The straight-line curve which resulted shows that under the conditions of the experiment the o-phenylphenol residues vary directly with concentration of the treatment solution.

All samples were examined for chemical peel injury after storage for 1 week at 70° F. Only the few samples having residues of o-phenylphenol greater than 15 p.p.m. had appreciable peel injury.

Discussion

Residues of o-phenylphenol in oranges increase with concentration, temperature, and length of treatment but decrease as the pH of the Dowicide A solution is raised. By proper control of treatment conditions almost any desired level of residues can be maintained. The time-tested Dowicide A–hexamine method (5) gives good control of decay at residue levels of about 2 p.p.m. and the legal tolerance for o-phenylphenol in citrus fruits (7) is 10 p.p.m. As no peel injury was found at levels below the legal limit, residues in this range should give good decay control without injury. For hydrocooling of oranges, a 30-minute treatment at 40° F. with 0.1% Dowicide A at pH 10.5, resulting in a residue level of about 4 p.p.m., has been found satisfactory.

These experiments have shown the importance of pH control in the use of Dowicide A as a fungicide for oranges. This factor is especially critical, as the pH of the solution tends to decrease because of absorption of carbon dioxide from the air and reaction with citric acid from damaged fruit. Unless checked, this could lead to residues in excess of the legal tolerance, serious peel injury, and ultimate precipitation of the fungicide.

The pronounced effect of pH on residues is probably due to absorption by the fruit of fungicide in the form of

Figure 4. Effect of pH on o-phenylphenol residues in oranges treated for 3 minutes with 2.0% Dowicide A at 90° F.

free o-phenylphenol which is formed by hydrolysis of the sodium o-phenylphenate in solution. Lower pH would tend to favor this hydrolysis and higher pH to suppress it. The absorption of fungicide by waxed fruit in the hydrocooling experiment supports this view.

Literature Cited

(1) Federal Register 21, 1172 (Feb. 21, 1956).
(2) Gottlieb, S., Marsh, P. B., Ind. Eng. Chem., Anal. Ed. 18, 16 (1946).
(3) Grierson, W., Proc. Florida State Hort. Soc. 70, 264–72 (1957).
(4) Grierson, W., Hayward, F. W., Ibid., 71, 205–15 (1958).
(5) Hopkins, E. F., Loucks, K. W., Citrus Ind. 34 (10), 5–14 (1953).
(6) Long, J. K., Roberts, E. A., Australian J. Agr. Research 9, 609–28 (1958).
(7) Rattray, J. M., Dept. Agr. and Forestry, Union S. Africa, Rept. Low-Temp. Research Lab. (1937–8), 170–6 (1939).
(8) Van der Plank, J. E., Rattray, J. M., Citrus Grower (S. Africa) 65, 13–14 (1939).
(9) Van der Plank, J. E., Rattray, J. M., Dept. Agr. and Forestry, Union S. Africa, Ann. Rept. Low-Temp. Research Lab., Capetown (1938–9), 93–8 (pub. 1940).

FERTILIZER TECHNOLOGY

High-Analysis Superphosphate by the Reaction of Phosphate Rock with Superphosphoric Acid

A. B. PHILLIPS, R. D. YOUNG, F. G. HEIL, and M. M. NORTON

Tennessee Valley Authority, Wilson Dam, Ala.

A NEW SUPERPHOSPHATE that contains about 54% available P_2O_5 has been introduced to the fertilizer industry by TVA. Because of its higher grade, this material is referred to as "high-analysis superphosphate." It is produced by acidulating phosphate rock with superphosphoric acid. Superphosphoric acid, also a TVA development, is

an electric furnace acid that contains about 76% P_2O_5, which is equivalent to about 105% orthophosphoric acid (H_3PO_4). This compares with 54 to 56% P_2O_5 for the usual furnace and wet-process phosphoric acids used in the fertilizer industry. Chemically, the superphosphoric acid contains about 49% of its phosphate as orthophosphate,

42% as pyrophosphate, and the remainder as higher polyphosphates. TVA has done considerable work in studying the production, properties, and use of superphosphoric acid (3, 5, 6); first application was in liquid fertilizer processes.

