Use of Concentrated Sulfuric Acid in Production of Granular Normal Superphosphate

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A process for use of strong sulfuric acid in production of granular normal superphosphate was studied in the laboratory. The process involved mixing the rock and acid, denning for about 30 minutes, granulating by spraying water on the acidulate in a rotary drum, and curing. With the proper combination of acid strength and rock particle size, the physical properties of the den product (dry and semigranular) were suitable for further granulation; regular grind rock was satisfactory with fuming acid. With the best combination of variables, over 85% of the granules were in the size range −6 +20 mesh, evolution of by-product fluorine was over 60%, P_2O_5 availability was 97%, and moisture content was 2% or lower. In comparison with the usual granular superphosphate process, this method simplifies operation and increases fluorine evolution substantially.

THE CUSTOMARY METHOD for producing normal superphosphate consists of acidulating phosphate rock with sulfuric acid of about 70% H_2SO_4 concentration, denning the acidulate until it sets up, and then curing it in storage piles for several weeks. To make granular normal superphosphate, which is preferred for direct application because of good handling and storage properties, the usual practice is to process the cured material by adding water to it in a rotary drum and then drying the granules. This method of operation has a number of drawbacks. The fresh superphosphate sets up very hard in the curing pile; it often must be removed by blasting and then must be ground before it can be fed to the granulator. The granulation operation is fairly difficult to control, and a considerable amount of oversize must be crushed and recycled with fines to the granulator. Also, a considerable amount of heat is required to remove the water added to accomplish granulation. Thus, a less troublesome method for granulating superphosphate would be very desirable.

Ordinarily, 25 to 30% of the fluorine in phosphate rock is evolved in gaseous form (HF and SiF_4) when the rock is acidulated with 70% acid. Increased fluorine evolution would be desirable because the fluorine serves no useful purpose in the superphosphate and because it can, under some circumstances, contribute to bag rot or to reversion of the phosphate to unavailable forms. Furthermore, fluorine is a potentially valuable by-product because of rapidly growing uses in new and expanding fields. If a practical means of increasing fluorine evolution could be devised, the economics of fluorine recovery would be improved as a result of decreased unit production costs.

A number of investigators have studied the manufacture of normal superphosphate with the objectives of increasing the proportion of fluorine evolved and/or producing a granular product. Fox and Hill (*2*) showed that the evolution of fluorine can be increased to about 50% by acidulating phosphate rock with strong acid of 98% H_2SO_4 content. Wight and Tongue (*6*) also found that use of strong acid instead of the usual 70% acid increased fluorine evolution. However, the sticky and hygroscopic nature of the acidulate made a heating step necessary. The heat-treated product was ground, treated with water to complete the reaction of acid and rock, and grained during the time the water was added.

In the work reported here, a dry, nonsticky acidulate could be obtained with strong sulfuric acid if the phosphate rock were of sufficiently fine particle size. The need for heating or calcining the acidulate was avoided, and a closely sized granular product was obtained by spraying water on the den product in a rotary drum. The availability of the P_2O_5 in the granular product after curing was as good as or better than in conventional normal superphosphate, and 50% or more of the fluorine in the phosphate rock was evolved.

Tests were carried out on a small scale, but the procedure used was designed to give the same conversion and product properties as obtained in large plants. Sulfuric acid preheated to the desired temperature was mixed with phosphate rock (200 grams) for about 30 seconds in a kitchen mixer. The acidulate was transferred immediately to a Dewar flask, which was then loosely sealed with a cork stopper, and held there for a period of time to simulate denning. With proportions and concentrations of reactants similar to those used in commercial practice, the maximum temperature reached in the flask was about 245° F. After the denning period, the superphosphate was cured in closed jars in an oven maintained at 150° F. Samples were taken for chemical analyses after denning and after 1, 3, 5, and 7 weeks of curing. Total and available P_2O_5 were determined by standard A.O.A.C. methods.

Two types of Florida phosphate rock were used, a low grade (32% P_2O_5) and a high grade (35% P_2O_5); analyses are shown in the following tabulation.

	Per Cent			
	P_2O_5	CaO	*Acid Insoluble*	F
Low grade	32.0	46.0	7.6–11.3[a]	3.7
High grade	35.0	49.5	4.0	3.9

[a] Typical range for this type of rock.

Except where noted, tests were made under the following conditions: acid, 96% H_2SO_4 and 200° F.; acidulation mole ratio [$(P_2O_5 + SO_3)$: CaO], 0.98; denning time, 1 hour; and curing time, 3 to 7 weeks.

