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FERTILIZER TECHNOLOGY

Calcium Superphosphate Manufacture by a Low Acidulation-Quick Conversion Process

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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 ₂ O ₅	34.23	33.95	34.07
Citrate-insol. P ₂ O ₅	31.09	31.29	...
CaO	49.30	...	50.90
R ₂ O 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

Table II. Analysis of Crude Chamber Sulfuric Acid

	%	
	(Product from Factory No. 2)	
H ₂ SO 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 ₂ O 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 vapor-tight. 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

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

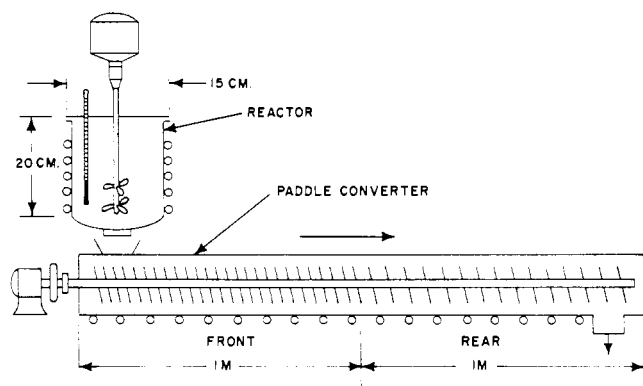


Figure 1. Arrangement of pilot plant

Reactor. 304 stainless steel with embedded Nichrome wire heater
 Paddle converter. Casing and paddle of mild and 304 stainless steel, respectively. Nichrome wire heater, 1 kw. for front section and 0.8 kw. for rear section. Pitches of paddles, 3.5 and 7 cm. for front and rear sections, respectively. Rotating speed of paddle shaft, 73 seconds per revolution. Driving motor, 1 hp.

Table III. Effect of Conversion Temperature,^a Conversion Time,^b and Number of Cycles^c

Expt.	No. of Runs	Converter	Conversion Temp., ° C.	Moist., %	Acidity, %	P ₂ O ₅ in Product, %				Availability, %	
						Total	Citrate-insol.	Available	Water-sol.		As DCP ^d
SERIES A ^e											
T-147	...	Oven	90-5, 4 hr.	16.78	...	19.51	3.55	15.96	12.96	3.00(15.4)	81.8
T-140	...	Pad.	127-37	1.82	1.64	23.28	4.81	18.47	12.53	4.93(21.2)	79.3
		Oven	150, 30 min.	1.75	1.94	23.75	5.76	17.99	11.88	6.11(25.7)	75.8
T-134	...	Pad.	156-9	2.83	0.95	22.48	4.71	17.77	13.09	4.68(20.8)	79.0
		Oven	130, 30 min.	2.31	0.92	22.70	4.21	18.49	14.62	3.87(16.7)	81.5
T-133	...	Pad.	150-8	3.59	1.11	22.32	4.57	17.75	13.40	4.35(19.5)	79.7
SERIES B ^f											
T-148	...	Oven	90-5, 4 hr.	17.22	...	18.53	3.01	15.52	11.84	3.68(19.9)	83.8
T-139	...	Pad.	125-35	1.63	1.56	22.32	3.60	18.72	14.36	4.36(19.6)	84.0
		Oven	150, 30 min.	1.32	1.45	23.01	3.80	19.18	14.14	5.04(21.9)	83.0
T-138	...	Pad.	122-38	2.41	1.26	21.95	3.21	18.74	15.00	3.74(17.1)	85.00
		Oven	150, 30 min.	0.74	2.15	22.61	3.61	19.00	13.91	5.09(22.5)	84.1
T-132	...	Pad.	143-57	1.41	2.40	22.75	3.72	19.03	11.13	7.90(34.8)	83.1
		Oven	130, 30 min.	3.74	1.32	22.28	2.47	19.81	15.95	3.86(17.3)	88.8
T-131	...	Pad.	160-55	1.97	2.29	21.63	3.73	17.90	10.92	6.98(32.4)	82.8
SERIES C ^g											
	No. of Passages										
T-142	1	...	110-38	2.70	1.34	22.96	4.42	18.54	14.43	4.11(17.9)	80.8
	2	...	112-39	1.00	1.66	23.49	5.39	18.10	11.63	6.53(27.8)	77.1
T-143	1	...	112-35	2.63	1.19	22.67	4.93	17.73	13.29	4.45(19.6)	78.2
	2	...	111-34	1.06	1.56	23.40	5.82	17.58	10.78	6.80(29.1)	75.2
SERIES D ^h											
T-144	1	...	105-30	4.57	1.45	21.27	3.24	18.03	14.70	3.33(15.6)	84.7
	2	...	109-34	2.72	2.01	22.45	3.90	18.55	12.98	5.57(24.8)	82.5
T-145	1	...	115-39	3.24	1.94	22.12	3.65	18.47	14.09	4.38(19.8)	83.7
	2	...	116-40	2.48	2.69	22.18	4.11	18.70	12.18	6.52(29.4)	82.1
SERIES E ⁱ											
	No. of Cycles										
T-146	1	...	120-10	2.64	2.07	21.23	3.21	18.02	15.08	2.94(13.9)	84.8
T-147 ^j	2	...	119-14	2.31	1.55	21.31	2.91	18.40	14.58	3.82(17.9)	86.3
T-148	2	...	121-15	2.42	1.41	21.49	2.89	18.51	14.67	3.84(17.9)	86.1
T-149	1	...	118-08	2.98	2.18	21.12	3.35	17.77	14.65	3.12(14.8)	84.2
	2	...	120-11	3.23	1.80	20.90	2.81	18.09	14.45	3.64(17.4)	86.7
	3	...	128-35	2.56	1.96	21.02	2.48	18.54	13.94	4.60(21.9)	88.3
T-151	1	...	120-18	3.42	2.53	21.00	3.25	17.75	14.94	2.81(13.4)	84.6
	2	...	118-31	2.91	2.08	21.13	2.81	18.32	14.99	3.33(15.8)	86.8
	3	...	126-29	2.36	1.53	21.30	2.53	18.77	15.00	3.77(17.7)	88.2