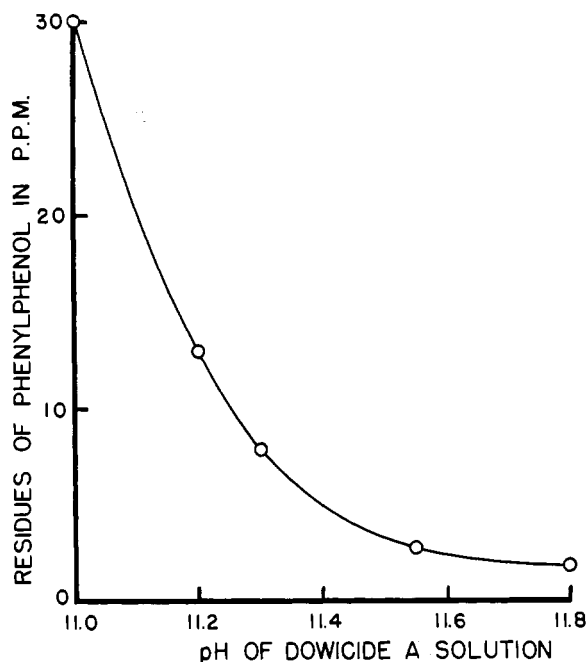In considering the use of superphosphoric acid in the production of super-

Production of high-analysis superphosphate (54 to 56% P_2O_5) by reaction of phosphate rock with superphosphoric acid was studied in bench scale, pilot plant, and plant scale equipment. Results were best when the acid concentration was about 74% P_2O_5 and the acid was preheated at 180° to 225° F. When the superphosphate was held in a den or storage pile, its temperature reached a maximum of 300° to 350° F. in about 40 minutes. This high temperature promoted fluorine volatilization and rapid conversion of the P_2O_5 to an available form. The superphosphate contained 1% or less of free moisture, and the P_2O_5 was chiefly in the form of anhydrous monocalcium phosphate. About 60% of the fluorine was evolved, compared with about 15% in the production of conventional triple superphosphate. The comparatively anhydrous nature of the product and evolution of fluorine compounds account for the substantially higher P_2O_5 content. Good ammoniating and processing characteristics have been demonstrated in pilot plant scale production of granular fertilizers. Economies should be realized in handling and shipping the more concentrated superphosphate and in the higher grades of fertilizers that can be prepared.

phosphate, some doubt of obtaining good results existed because conversion of the P_2O_5 in phosphate rock had been poor in earlier studies with stronger than usual phosphoric acid in the range of 80 to 90% H_3PO_4 (7). Also nothing was known about the acidulation properties of the nonortho acids in the superphosphoric acid. However, in exploratory small scale tests, conversion of rock P_2O_5 was high when the acid was diluted slightly to about 102% H_3PO_4 and heated to 170° F. prior to mixing with the rock. The superphosphate thus produced contained 54 to 55% available P_2O_5 when the proportions of acid and rock were about the same as those normally used for the production of triple superphosphate. This represents a substantial increase in grade, compared with 46 to 48% for conventional triple superphosphate. This paper describes the development of the process for production of high-analysis superphosphate.

Small Scale Studies

In the small scale tests, superphosphoric acid and pulverized phosphate rock in amounts sufficient to produce 1 to 2 pounds of superphosphate were mixed for 15 to 30 seconds in a kitchen mixer. The mixture was transferred to a Dewar flask, where it was held for an hour or longer to avoid loss of heat and to simulate denning. It then was removed from the flask and placed in a closed jar in an oven for curing at 250° to 300° F. for 3 days and 150° F. thereafter for a total of 2 to 4 weeks. In tests made to determine the setting time, or the time required for the superphosphate to become firm, the mixture was allowed to remain in the mixer bowl until it solidified. Samples were taken after simulated denning and after curing for various periods.

The superphosphoric acid was obtained from TVA plant operations at the usual strength of about 75.5% P_2O_5 (104.5% H_3PO_4) and used as received or diluted slightly with water to the desired concentration. The phosphate rock used in most tests was Florida land pebble that contained about 32% P_2O_5 and had been ground to the size commonly used in the prodution of superphosphate (75% -200 mesh). Chemical analysis typical of the rock used in the tests showed:

	%		%
P_2O_5	32.2	Al_2O_3	1.7
CaO	46.0	F	3.6
SiO_2	7.1	CO_2	2.8
Fe_2O_3	2.1	H_2O	0.8
Ignition loss	6.6		

Effects of Acid Concentration, Temperature, and Acidulation Ratio (Table I). At 0.98 acidulation ratio and 175° F. highest conversion was obtained with 102% H_3PO_4 concentration. Setting time decreased with decrease in acid concentration.

