Fertilizer by Fusion of Phosphate Rock and Gypsum

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Phosphate rock containing 33.6% phosphorus pentoxide was fused with gypsum, dehydrated by heating at 500° F. for 3 hours, in various proportions in a gas-fired laboratory furnace. The molten product was quenched in water and subsequently dried. Products of high phosphorus pentoxide availability (>90%) were obtained when mixtures of phosphate rock and gypsum containing at least 65% dehydrated gypsum were fused. In the early fusions various proportions of langbeinite, muriate, or glasserite were used as fluxing agents. As addition of the flux decreased phosphorus pentoxide availability, subsequent fusions were made with rock and dehydrated gypsum alone. Typical products, made by fusing a mixture containing 30% phosphate rock and 70% dehydrated gypsum, contained at least 10.5% total phosphorus pentoxide and 10.4% available phosphorus pentoxide as determined by 2% citric acid. The product was granular, nonhygroscopic, and easily ground. Production of phosphate fertilizer by this process is believed to have definite economic advantages for certain areas and is especially suited to Iowa, where large deposits of gypsum are available. The process represents a possible means of conserving sulfur.

PART OF THE FERTILIZER RESEARCH program at Iowa State College is directed towards "thermal" processing of phosphate rock. The phosphorus pentoxide content of the rock is made available by heat treatment in contrast to acid treatment, as is common in the manufacture of superphosphate.

Many workers have been interested in thermal processing of phosphate rock (9, 10, 17, 21, 22) and at least two distinct types of processes have evolved. The defluorination process is dependent upon the removal of the fluorine content of the rock in a calcined or molten state (7, 8, 11, 18, 20). The fusion process is dependent upon the fusion of the rock with certain addition agents, such as silicate or sulfates, without the removal of fluorine (5, 14-16, 19, 23).

The fusion process is a relatively new approach to the manufacture of fertilizer and has some significant aspects. No acid is required. Physical properties are superior to those of acidulated fertilizers, in that the product is granular, nonhygroscopic, and nonacidic, and can be produced as mixed goods directly containing phosphorus and other plant nutrients. The process is comparatively simple and the economics may be favorable in certain areas, compared with superphosphate manufacture. The especial significance of gypsum in the fusion process is that it represents a raw material of lower cost, more widely available than other addition agents, and may encourage industrial development of this type of fertilizer.

Materials and Procedures

Raw Materials. The phosphate rock used in these studies was obtained ground from the Davison Chemical Corp., and was dried at 100° C. for 5 hours before use. The gypsum was a commercial product from the U. S. Gypsum Co., Fort Dodge, Iowa, which was ground in a roll mill and subsequently in a laboratory Mikro Samplmill before use. Chemical and screen analyses of these materials are given in Table I.

To prevent sample losses resulting from the rapid dehydration of the gypsum in the furnace, it was heated at 500° F. for 3 hours before use, to remove the water of hydration. The material resulting from this heat treatment is referred to in this paper as dehydrated gypsum, as distinguished from calcined gypsum, which might suggest the removal of sulfate. The term "anhydrite" is not appropriate to this material, as a very particular crystal structure would be implied. In the preheating step no attempt was made to ensure a definite crystal compound.

Fusion Furnace. A small scale gas-fired refractory furnace was used for the fusions. This furnace was built of Babcock & Wilcox K-28 high temperature insulating brick, as shown in Figure 1. One of the bricks in the front was cut, so that a portion could be removed for inserting and removing the crucibles containing the charge. A laboratory blast burner was used. By impinging

Table I. Chemical and Screen Analyses of Raw Materials

Constituent	% of Sample (Dry Basis)[a]	
	Phosphate rock	Gypsum
H₂O (combined)	. . .	19.9
P_2O_5	33.6	. . .
CaO	47.8	32.1
SO_3	. . .	44.8
MgO	0.40	. . .
SiO_2	9.1	2.5
R_2O_3	2.41	0.4
CO_2	. . .	0.6
F	4.6	. . .
Screen size		
−48 +60	0.3	. . .
−48 +65	. . .	0.7
−60 +100	10.3	. . .
−65 +100	. . .	6.8
−100 +150	11.4	10.9
−150 +200	22.8	13.1
−200	. . .	68.5
−200 + 325	43.5	
−325	11.7	

