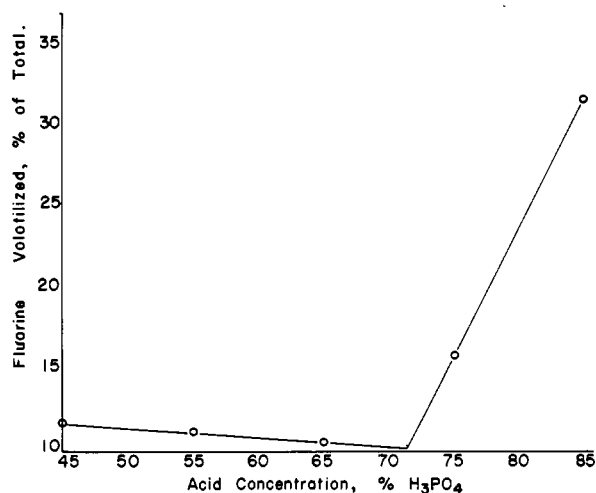


Figure 6. Influence of concentration of phosphoric acid on fluorine volatilization, 106% acidulation of Florida rock, lot 1934

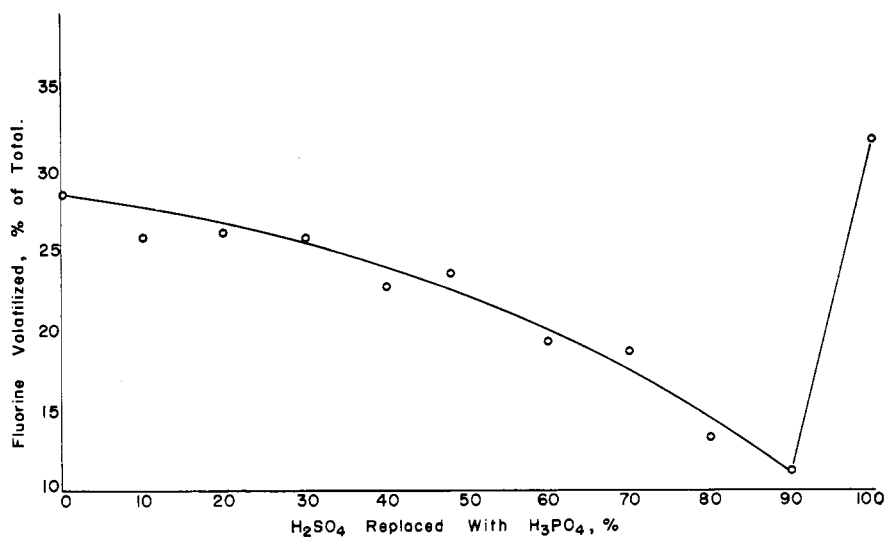


Figure 7. Influence of phosphoric acid replacement of sulfuric acid on fluorine volatilization from Florida rock, lot 1934, 106% acidulation

had no significant effect on fluorine volatilizations. Increasing the temperature of 60% acid from 12° to 70° C. increased volatilization from 15 to 20%; of 70% acid from 8° to 60° C. increased volatilization from 25 to 42%; of 80% acid from 11° to 68° increased the volatilization from 38 to 46%. Above 80% acid, the volatilizations at low temperatures were almost as great as at high temperatures. Thus, raising the temperature of 90% acid from 8° to 58° C. increased the volatilization only from 56 to 59%; and of 95% acid from 10° to 63° C. increased volatilization from 65 to 67%. From these observations it is evident that the concentration of the acid (11, 12) is of far greater significance than the initial acid temperature.

Influence of Phosphoric Acid Concentration

The influence of phosphoric acid concentration on fluorine volatilization is of interest not only in the interpretation of results attributable to the secondary reaction in ordinary superphosphate preparation, but also in the development of conditions favorable to fluorine volatilization in the manufacture of wet-process phosphoric acid and concentrated superphosphate. The acid used in these studies (c.p. reagent acid grade) was made from elemental phosphorus produced by the phosphate reduction furnace process and was substantially free from fluorine. Varying the concentration of this acid over the range 45 to 72% phosphoric acid produced little change in fluorine volatilization from phosphate rock-phosphoric acid mixtures. But increasing the concentration from 75 to 85% caused a rapid increase in volatilization up to one third of the total in the rock, in accordance with equilibrium Equation 1. The results shown in Figure 6 indicate that the water formed by reaction between the rock and phosphoric acid is about equal to that consumed in the hydration of the fluosilicic acid released by the reaction.