^a Experimental conditions for A and B. One cycle. One passage through converter. Hydrolysis time, 5 hours. Hydrolysis temp., 100-20° C.

^b Experimental conditions for C and D. Hydrolysis time for 1st cycle, 5 hr. Hydrolysis temp., 100-03° C.

^c Experimental conditions for E. Hydrolysis time. For 1st cycle 5 hr., for 2nd and 3rd cycles 1 hr. Hydrolysis temp. 100-03° C.

^d Dicalcium phosphate. Figures in parentheses indicate percentage on total P₂O₅ basis.

^e Acidulation mole ratio 1.9, phosphate rock (P₁) 1430 g., H₂SO₄ 50° Be.' 1040 g., water 500 cc. (free moist. 30%).

^f Acidulation mole ratio 2.1, phosphate rock (P₁) 1430 g., H₂SO₄ 50° Be.' 1140 g., water 500 cc. (free moist. 30%).

^g Acidulation mole ratio 1.9, phosphate rock (P₂) 1430 g., H₂SO₄ 50° Be.' 1020 g., water 500 cc. (free moist. 30%).

^h Acidulation mole ratio 2.1, phosphate rock (P₂) 1430 g., H₂SO₄ 50° Be.' 1120 g., water 500 cc. (free moist. 30%).

ⁱ Acidulation mole ratio 2.1, phosphate rock (P₃) 1072.5 g. H₂SO₄ 50° Be.' 847.5 g.

^j Grinding of 1st cycle product, all passing 80 mesh.

Table IV. Average Results of Conversion

Acidulation Ratio, Moles H ₂ SO ₄ /P ₂ O ₅ Cycle	No. of Product	Moisture, %	Product Acidity, %	% P ₂ O ₅ in Product					P ₂ O ₅ Avail., ability %
				Total	Citrate-insol.	Available	Water-sol.	DCP	
1.9	1	2.15	1.24	22.74	4.09	18.05	13.55	4.50	79.4
2.1	1	2.98	2.18	21.12	3.35	17.77	14.65	3.12	84.2
	2	3.23	1.80	20.90	2.81	18.09	14.45	3.65	86.7
	3	2.56	1.96	21.02	2.48	18.54	13.94	4.60	88.3

Table V. Comparison of Results of Proposed Process with Conventional Process

Phosphate Rock, P ₃			Acidulation Ratio			P ₂ O ₅ Conversion, %	
Composition, %	Gram Moles/Kg. Rock	Gram Moles/Kg. Rock	Gram Moles/Kg. Rock		% theoretical	Result obtained	Conventional
			Theoretical	Actually used			
P ₂ O ₅	34.07	2.4	4.8	2.1 mole	79.6	88.3	110.6
CaO	50.90	9.08	1.53	ratio series			
F	3.94	0.35 ^a					
			6.33	5.04			

^a As SiF₆.

granulated in the converter. In normal operation the material took 60 minutes to pass through the paddle converter.