[a] 100° C. for 5 hours for phosphate rock, 45° C. for 2 hours for gypsum.
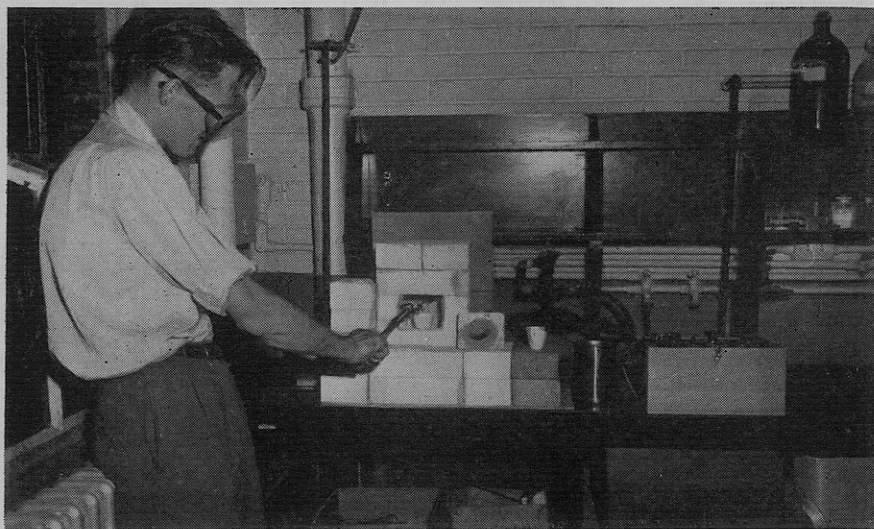
Figure 1. Laboratory fusion furnace

the mixed stream of air and natural gas on an incandescent surface, temperatures of 2800° F. inside the furnace could be obtained.

Crucibles. Tungsten, graphite, and porcelain crucibles were used. However, as most of the fusions were made at temperatures below 2500° F., porcelain crucibles were generally more convenient.

Procedure. Phosphate rock was intimately mixed with various proportions of dehydrated gypsum in either 20- or 30-gram charges. The mixture was placed in the crucible and inserted in the furnace through the opening. As the charge melted, bubbles appeared. The charge was left in the furnace from 5 to 10 minutes and then removed by tongs and immediately quenched by pouring into a beaker of water. The quenched product was filtered, dried, and analyzed.

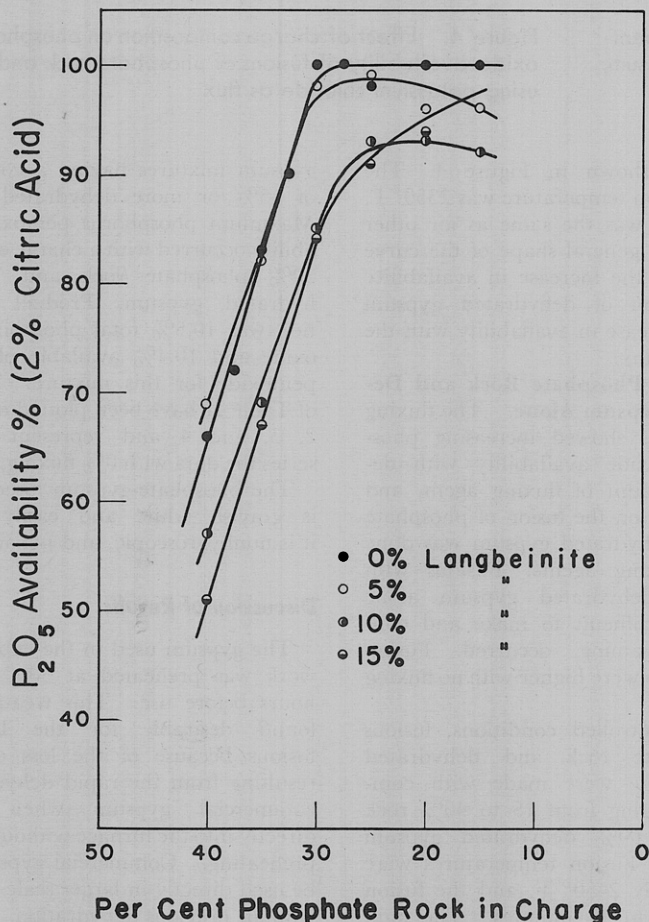**Analyses.** The methods of analyses set forth by the Association of Official Agricultural Chemists (3) were used for carbon dioxide, magnesia, and the separations for phosphorus pentoxide. A colorimetric procedure (6) was used for the actual phosphorus pentoxide determinations. Available phosphorus pentoxide was determined by the modified 2% citric acid method proposed by MacIntire and associates (13). Iron, alumina, and silica were determined according to the methods of the Association of Florida Phosphate Mining Chemists (2). Fluorine was determined by the method of Brabson, Smith, and Darrow (4), in which perchloric acid digestion alone is used. Calcium was determined by the method of Hoffman and Lundell (12). Samples of the fused products were ground to pass an 80-mesh screen before analysis.