The percentage of fluorine evolved from the rock was calculated from analyses of the phosphate rock and of the product, and was based on an F:CaO balance. A difference of 0.1% fluorine as determined by analysis made a difference of 4 percentage points in the calculated value for fluorine evolved; therefore, the accuracy of the calculated values was assumed to be ±4 percentage points.

Acidulation and Denning

Acid Concentration. Initial tests were made to study the effects of sulfuric acid concentration on the chemical

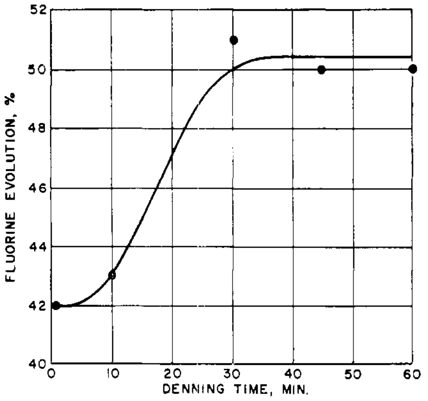

Figure 1. Effect of denning time on fluorine evolution

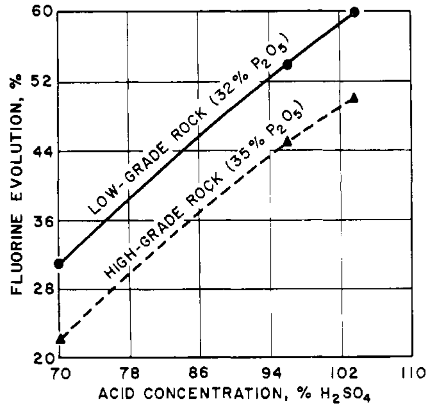

Figure 2. Effect of acid concentration on fluorine evolution

Table II. Effect of Supplemental Silica on Fluorine Evolution[a]

Silica Added, % by Wt.	Fluorine Evolved,[b] % Low-grade rock (32% P_2O_5)	High-grade rock (35% P_2O_5)
0	54	45
1	59	49
2	58	..
3	..	56
5	..	55

[a] 96% acid; particle size of rock, 95% −200 mesh.
[b] During mixing and denning for 1 hour.

Table I. Effect of Particle Size of Rock on Physical Condition of Acidulate, Fluorine Evolution, and P_2O_5 Availability of Cured Product[a]

Rock Size, % −200 Mesh	Acid Concentration, % H_2SO_4	Physical Condition of Denned Acidulate[b]	Fluorine Evolution,[c] %	P_2O_5 Availability of Cured Product,[d] %
		Low-Grade (32% P_2O_5) Rock		
79	96	Lumpy, sticky	57	87
86	96	Lumpy, sticky	55	..
93	96	Dry, semigranular	55	..
96	96	Dry, semigranular	54	92
96	103.6[e]	Dry, powdery	64	92
79	103.6[e]	Dry, semigranular	63	83
		High-Grade (35% P_2O_5) Rock		
77	96	Lumpy, sticky	44	77
94	96	Dry, semigranular	46	87
94	103.6[e]	Dry, powdery	50	82

[a] Acidulation mole ratio [(P_2O_5 + SO_3):CaO] = 0.98.
[b] After denning for 1 hour.
[c] During mixing and denning.
[d] After curing 3 to 7 weeks.
[e] Fuming sulfuric acid (15 to 18% SO_3).

and physical properties of the denned and cured products. Tests were made with low-grade Florida rock ground to the size generally used in the production of normal superphosphate (about 79% −200 mesh). The acidulation mole ratio [(P_2O_5 + SO_3):CaO] was 0.98. With low-grade rock and 70% acid, the fresh acidulate was in the form of a fluid mud which set up in about 5 minutes. After denning, the material was firm, friable, and porous. These results were the same as in plant practice with this strength acid. When 90 or 96% acid was used, there was no fluid stage. A lumpy, sticky material was formed immediately upon addition of the rock to the acid. After denning, the material was still slightly sticky, and the lumps were quite soft. When fuming sulfuric acid (15 to 18% SO_3) was used, a dry, nonsticky, semigranular material formed immediately.

As expected, the P_2O_5 availability of the product after curing for 3 to 7 weeks was relatively low when strong acid was used—87 and 83%, respectively, for 96% and fuming acid.