Mixed Acid Superphosphate Preparations

Considerable interest has been shown in recent years in the production of enriched superphosphates using mixtures of phosphoric and sulfuric acids (20). The data shown in Figure 7 are for fluorine volatilizations from a series of such mixtures in which 2 moles of 85% phosphoric acid were substituted for each mole of 70.6% sulfuric acid replaced in preparations made with Florida rock 1934. Diluting sulfuric acid with phosphoric acid tends to retain silicon tetrafluoride in the mixture and the reaction between the rock and phosphoric acid is retarded by the presence of calcium sulfate produced in the reaction between the rock and sulfuric

acid. But, in the absence of the interfering sulfate, the concentrated phosphoric acid attacks the rock with vigor and releases fluosilicic acid in concentrations that undergo substantial decomposition before it has an opportunity to recombine with the phosphate rock.

The influence of relatively small concentrations of sulfuric acid in phosphoric acid has a practical bearing on fluorine evolution in the manufacture of superphosphate with wet-process phosphoric acid. For example, an acid containing 2.6% sulfur trioxide and 52.5% phosphorus pentoxide corresponds to an 8% replacement of phosphoric acid with sulfuric acid. This could cause an appreciable reduction in fluorine volatilization, according to the results shown in Figure 7.

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Received for review September 26, 1958.
Accepted March 30, 1959. Division of Fertilizer and Soil Chemistry, 134th Meeting, ACS, Chicago, Ill., September 1958.

INSECTICIDE EVALUATION

Dermal and Oral Treatments of Cattle with Phosphorus-32-Labeled Co-Ral

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Only small amounts of phosphorus-32 were absorbed through the skin and eliminated in the urine following dermal application of the compound to cattle. High levels of the unchanged toxicant were found on the hair several weeks after treatment. The compound was ineffective as a systemic against stable flies and screwworm larvae but highly effective against these insects by contact. On oral treatments, at 10 and 20 mg. per kg., approximately 38% of the dose was excreted in urine as polar degradation products and about 35% in the feces 7 days after treatment.

CO-RAL *O*-(3-chloro-4-methylumbelliferone) *O,O*-diethyl phosphorothioate, has been shown by several workers (7, 8) to be a promising insecticide for the control of second- and third-instar cattle grubs when applied dermally to cattle. Brundrett, McGregor, and Bushland (1) have found this compound to be effective against grubs prior to their encystment. To obtain information on the absorption, excretion, and systemic action of this compound, several cattle were treated both dermally and orally with phosphorus-32-labeled Co-Ral at Kerrville, Tex.

Materials and Methods

The phosphorus-32-labeled Co-Ral used in these studies had a specific

activity of 426 to 923 counts per minute per microgram and a radiochemical purity greater than 97.5%.

The compound was applied dermally to three Hereford steers as an emulsion prepared from 20% xylene-Triton X-100 concentrate, using a 2-gallon pressure sprayer equipped with a brush on the nozzle.

To prevent ingestion of the insecticide and contamination of the urine, the head and underside of the animals were not treated. The runoff was collected and assayed radiometrically. A summary of dermal treatment data is given in Table I. Precautionary measures were taken throughout the experimental period to

Table I. Dermal Treatment Data with P³²-Labeled Co-Ral on Three Hereford Steers

1956-7	Weight of Animal, Kg.	Active Ingredient, %	Intended Dose		Applied Dose		Runoff	
			Grams	Mg./Kg.	Grams	Mg./Kg.	Grams	%
November	152	2	11.4	75	9.8	64.5	1.7	14.9
February	156	2	11.7	75	7.6	48.8	4.1	35.0
March	147	1	4.4	30	4.0	27.2	0.4	9.1