The gypsum was analyzed according to the standard methods of the American Society for Testing Materials (1).

Experimental Results

Fusion of Phosphate Rock and Gypsum Using Fluxing Agents. In the early work small amounts of fluxing agents were added to the mixture of rock and dehydrated gypsum to promote a fluid melt. Fluxing agents were commercial langbeinite ($K_2SO_4 . 2Mg_2SO_4$), commercial glasserite ($3K_2SO_4 . Na_2SO_4$), and c.p. potassium chloride. These materials were selected from the results of previous fusion studies using them as addition agents alone. In addition to promoting a more fluid melt, these materials also contained potash (K_2O), which was desirable in the product.

Fusions made with mixtures of phosphate rock and dehydrated gypsum using langbeinite as a flux had charge compositions varying from 15 to 40% phosphate rock, 45 to 80% dehydrated gypsum, and 5 to 15% langbeinite. The results, in terms of the phosphorus pentoxide availability of the product (ratio of available phosphorus pentoxide to total phosphorus pentoxide), are shown in Figure 2, where each point represents an average of at least two fusions. Fusion temperatures were approximately 2350° F. and fusion time was approximately 5 minutes after appearance of initial bubbling. The data indicate that the addition of dehydrated gypsum considerably increased the phosphorus pentoxide availability of the product but that the addition of langbeinite as a flux decreased it. Optimum charge composition was approximately 30% phosphate rock, 65% dehydrated gypsum, and 5% langbeinite. Product analyses from a charge of this composition showed 10.6% total phosphorus pentoxide and 10.4% available phosphorus pentoxide as determined by 2% citric acid, equivalent to a