In tests with acid of 102% H_3PO_4 concentration and an acidulation mole ratio of 0.96, at 200° F. and above, the conversion was 90%. Varying the acid temperature proved an effective means of controlling the setting time.

At acid strength of 102% H_3PO_4 and acid temperature of 150° F., conversion increased from 75 to 99% as the acidulation ratio was increased to 1.10. The setting time, 135 to 180 seconds, was not greatly affected by changes in acidulation. The grade of the product increased from 48 to 56.5% as the acidulation mole ratio was increased from 0.85 to 1.10. Superphosphate made using an acidulation ratio higher than 1.05 was excessively sticky and was considered unsatisfactory.

Particle Size, Grade, and Type of Phosphate Rock. In a few tests with more finely pulverized Florida rock, the most pronounced difference was that the set time decreased with decrease in size of rock. Conversion increased slightly. In these tests, the P_2O_5:CaO

mole ratio was 0.96 and the 102% acid was heated to 200° F.

Fineness of Phosphate Rock, % through 200 Mesh	Set Time, Sec.	Conversion, %
75	90	90
85	70	91
93	60	91
96	45	94

In tests with higher grades of Florida phosphate rock (34 to 35% P_2O_5), fluidity during mixing was increased and the set time of the acidulate was prolonged. Conversion was about the same as with 32% rock; however, as expected, higher grades of superphosphate were produced. The acid concentration was 102% H_3PO_4 and the P_2O_5:CaO mole ratio was 1.0.

P_2O_5 Content of Phosphate Rock, %	Grade of High-Analysis Superphosphate Produced, % Available P_2O_5
32	54
34	56
35	57

In a few tests with Wyoming and Idaho rocks of about the same grade and particle size as the ground Florida pebble (75% -200 mesh), results were similar except that, when the western rocks were used, the set time was about twice as long as with Florida rock under the same test conditions. Conversion was slightly lower with the western phosphates. Calcination of Idaho phosphate at about 1200° F. resulted in very hard and very dense superphosphate. It appeared to be too hard to cut from a den with the equipment generally used.

Temperature of Reaction. With acids of some concentrations, exceptionally high temperatures developed in the acidulates during the first hour after mixing, and copious evolution of fluorine was observed. Small scale tests, therefore, were made to study reaction temperature in more detail. The procedure used was the same as described. During
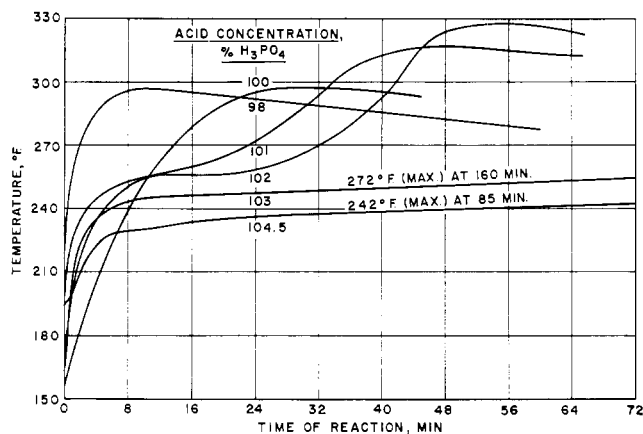
Figure 1. Temperature curves for acidulates of high-analysis superphosphates from acids of different concentrations

Figure 2. Effect of denning time on temperature, evolution of fluorine, and conversion of rock P_2O_5

Table I. Effect of Acid Concentration, Acid Temperature, and Acidulation Ratio on P_2O_5 Conversion and Setting Time