The proportion of fluorine evolved during mixing and denning for 1 hour increased from 31 to 63% as the concentration of the acid used was increased from 70 to 103.6% (fuming). With 96% acid, about 57% of the fluorine was evolved in 1 hour. These results were similar to those reported by Fox and Hill (*2*).

To obtain further information on evolution of fluorine, the chemical reaction between low-grade rock and 96% acid was stopped at specified times after mixing the rock and acid. The results, plotted in Figure 1, show that about 42% of the fluorine was released almost instantaneously and another 8 to 10% within 30 minutes. Evolution after the first 30 minutes was negligible. This is about the same length of time allowed for evolution of fluorine in the regular production of normal superphosphate (*1*).

Particle Size and Grade of Rock. Tests with both low- and high-grade rocks ground to various degrees of fineness (Table I) showed that both the physical condition of the denned product and the P_2O_5 availability of the cured product were improved by decreasing the particle size of the rock. With 96% acid, decreasing the size of the rock from 79% through 200 mesh to 93 or 97% through 200 mesh changed the condition of the denned product from a sticky, lumpy material to a dry, semigranular material, which could be handled directly in granulation. This material was similar to that obtained when fuming acid was used with rock of regular grind.

The particle size of the rock had little effect on the fluorine evolved during mixing and denning. However, as shown in Figure 2, more fluorine was evolved from low-grade than from high-grade rock under the same conditions of acidulation.

As stated earlier, increasing the concentration of the acid resulted in poor conversion of the rock P_2O_5 to an available form. The use of finely ground rock with strong acid resulted in some increase in P_2O_5 availability. However, satisfactorily high availability was obtained only when sufficient moisture was provided during curing to permit the acid-rock mixture to react further.

Supplemental Silica. Data reported by Patsourides (*5*) show that the amount of evolved fluorine which is combined in some form with silica, such as SiF_4, varies with the type of rock. Thus, differences in the amounts or fineness of the silica in the rocks in the above tests may have caused the differences in the proportions of fluorine evolved; the high-grade rock had a much lower acid-insoluble content than did the low-grade rock. It has been reported also that addition of silica does not increase fluorine evolution during the manufacture of superphosphate (*3*) but does give an increase when the superphosphate is heated subsequent to manufacture (*4*). Tests in the present work (Table II) showed that adding 3% by weight of silica to finely ground high-grade Florida rock prior to acidulation with strong acid increased the evolution of fluorine to that obtained with finely ground low-grade rock and strong acid. Addition of silica to the low-grade rock gave only 4 to 5 percentage points increase in evolution, which may have been within the limit of experimental error. Three different types of silica were used: powdered silicic acid, by-product silica from a fluorine recovery pilot plant, and diatomaceous earth. There was no appreciable difference in the effect of the different types. Quartz was not tested.

Granulation

The tests described in the preceding discussion confirmed the advantage of strong acid in promoting fluorine evolution and showed that a nonsticky, semigranular acidulate could be obtained by properly correlating acid strength with rock particle size. However, the highest P_2O_5 availability (92%) was lower than that usually obtained in the manufacture of normal superphosphate (95% or higher). Moreover, the semigranular acidulate needed further granulation. Therefore, addition of water after denning was tested as a means of improving both availability and granulation.

Table III. Effect of Adding Water After Denning on P_2O_5 Availability

Acid Concentration, % H_2SO_4	*P_2O_5 Availability,[a] %*	
	Without water addition	*With water added after denning[b]*
LOW-GRADE ROCK (32% P_2O_5; 96% −200 MESH)		
96	92	96
103.6[c]	92	95
HIGH-GRADE ROCK (35% P_2O_5; 94% −200 MESH)		
96	87	98
103.6[c]	82	97

[a] After curing 3 to 7 weeks.

[b] Water sufficient to dilute acid to 75% H_2SO_4.

[c] Fuming sulfuric acid.

The effect of post-den water addition on availability is shown in Table III. In these tests, denned acidulate made from finely ground rock was mixed with water in an amount that would have diluted the acids to 75% H_2SO_4 in a kitchen mixer, and the mixture was allowed to cure for several weeks. Good availability (95 to 98%) was obtained with both low- and high-grade rock and with both 96% and fuming acids. Availability was improved the most for the high-grade rock.

Preliminary granulation tests were carried out by spraying water on the denned acidulate in a small rotating drum (10-inch diameter and 6 inches long). Good granulation was obtained when the acidulate was dry and nonsticky; any degree of stickiness interfered with granulation. Both powdery and semigranular acidulate gave good results.