Figure 2. Effect of charge composition on phosphorus pentoxide availability of fusions of phosphate rock and gypsum, using langbeinite as flux
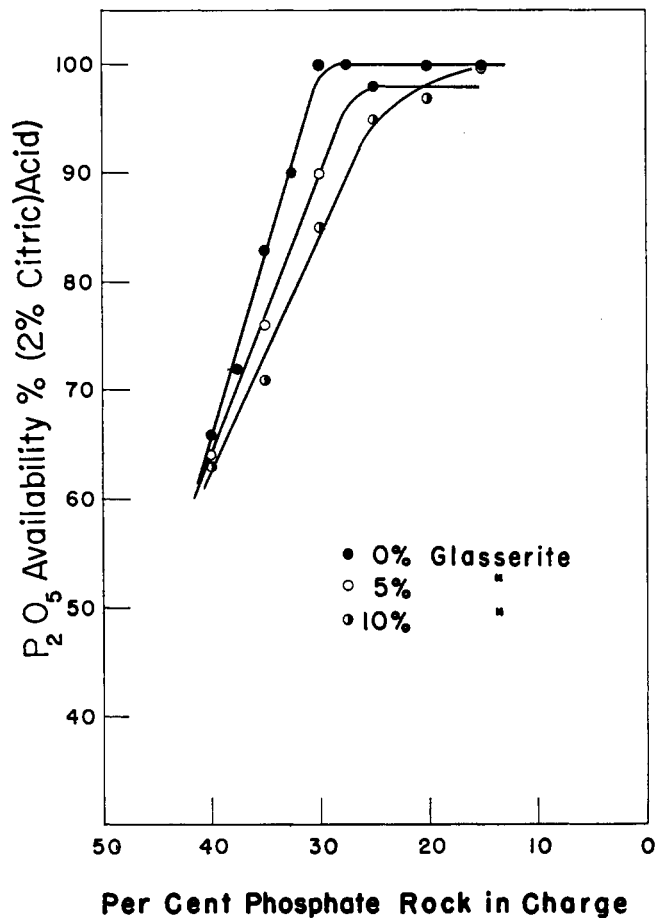
Figure 3. Effect of charge composition on phosphorus pentoxide availability of fusions of phosphate rock and gypsum, using glasserite as flux
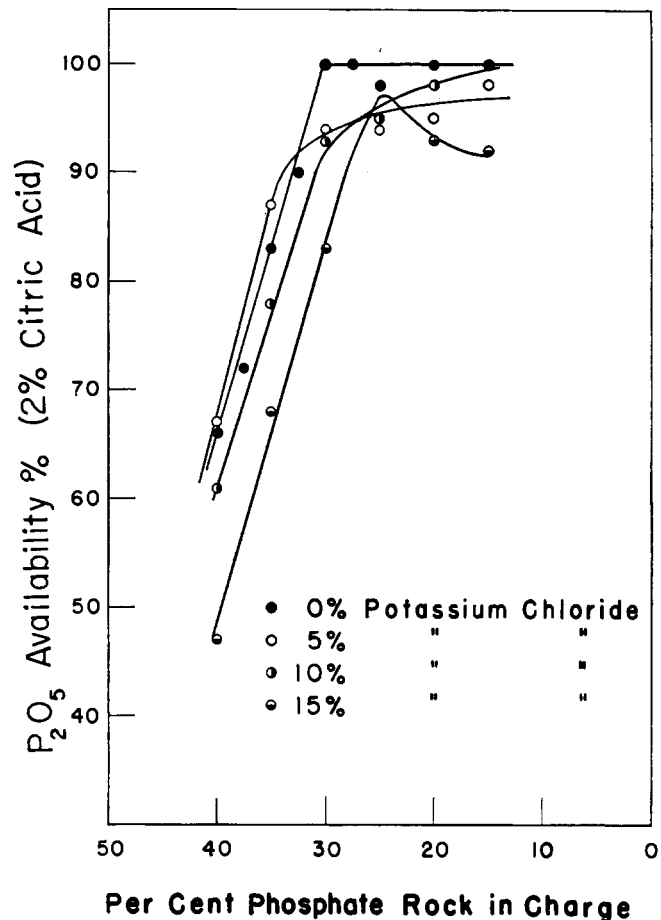

Figure 4. Effect of charge composition on phosphorus pentoxide availability of fusions of phosphate rock and gypsum, using potassium chloride as flux

phosphorus pentoxide availability of 98%.

Fusions made with mixtures of phosphate rock and dehydrated gypsum, using glasserite as a flux, had charge compositions ranging from 15 to 40% phosphate rock, 50 to 80% dehydrated gypsum, and 5 to 10% glasserite. The averaged results of a number of fusions are shown in Figure 3. Fusion temperatures were approximately 2400° F. and the time beyond appearance of bubbling was approximately 5 minutes. The curves are similar to those of Figure 2 and also show the decrease in phosphorus pentoxide availability with increased fluxing agent. Optimum composition of charge was 25% phosphate rock, 70% dehydrated gypsum, and 5% glasserite. The phosphorus pentoxide analyses of products from this charge composition were 6.6% total phosphorus pentoxide and 6.4% available phosphorus pentoxide, or an availability of 97%.