Acid % H_3PO_4	Acid Temp., ° F.	P_2O_5:CaO Mole Ratio	Setting Time, Sec.	P_2O_5 Conversion, %	Grade of Superphosphate, % Available P_2O_5
		Effect of Acid Concentration			
104.5	175	0.98	390	65	. . .
103	175	0.98	210	86	. . .
102	175	0.98	180	92	. . .
101	175	0.98	. . .	90	. . .
100	175	0.98	180	90	. . .
98	175	0.98	120	90	. . .
		Effect of Acid Temperature			
102	125	0.96	240	83	. . .
	150	0.96	180	87	. . .
	175	0.96	120	89	. . .
	200	0.96	90	90	. . .
	225	0.96	75	90	. . .
	250	0.96	75	90	. . .
	275	0.96	45	90	. . .
	300	0.96	45	90	. . .
		Effect of Acidulation Ratio			
102	150	0.85	135	75	48
		0.90	135	78	50
		0.95	180	85	52
		1.00	150	93	54
		1.05	180	97	55
		1.10	150	99	56 5

the simulated denning period, the temperature of the material in the Dewar flask was measured at 5-minute intervals for 45 to 160 minutes until the maximum temperature was reached. Acidulates were prepared with acids containing the equivalent of 98, 100, 101, 102, 103, and 104.5% H_3PO_4. The acid was heated to 225° F. and an acidulation mole ratio of 0.98 was used in each test. Curves showing the time-temperature relationship for the various acid concentrations are given in Figure 1.

Acid concentration had a pronounced effect on the maximum temperature and the time required to reach the peak temperature after mixing.

In subsequent work, the autogenous rise in temperature of the acidulate was found to be very important in obtaining good conversion and high grade of product and to have a pronounced effect on the evolution of fluorine during processing and storage. Pilot plant tests were made to study further the temperature rise phenomena and their effects on the physical and chemical properties of the superphosphate.

Pilot Plant Tests

The pilot plant, which has been described in detail (8), consisted of a cone mixer and a continuous den of the Broadfield type. Capacity was about 1 ton per hour. Tests were made under conditions that had given best results in small scale tests; superphosphoric acid diluted to 102% H_3PO_4 was used to acidulate pulverized phosphate rock (32% P_2O_5, 75% −200 mesh) at a P_2O_5:CaO mole
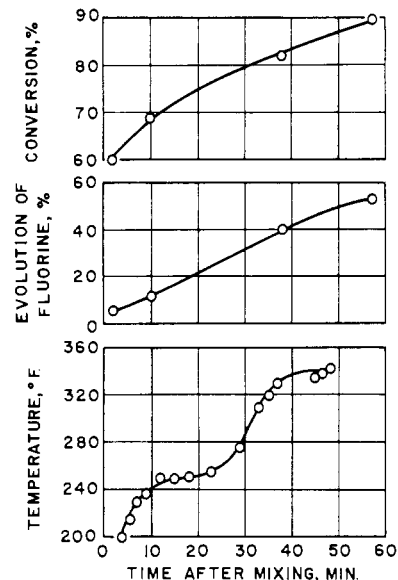
ratio of 0.98 to 1.05. The acid was heated to 170° F. prior to mixing with the rock.

The unit was operated at a production rate to 1 ton per hour, with the speed of the den regulated to allow a retention time of about 1 hour. The block of superphosphate formed in the den was about 18 inches deep and 24 inches wide. The material was very porous and was friable after a few minutes in the den. Temperature of the block was measured periodically, and samples were taken 2, 10, 38, and 57 minutes after mixing. The samples were crushed to simulate cutting and were spread out to cool to interrupt the high-temperature reaction. These samples were submitted for chemical analyses to determine conversion and fluorine content. Data showing the time-temperature curve obtained, the extent of the fluorine evolution, and conversion at the various times are plotted in Figure 2.

The temperature curve was similar to the one obtained in small-scale tests with 102% acid. Conversion was 90% immediately after denning and increased to 92% after 24 hours in a storage pile.

The pilot-plant product was much more porous and, consequently, had a considerably lower bulk density than conventional triple superphosphate as it solidified in the den. It was very friable and could be cut from the den by the usual method. The bulk density was about 25 pounds per cubic foot while in the den and 35 pounds after cutting from the den. After milling in a cage mill and screening at 6 mesh, the bulk density was about 55 pounds per cubic foot, which is not much lower than that of other superphosphates. Somewhat larger denning and storage capacity than is needed for conventional triple superphosphate would be required for proc-

essing high-analysis superphosphate because of its low bulk density before milling.

Recovery of fluorine from the den has been studied extensively in the pilot plant (2).