Since these tests were promising, a further series of tests (Table IV) was carried out to determine the effects of variables on availability and granulation.

In tests of granulating denned acidulate made with 96% acid and finely ground rock, good availability was obtained by adding water to give 75 to 85% equivalent acid concentration. Other tests indicated that use of less water would have given an acidulate too dry to cure properly. Adding water sufficient to dilute the acid to 75% appeared to be ideal for granulation; 78 to 86% of the product was in the range −6 +20 mesh. Less water increased the amount of fines, and, in preliminary tests, use of more water caused overgranulation and unnecessarily increased the moisture content of the product. Tests were not made with acidulates from 96% acid and coarse rock because, as pointed out earlier, these denned acidulates were lumpy and sticky.

In tests with fuming acid at the normal acidulation [$(P_2O_5 + SO_3):CaO = 0.98$], addition of water to 75% equivalent acid concentration gave good availability and granulation when finely ground rock was used. Availability was poor with coarse rock even when extra water to dilute to 65% equivalent concentration was used. However, with coarse rock, good availability (96%) was obtained by increasing the acidulation ratio to 1.02 (equivalent to increasing the amount of acid used by 6%).

If separation of the offsize before curing were desired, some difficulty might be encountered because of stickiness of the fresh granules. Tests were made in which the granules were subjected to mild drying to surface dry or case harden them. Warm air (100° to 150° F.) was passed over the rolling bed of granules after the water addition was completed.

From 10 to 15 minutes' contact with the warm air was required to completely eliminate stickiness. However, this reduced the moisture content of the granules to about 3%, which is lower than permissible for good curing (Table V). A period as short as 4 minutes reduced stickiness sufficiently to allow screening; at the resulting moisture content (about 5%), the granules cured well and the availability was little lower than in tests without drying.

A further advantage of the drying would be to reduce any caking that might occur during storage for curing. Whether or not such caking would occur to a degree that would cause any significant difficulty was not established; large-scale tests would be necessary to clarify this point.

Discussion

In the process developed, good granulation and availability were obtained

Table IV. Use of Strong Acid Followed by Water Addition After Denning: Effect of Process Variables on Granulation and P_2O_5 Availability

Acid Concentration, % H_2SO_4		*Particle Size of Rock, % −200 Mesh*	*$(P_2O_5 + SO_3)$:CaO Mole Ratio*	*Composition of Product, %*				*P_2O_5 Availability,[b] %*	*Screen Analysis of Product, %*		
					Cured						
Initial	*Equivalent[a]*			*Fresh H_2O*	*Total P_2O_5*	*A.P.A.*	*H_2O*		*+6*	*−6 +20*	*−20*
96	75	96[c]	0.98	7.9	21.9	21.0	1.3	96		[d]	
	75	96[c]	0.98	7.3	21.2	20.1	0.8	95	7.3	78.7	14.0
	75	93[c]	0.98	8.6	21.5	20.4	5.1	95		[d]	
	75	94	0.98	5.8	22.2	21.9	1.2	99	11.0	86.3	2.7
	75	94	0.98	6.5	22.2	21.7	4.4	98	8.8	83.6	7.6
	80	94	0.98	5.1	22.2	21.7	3.5	98	18.5	64.9	16.6
	85	94	0.98	4.6	22.4	21.9	2.5	98	10.0	59.6	30.4
103.6[e]	75	94	0.98	4.5	22.0	21.3	2.0	97	2.1	78.0	19.9
	65	77	0.98	6.3	22.8	20.3	3.9	89		[d]	
	75	77	0.98	4.9	25.1	22.9	0.8	91	7.4	61.5	31.1
	75	77	1.0	6.7	22.6	21.5	0.5	95	19.8	74.9	5.3
	75	77	1.02	6.9	22.3	21.4	1.0	96	10.0	77.0	13.0

[a] After addition of water to denned acidulate.

[b] After curing 3 to 7 weeks.

[c] Low-grade rock; other tests were with high-grade rock.

[d] No granulation attempted; tests included for comparison.

[e] Fuming sulfuric acid.