Fusions made with mixtures of phosphate rock and dehydrated gypsum using potassium chloride as a flux had charge compositions ranging from 15 to 40% rock, 45 to 80% dehydrated gypsum, and 5 to 15% potassium chloride. The effect of charge com-

position is shown in Figure 4. The average fusion temperature was 2350° F. Fusion time was the same as for other fluxes. The general shape of the curve shows again the increase in availability with addition of dehydrated gypsum and the decrease in availability with the addition of flux.

Fusion of Phosphate Rock and Dehydrated Gypsum Alone. The fluxing agent studies showed increasing phosphate pentoxide availability with decreasing amount of fluxing agent, and further work on the fusion of phosphate rock and dehydrated gypsum was done without fluxing agents. Fusions with rock and dehydrated gypsum alone were more difficult to make and considerable foaming occurred. Fusion temperatures were higher with no fluxing agent.

Under controlled conditions, fusions of phosphate rock and dehydrated gypsum alone were made with composition ranging from 15 to 40% rock and 85 to 60% dehydrated gypsum (Table II). Fusion temperatures were approximately 2450° F. and the fusion time was 8 to 12 minutes. The data show that a product of high phosphorus pentoxide availability can be obtained by fusing phosphate rock and dehydrated

gypsum mixtures having a composition of 65% or more dehydrated gypsum. Maximum phosphorus pentoxide availability occurred with a charge containing 30% phosphate rock and 70% dehydrated gypsum. Product composition was 10.5% total phosphorus pentoxide and 10.4% available phosphorus pentoxide for this mixture. The data of Table II have been plotted on Figures 2, 3, and 4 and represent for each series the data with 0% fluxing agent.

The phosphate-gypsum fused product is grayish white and easily ground; it is nonhygroscopic, and nonacidic.

Discussion of Results

The gypsum used in the experimental work was preheated at 500° F. for 3 hours before use. This treatment was found desirable for the laboratory fusions because of the loss of sample resulting from the rapid dehydration of commercial gypsum when inserted directly into the furnace without previous preheating. Commercial gypsum could be used directly in larger scale operation without previous dehydration.

The consistent character of the curves of Figures 2, 3, and 4 suggested that the availability of the product was a function

of some molecular ratio of the compounds in the rock and addition agent in the charge, giving rise to a soluble structure in the molten state, which was preserved by quenching. It was postulated that the anion mole ratio would be controlling, as both phosphate and sulfate anions have a tetrahedral arrangement of atoms. Such an arrangement— i.e., a phosphorus or sulfur atom with four oxygen atoms arranged around it at the corners of a tetrahedron—would make the anion grouping relatively large fompared to the cation itself and therecore the effect, structurally, would be dependent on these large groups. To test this postulate, the mole ratio of sulfur trioxide to phosphorus pentoxide in the charge was plotted against 2% citric acid availability for all the fusions (Figure 5). Included on this plot are points taken from previous work on langbeinite phosphate fusions (5). This plot shows that the anion mole ratio, SO_3/P_2O_5, is a good correlation for phosphorus pentoxide availability in the product. It is evident that an SO_3/P_2O_5 ratio of at least 6.0 in the charge is necessary to obtain fused products of high phosphorus pentoxide availability. The close correlation of the SO_3/P_2O_5 ratio to availability in the langbeinite fusions to that in the dehydrated gypsum fusions offers further evidence that the cation plays a less important role than the large anion grouping.