Plant Scale Experience

High-analysis superphosphate was produced on a demonstration scale in the plant used previously to make conventional triple superphosphate from electric furnace phosphoric acid. The facilities, which were used with little modification, included a TVA cone mixer, a "wet belt" for retention of the material until it solidified, and conveying equipment to pile-storage curing. Although the product was satisfactory, the plant was inadequate in some respects. The cone mixer proved satisfactory. However, the lower bulk density and longer set time of the acidulate limited the capacity of the wet belt and it was necessary to operate at a considerably reduced rate of production. A large part of the fluorine was evolved after the material reached the storage piles; the maximum temperature occurred in the storage piles, because the material reached storage only about 10 minutes after mixing. Disposal or recovery of fluorine was impractical under these conditions. The product contained about 54% available P_2O_5 and conversion of the P_2O_5 in the phosphate rock averaged 92 to 94%.

Modified demonstration scale plant facilities that will overcome these deficiencies and provide part of the production as granular material are being constructed. A semigranular material will be produced by acidulating phosphate rock in a rotary drum. The plant will have facilities for denning the superphosphate to allow best conditions for reaction and to facilitate collection and recovery of fluorine. The granular and nongranular products will be obtained by screening the semigranular material after pile curing.

Production of High-Analysis Granular Fertilizers

High-analysis superphosphate was used in a pilot plant continuous ammoniator-granulator as a source of phosphate in formulating granular fertilizers. Several grades including 13–13–13, 6–24–24, 12–24–12, and 13–39–0, which are higher in analysis than can be produced with conventional triple superphosphate, were produced satisfactorily. Substantial tonnages of high-analysis superphosphate have been used in several commercial scale ammoniation-granulation plants, and good results have been reported in formulating a variety of grades. The degree of ammoniation has been about 3.5 pounds of ammonia per unit of available phosphate.

In addition to the advantage of using high-analysis superphosphate in formulating higher analysis mixed goods, this superphosphate is of economic advantage in formulations for conventional grades, because larger proportions of ordinary (20%) superphosphate can be used. It also is advantageous in granulating some grades because of its low moisture content and the high heat of reaction obtained during ammoniation. High-analysis superphosphate has been reported to be much less dusty than the usual superphosphates, and this has been a particular advantage in bulk handling in fertilizer plants.

Chemical Composition and Characteristics

Chemical Analysis of High-Analysis of Superphosphate from Demonstration Plant

	Wt. %		Wt. %
P_2O_5		CaO	21.2
Total	55.4	F	0.7
Available	54.3	Free mois-	
Water-soluble	53.0	ture	1.2
Free acid	3.2		

High-analysis superphosphate usually contains only about 1% of free moisture and is mainly in the form of anhydrous monocalcium phosphate. Only small quantities of nonorthophosphates have been found in the product. The low proportion of free moisture and water of hydration accounts largely for the higher grade. The greater evolution of fluorine, mainly as SiF_4, adds further to the increased grade. Only 10 to 15% of the fluorine in the rock is released in making conventional triple superphosphate, while about 60% is released in making high-analysis superphosphate. The water solubility of the phosphate usually is 92 to 95%, somewhat higher than for conventional triple superphosphate.

High-analysis superphosphate is more hygroscopic than conventional triple superphosphate and will absorb moisture from the air, particularly if small samples are exposed for extended periods during humid weather. The absorption of moisture will decrease the grade of the product but not impair its physical condition. Care is exercised to avoid undue exposure of samples of the material during preparation and handling for chemical analysis, to minimize the effect of absorption of moisture on the analytical results.

Storage and Handling Properties

High-analysis superphosphate stored very well in bulk. It caked less than conventional triple superphosphate. The lumps that formed were easy to

crush, and the fine material was not as dusty as the usual superphosphates. Although it absorbed moisture more readily than conventional superphosphate, the absorption was confined to the outer layer of the storage pile. The absorption of moisture during storage did not result in the formation of wet, sticky material, as a large part of the moisture combined chemically with the anhydrous monocalcium phosphate as water of hydration.

Bag-storage tests were made of nongranular high-analysis superphosphate that had been cured in storage piles for 2 to 3 months. The bags were stored in stacks 12 bags high in a well-ventilated building. At the time of inspection, the bags were dropped four times from a height of 3 feet to simulate handling in regular plant and shipping operations. Any failure of the bags on dropping was noted and the amount of +2-mesh lumps remaining after dropping was determined as a measure of caking.