Table V. Effect of Granule Drying Time on P_2O_5 Availability of Cured Product[a]

Drying Time,[b] Min.	Moisture Content of Granules After Drying, %	Composition of Cured Product,[c] %					P_2O_5 Availability, %
		P_2O_5					
		Total	A.P.A.	W.S.	F.A.	H_2O	
15	2.9	22.3	21.5	19.3	1.2	1.5	96
4	4.8	21.7	21.2	19.5	1.1	1.9	98
0	5.8	22.2	21.9	19.8	0.7	1.2	99

[a] High-grade rock; 96% H_2SO_4.
[b] With warm (100° to 150° F.) air.
[c] Cured 3 to 7 weeks.

with either 96% acid and finely ground rock or with fuming acid and a standard grind of rock. It was necessary to use slightly more acid with the latter combination. It has been estimated that fine grinding of rock to the size desired for this process would increase the cost of the rock by about 40 cents per ton or about 25 cents per ton of superphosphate. At published prices, the use of a higher acidulation with fuming acid and the standard grind of rock would increase production cost approximately the same amount. Thus, the choice between the two might depend on the cost of acid at the particular plant location.

The process has the following advantages over the usual method for granulating superphosphate. The usual acid dilution equipment is eliminated, as well as the cutter commonly used with mechanical dens. The superphosphate is granulated before curing, thereby eliminating the extra handling involved in digging cured superphosphate from the pile, transferring to the granulation area, and grinding prior to granulation. The cost of drying the granulated superphosphate is reduced or eliminated. Any surface drying required to facilitate screening or reduce caking in the pile can be accomplished by short contact with warm air, possibly within the granulating drum. Although little or no drying is required, the moisture content of the product is relatively low and it is therefore easier to make standard 0-20-0 from low-grade rock. The evolution of fluorine is increased by twofold or more, thereby improving the economics of fluorine recovery.

Although the procedures were designed to simulate commercial operation, a larger scale investigation of the process appears warranted. Points on which further information is needed include the type of mixer best suited to mixing of strong acid and rock, granulation efficiency obtainable in larger equipment, the degree of surface drying, if any, needed to prevent caking in the pile, and ammoniation characteristics of the product. Four to 5 pounds of ammonia per unit of P_2O_5 were held in small-scale tests.

The process should be adaptable to existing superphosphate granulation plants with little change in equipment, assuming that the rock-acid mixer is suitable. Standard dens (perhaps with cutter eliminated) should be appropriate for the dry, semigranular acidulate, and the rotary drum commonly used in granulation plants should be suitable for granulation of the acidulate.

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Received for review February 7, 1962. Accepted May 7, 1962. Division of Fertilizer and Soil Chemistry, 140th Meeting, ACS, Chicago, September 1961.

ISOTOPE-LABELED INSECTICIDES

The Synthesis of Tertiary Carbon Deuterated DDT and DDT Analogs

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To utilize one of several contemplated experimental approaches to the testing of a new chemical hypothesis (*10*) on the toxic action of certain contact insecticides, it was necessary to prepare the deuterated analogs of some of these. The reactivity of DDT under certain conditions which ordinarily favor free radical reactions had led the authors to believe that the toxic action of DDT might be the result of an in vivo free radical reaction of DDT at the susceptible site.

The nature of several reported metabolites of DDT, viz., DDE (*21*), *p,p′*-dichlorobenzophenone (*14*), *p,p′*-dichlorobenzyhydrol (*20*), and Kelthane (*14, 22*) suggests that detoxication proceeds via enzymatic processes which may also be free radical in type.

The first two of these metabolites have been obtained in this laboratory by the bromine-sensitized photoelimination and autooxidation reaction.

Barker (*2*) reacted deuterochloral and 1-deuterodichloroacetaldehyde with chlorobenzene to prepare 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane-2-d(d-DDT, d-I) and 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethane-2-d(d-DDT, d-I) and 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane-2-d (d-TDE, d-II), respectively.

Among the products of the sulfuric acid condensation of chloral and chlorobenzene is the compound, *p*-chloro-α-trichloromethylbenzyl alcohol (IA), which is probably an intermediate in the formation of I (*3*). The preparation of the 1-d analog of this compound by the reduction of 2,2,2,4′-tetrachloroacetophenone (IK) with lithium aluminum deuteride to yield d-IA appeared feasible in the light of the successful reduction of hexachloroacetone to 1,1,1,3,3,3-hexachloro-2-propanol (*8*) and of 2-fluoro-2,2,4′-trichloroacetophenone to *p*-chloro - α - (dichlorofluoromethyl)-benzyl alcohol (*5*).

Chlorination of *p*-chloroacetophenone gave IK and 2,2,4′-trichloroacetophenone (IIK). A model reduction with lithium aluminum hydride of IK and of IIK gave IA and IIA, respectively, in