A process flowsheet for a large scale operation is shown in Figure 6. The raw materials are brought into the plant by railroad cars and unloaded into storage. The gypsum is reclaimed from storage by a screw conveyor and agglomerated with the rock to a size averaging 1- to 2-inch lumps. The agglomerated material is introduced into the top of a fuel-fired shaft furnace, where the fusion takes place and the molten product is tapped into a high velocity stream of water. The water stream granulates the molten product, quenches it, and carries it to a settling basin. From the settling basin the product is dewatered, dried, and bagged for shipment. The production costs for such a plant, located in the Midwest and producing a 0-10-0 fertilizer, are estimated to be $16.74 per ton for a 50-ton-per-day plant and $14.83 for a 100-ton-per-day plant. This is equivalent to $1.67 and $1.48 per unit, respectively, for the two plants. As superphosphate can be purchased by mixing plants in the Midwest for $1.00 to $1.20 per unit, this process would not be competitive at present. However, it might be competitive in other parts of the world, where the sulfur supply is short or an abundance of gypsum is available at low cost. The physical properties of the product—granular, noncaking, and nonacidic—may make it attractive in other areas.
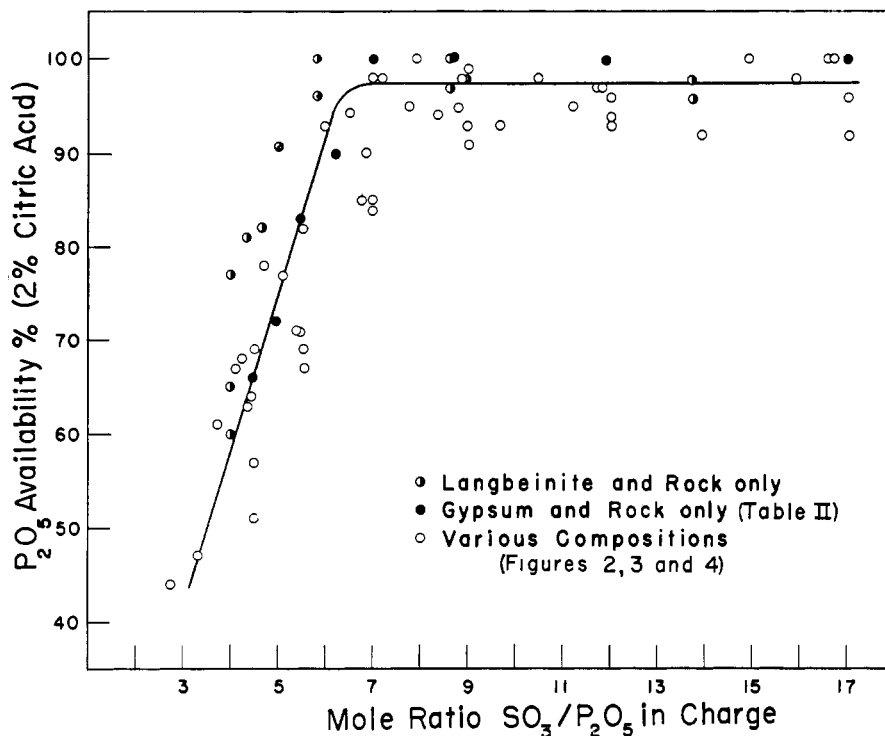

Figure 5. Effect of SO_3/P_2O_5 mole ratio on phosphorus pentoxide availability in fused products

Table II. Composition of Products from Fusion of Phosphate Rock and Dehydrated Gypsum

(Fusion at 2450° F.)

| Phosphate Rock, % | Gypsum[a], % | % P₂O₅ | | | Availability, % | |
| | | | Available | | | |
		Total	2% citric acid	Neutral NH₃ citrate	2% citric acid	Neutral NH₃ citrate
40.0	60.0	13.2	8.7	...	66	...
37.5	62.5	13.8	10.0	5.9	72	43
35.0	65.0	11.7	9.7	...	83	...
32.5	67.5	12.0	10.8	8.2	90	68
30.0	70.0	10.4	10.4	8.1	100	78
27.5	72.5	10.4	10.4	10.5	100	100
25.0	75.0	9.6	9.4	9.1	98	95
20.0	80.0	6.8	7.0	...	100	...
15.0	85.0	5.1	5.5	...	100	...