Storage in plain paper bags (no moisture barriers) was unsatisfactory. Because of the hygroscopicity of the superphosphate, it absorbed water through the bag walls and this resulted in lowering of the grade and in caking. The paper became dry and brittle and failed in a short time. This deterioration of the bag was apparently due to dehydration, the presence of free acid, and the continued slow release of fluorine. Fertilizer bags with one or two asphalt-laminated plies gave considerably better results, but failed in about 2 months. Bags with a polyethylene-coated inner ply failed along the bag folds; the rest of the bag was not attacked. It was found that folding of the bags had caused minute breaks in the polyethylene film and that this permitted passage of fluorine-bearing gas to the outer plies with resultant weakening and failure. Untreated cotton thread used in sewing bags containing high analysis superphosphate usually deteriorated during storage. Waxed cotton thread and Dacron thread were satisfactory. Little or no caking of the superphosphate occurred in any of the bags with asphalt-laminated or polyethylene moisture barriers.

Deterioration of bags could be decreased by mixing the cured superphosphate with 3% by weight of pulverized calcined dolomite or 5% by weight of pulverized limestone; however, dilution as a result of these treatments reduced P_2O_5 concentration of the product by 1.5 to 2.5 units. More promising results were obtained when the cured superphosphate was conditioned with 0.5 to 1.0% by weight of ammonia. Bag deterioration was decreased markedly and the available P_2O_5 content of the product was not decreased more than 1 unit by dilution and loss of availability. Treatment of cured product with 0.5%

of ammonia reduced free-acid P_2O_5 content from about 3% to about 1%. Use of 1% of ammonia reduced free-acid P_2O_5 to less than 0.5%. It is believed that conditioning with ammonia will satisfactorily solve the bag-storage problem.

Production of Granular High-Analysis Superphosphate

High-analysis superphosphate also has been produced in a granular form in pilot plant tests. Acidulation and granulation were accomplished simultaneously in a rotary drum by a technique similar to the one-step process developed by TVA for production of granular triple superphosphate (4). Granulation was controlled more easily in production of the high-analysis superphosphate. No recycle was required for control, because of the very low moisture content and rapid set time of the acidulate. The primary control of granulation was through regulation of the temperature of the acid. The acid was heated to a range of 225° to 300° F. and fed at a concentration equivalent to about 102% H_3PO_4. The superphosphoric acid was diluted to about 102% H_3PO_4 either in the feed tank or by continuous addition of water in a mixing wye on the acid distributor. Operation was satisfactory with proportioning of acid and rock to give P_2O_5:CaO mole ratios of 0.98 to 1.05.

Tests were made in the pilot plant with the distributor for acid located above the bed of material in the drum and located beneath the bed. Although results were reasonably good with the distributor above the bed, areas of excessive stickiness sometimes resulted and impaired granulation efficiency. The use of a submerged distributor that contained 20 holes 3/32 inch in diameter, which distributed acid over about the first half of the length of the drum, gave best results. The addition of about 40 pounds of steam per ton of product through a parallel distributor beneath the bed also assisted in control of granulation. Use of distributors beneath the bed allowed satisfactory operation with acid temperature as low as 225° F.; a temperature of 275° to 300° F. was required when the acid was distributed above the bed. With distributors beneath the bed, best results were obtained with a rotational speed of the drum of about 35% of critical speed. Critical speed in revolutions per minute is determined by the relationship, $76.5/\sqrt{D}$, where D is the diameter of the drum in feet (7). A higher rotational speed of 45 to 50% of critical speed was best when the acid was distributed above the bed.

With the distributors beneath the bed, it was possible to control granulation to produce a high percentage of granular product in the −6- +20-mesh range or to

produce a semigranular product containing about half granular material and half fines. The fine (−20-mesh) material produced in this manner ammoniated satisfactorily in the production of granular high-analysis fertilizers. The semigranular product could be screened to provide both granular superphosphate for direct application and fine material for ammoniation and use in complete fertilizer formulations.

Data for a typical test of the production of granular high-analysis superphosphate in the pilot plant are given in Table II.

As in the production of nongranular material, it was necessary to den the granular product at least 1 hour to obtain good conversion and a high product grade. The temperature of the granular product increased to a range of 300° to 350° F. during denning. The amount of fluorine evolved increased as the denning time was increased. The percentage of fluorine evolved, conversion, and grade of product at various denning times and after curing for 3 days are shown in the following tabulation. The acid concentration was 102% H_3PO_4 and the acid P_2O_5:CaO mole ratio was 0.98.

Time of Denning, Hr.	Evolution of Fluorine, %	Con-version, %	Grade, % Available P_2O_5
1	52	87	52.5
8	54	89	53.5
12	56	89	54
20	60	90	54
Cured 3 days at 250° F.	66	92	55

In producing the granular material, screening should be deferred until denning is completed or until after pile storage for a few days. This allows maximum evolution of fluorine and high denning and curing temperatures, which are favorable to conversion.

Bulk density of the granular product is about 65 pounds per cubic foot and the angle of repose is about 38°.

Materials of Construction

Type 316 stainless steel was satisfactory for the cone mixer for high-analysis superphosphate and for pumps and piping for handling the superphosphoric acid up to 200° F. Mild steel was satisfactory for the granulation drum in the pilot plant. Corrosion test data indicate that red brass should be satisfactory for handling heated superphosphoric acid at 250° to 300° F.; the corrosion rate was about 15 mils per year. Hastelloy B had a corrosion rate of 1 mil per year or less in this service. Stainless steels showed excessive corrosion in contact with superphosphoric acid at 250° F. and higher.

Conclusions

Superphosphoric acid can be used to

Table II. Production of Semigranular High-Analysis Superphosphate

Production rate, tons/hr.	1.7
Formulation, lb./ton product	
Phosphate rock (32.3% P_2O_5, 46.4% CaO, 0.5% H_2O)	921
Phosphoric acid, 102% H_3PO_4 (73.9% P_2O_5)	1047
Steam	30–60
Temperature, ° F.	
Acidulator product	326
Acid preheat	276
Screen analysis (Tyler), %	
+6 mesh	15.4
−6 +10 mesh	12.5
−10 +16 mesh	38.8
−16 +20 mesh	6.3
−20 +28 mesh	10.4
−28 mesh	16.6
Chemical analysis of product after curing 4 days at 250° F., %	
Total P_2O_5	55.8
Available P_2O_5	54.9
W.S. P_2O_5	52.1
Free acid P_2O_5	3.8
F	0.5
CaO	21.1
H_2O	2.0
Net conversion of P_2O_5 from rock, %	
Denned 20 hr.	89
Cured 4 days at 250° F.	94
Further cured 10 days at 150° F.	94
Fluorine evolved, %	
Denned 20 hr.	52
Cured 4 days at 250° F.	60
Further cured 10 days at 150° F.	60

acidulate phosphate rock to produce superphosphate of unusually high analysis. Both granular and nongranular products can be produced in equipment commonly used in the fertilizer industry. Heating of the acid and provisions for denning the material for at least 1 hour are required to obtain satisfactory reaction and to facilitate fluorine recovery, which is expected to become of more and more importance in the future. The high proportion of fluorine evolved, about 20 pounds per ton of high-analysis superphosphate, should make recovery particularly attractive.

Savings should result in handling and shipping the more concentrated superphosphate and the higher analysis grades of complete fertilizers that can be formulated with it. Additional economy in formulating the usual grades should result because more ordinary (20%) superphosphate can be used. The low moisture content, higher heat of reaction during ammoniation, and the fact that high-analysis superphosphate is less dusty in handling also are of importance in its use in fertilizer formulations. Satisfactory bulk handling has been demonstrated, and promising results have been obtained in treating the material to prevent excessive attack on bags.

Acknowledgment

plant tests, and George Hoffmeister, Jr., who supervised conditioning and storage tests. They are indebted also to T. P. Hignett, chief of the Applied Research Branch, whose advice helped direct the course of the work. A large part of the analytical work was done by R. D. Duncan and L. J. Sheffield.