[a] Preheated 3 hours at 500° F.
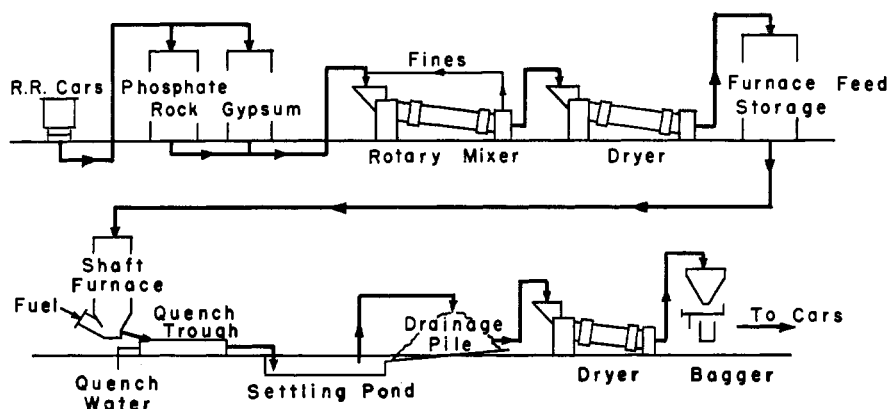[b] Averages of two or more fusions of 30 grams each.

Figure 6. Flowsheet for large scale fused phosphate rock gypsum plant

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ATMOSPHERIC POLLUTION

Relationship among Exposure Periods, Foliar Burn, and Fluorine Content of Plants Exposed to Hydrogen Fluoride

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Low concentrations of fluorides from industrial gases have been found in the atmosphere of some agricultural areas. Observations of a pathological condition attributed to fluorides in a wide range of plant species resulted in initiation of controlled fumigation experiments to determine the effects of environmental variables upon the rate of foliar response to hydrogen fluoride fumigation. Forty plant varieties were exposed to atmospheric concentrations of 1.5, 5, and 10 parts per billion of hydrogen fluoride in daylight and darkness. Correlation between exposure factor and accumulated foliar fluoride level for family, genus, and species has been calculated. The varieties fumigated averaged 91.3% as responsive to hydrogen fluoride in darkness as in daylight. Varieties fumigated were somewhat more responsive to a daily low fumigation concentration than to twice weekly higher concentrations of approximately equivalent exposure factor.

OBSERVATIONS OF A PATHOLOGICAL CONDITION in a wide range of species of plants have been made in seven areas within the state of Washington within the past decade. In each of the affected areas, air pollution in the form of gaseous fluorides has been diagnosed as the primary contributing cause of the observed leaf scorch (*14, 17, 19, 21, 22, 24, 28*).

Numerous reports concerning field observations of the visible effects of fluoride upon certain types of vegetation have been reviewed by Miller, Johnson, and Allmendinger (*22*) and Thomas (*30*). Others have contributed

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descriptions of field observations of the effects of fluoric effluents upon vegetation (*9, 11, 13, 15, 20, 23, 26*). Several papers within the past 5 years have reported the effects of controlled hydrogen fluoride fumigation on plants conducted in a concentration range of 0.05 to 10 p.p.m. of fluoride (*12, 16, 30, 32*).

Extensive field sampling for atmospheric fluorides has been conducted by the Division of Industrial Research of the State College of Washington between 1949 and 1954 in Spokane, Wash. (*5*); Longview, Tacoma, and Camas, Wash. (*2*); and Utah and Salt Lake Counties in Utah (*7*). The results of these surveys indicated that average 4-hour atmospheric concentrations were less than 5 p.p.b., with occasional max-

imum 4-hour average concentrations in the order of 10 to 20 p.p.b. of hydrogen fluoride. Other investigators in the field of air pollution (*10*) show agreement with these data. As these concentrations were considerably lower than those used in most of the fumigation work which had been reported, a need existed for fumigation studies using concentrations which had actually been found in the field, and which had been blamed for observed pathological conditions in plants growing in the field.

It is of practical importance to obtain information regarding minimum concentrations and exposure times required to produce visible foliar fluoride burn on a wide variety of vegetation. The development of such data must be based