Literature Cited

(1) Brook, A. T., "Granular Compound Fertilizers," Joint Technical-Agronomic Conference, International Superphosphate Manufacturers' Association, Lausanne, September 1956.
(2) Heil, F. G., Young, R. D., Stumpe, J. J., "Pilot-Plant Study of an Ammonium Fluoride Process for Recovery of Fluorine from Superphosphate," Division of Fertilizer and Soil Chemistry, 136th Meeting ACS, Atlantic City, N. J., September 1959.
(3) McKnight, David, Striplin, M. M., Jr., Agr. Chem. 13, 33–4 (August 1958).
(4) Phillips, A. B., Young, R. D., Lewis, J. S., Jr., Heil, F. G., J. Agr. Food Chem. 6, 584–7 (1958).
(5) Striplin, M. M., Jr., McKnight, David, Megar, G. H., Ibid., 6, 298–303 (1958).
(6) Striplin, M. M., Jr., Stinson, J. M., Wilbanks, J. A., Ibid., 7, 623–8 (1959).
(7) Tennessee Valley Authority, Chem. Eng. Rept. 5, compiled by G. L. Bridger, p. 53, U. S. Government Printing Office, Washington, D. C., 1949.
(8) Young, R. D., Heil, F. G., J. Agr. Food Chem. 5, 682–7 (1957).

FERTILIZER TECHNOLOGY

Calcium Superphosphate Manufacture by a Low Acidulation-Quick Conversion Process

SHAW-CHEN LEE and CHIU-CHIN LIN

Factory No. 2, Taiwan Fertilizer Co., Ltd., Keelung, Taiwan, China

A low acidulation and quick conversion process for the manufacture of calcium superphosphate was developed on a pilot plant scale, starting with acidulation of phosphate rock with a comparatively low acid-rock ratio. The acidulated mass was then autoclaved, concentrated, and converted under controlled conditions. Good conversion was obtained in various experiments, and the product contained 3 to 7% of citrate-soluble phosphorus pentoxide and 11 to 15% of water-soluble phosphorus pentoxide with excellent physical properties.

THE CONVENTIONAL PROCESS for calcium superphosphate requires acidulation of phosphate rock for the formation of monocalcium phosphate and subsequent curing of the green product for 4 to 6 weeks. To save curing space and time, a quick-curing process (2, 4) was developed. To save the mineral acid required in acidulation, experimental work on dicalcium phosphate has been done. Based on previous work on dicalcium phosphate (3) and superphosphate (7), a low acidulation-quick conversion process for the manufacture of calcium superphosphate is presented.

Materials, Equipment, and Methods

Three phosphate rock samples and crude chamber sulfuric acid were used (Tables I and II).

The equipment (Figure 1) consisted essentially of an autoclave reactor and an electrically heated paddle-type continuous converter. The function of the reactor was to perform the acidulation and hydrolysis reactions and that of the converter was to evaporate and to convert the partially hydrolyzed mixture.

Total water was determined by heating 5 grams of the sample at 99 to 101°

Table I. Analysis of Phosphate Rock

	Phosphate Rock		
	P_1, Florida	P_2, Florida	P_3, Morocco
Chemical Analysis (Air-Dry Basis), %			
Total P_2O_5	34.23	33.95	34.07
Citrate-insol. P_2O_5	31.09	31.29	...
CaO	49.30	...	50.90
R_2O_3	2.52	...	0.65
CO_2	3.21	...	3.89
F	3.87	...	3.94

Screen Analysis (Tyler Standard), Weight %

Mesh				
	+ 60	...	6.00	3.32
− 60	+ 80	6.0	6.60	5.73
− 80	+100	1.5	8.40	5.03
−100	+150	12.0	18.85	29.11
−150	+200	13.5	11.15	22.35
−200		67.0	49.00	34.46

C. for 5 hours. For free acid determinations a 2-gram sample was extracted with 50 ml. of 95% alcohol instead of acetone. The total, citrate-insoluble, and water-soluble phosphorus pentoxides were determined by the AOAC volumetric titration method (7), calcium oxide and combined oxides by

Table II. Analysis of Crude Chamber Sulfuric Acid

(Product from Factory No. 2)

	%
H_2SO_4	62.53
Total solids	0.15 −0.35
Suspension solids	0.04 −0.05
Total Fe	0.0053–0.00248
Soluble Fe	0.0047–0.00246
N_2O_3	0.023 −0.03
As	0.0259–0.0929

the usual method, and fluorine by the Willard-Winter method (6).

Procedure

Phosphate rock and 50° Be'. sulfuric acid were mixed, and water was added in the reactor which was made vaportight. The reactor was then kept at 100° to 105° C. by the embedded electric heater for the hydrolysis of the mixture. Speed of the stirrer in the reactor was 1300 to 1500 r.p.m. After heating, the material was discharged through the bottom outlet of the reactor into the paddle converter, the temperature of which had been regulated in the range of 110° to 150° C. by rheostat. The material was then continuously dried and