Results

Experiments were made with an acidulation mole ratio equivalent to 1.9 and 2.1 moles of sulfuric acid per mole of phosphorus pentoxide, and a heating period of 5 hours for the first cycle and 1 hour for subsequent cycles in the autoclave for each series of experiments. The conditions for the acidulation step were kept almost constant as specified in each series of experiments. Other conditions of acidulation and heating time have been tried with poor results. Impurities in acidulation gave obscure experimental results. Results in Table III are arranged according to the order of the influence of varying conditions.

Effect of Conversion Temperature

In this series of experiments, conversion temperature for the partially hydrolyzed mixture varied from 95° to 150° C. (Table III, A and B). For comparison of performance, the conversion step for each hydrolyzed mass was run in parallel with both the continuous paddle converter and the laboratory electric drying oven with automatic temperature-controlling device. These results show that a suitable conversion temperature is 110° to 130° C., while the formation of dicalcium phosphate increases with increasing temperature and time of conversion. Apparently reversion of available phosphate occurred above 130° C. in the continuous paddle converter.

Effect of Conversion Time

Conversion time for the hydrolyzed mass was varied from 1 hour for single passage through the continuous paddle converter to 2 hours for double passage, by which the product discharged from the first passage was subjected to second passage through the paddle converter without intermediate grinding and moistening (Table III, C and D). Although time intervals for conversion shorter than 1 hour have not been tried, time required for conversion between 110° and 130° C. in the paddle converter should be from 30 minutes to 1 hour. Citrate-soluble phosphorus pentoxide mainly as dicalcium phosphate increased from 3% to around 7% at the expense of total phosphorus pentoxide when the first passage product was put through the double passage.

Effect of Number of Cycles

Experiments were made with an acidulation mole ratio of 2.1, and recycling of hydrolysis and conversion steps were carried out without intermediate grinding of the first cycle product in most instances (Table III, E). Up to 3 cycles of processing an increment of more than 2% in phosphorus pentoxide availability and 3% in citrate-soluble phosphorus pentoxide can be effected through each cycle.

Conversion temperature seems to be the most important factor influencing phosphorus pentoxide availability. The resultant data are averaged in Table IV.

The product from the continuous converter had good physical properties with a granular size yield of around 70%. The screen analyses of the product from experiments 143 and 145 are:

Size, Tyler Mesh		Wt., %	
		T-143	T-145
	+ 3	14.1	16.8
- 3	+10	62.5	63.7
-10	+20	12.1	11.3
-20	+35	4.4	4.4
-35		6.9	3.8

Discussion

When the proposed process is considered as underacidulation in which calcium fluorosilicate in rock does not consume sulfuric acid, the degree of acidulation and resultant conversion of the proposed process are compared with those of the conventional process in Table V.

As compared with the conventional process for calcium superphosphate, the proposed process requires an acidulation mole ratio of around 2.1 instead of 2.6 and a reaction time of about 10 hours instead of 4 to 6 weeks for curing. Although the loss in insoluble phosphorus pentoxide and the processing and equipment cost of the proposed process may seem higher than those of the conventional process, the net savings of about 15% in acidulation and in the costs of storage, curing, handling, and granulation should be appreciable.

As compared with the process for dicalcium phosphate, the proposed process seems to be more convenient, direct, and feasible, with comparable results.

The proposed process for calcium superphosphate includes direct acidulation, hydrolysis, and thermal conversion performed in a simple and continuous operation. Because good conversion can be obtained with less sulfuric acid, the process seems to be adaptable for superphosphate manufacture.

As the process converts only 15 to 30% of the phosphorus pentoxide in phosphate rock to dicalcium phosphate and the remainder to monocalcium phosphate, the product should be less liable to water loss than ordinary superphosphate and more effective than dicalcium phosphate fertilizer. However, this experiment is only a preliminary new approach to calcium superphosphate. Process conditions and plant equipment need to be further explored and developed.

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TRACE ELEMENTS ANALYSIS

Preparation of Plant Tissues for Micronutrient Analysis. Removal of Dust and Spray Contaminants

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Procedures for removal of contamination from dust and spray residues from plant tissues prior to analysis for micronutrients are described. Three herbaceous plants—rye, tomato, and sugar beet—were dusted with soil or sprayed with a simulated Bordeaux spray containing copper, iron, manganese, molybdenum, and zinc. Effectiveness of removal of contamination by dilute hydrochloric acid or dilute hydrochloric acid plus detergent was measured. Dust contamination was removed satisfactorily by both wash solutions. Spray contamination was difficult to remove by washing. The wash solutions and procedures used did not result in loss of elements from within the tissues.

REPORTS on the need for removal of surface contamination from plant tissue prior to determination of micronutrients have largely been confined to work with iron in tissues such as leaves of citrus (7) and pears (2). Jacobson (2) considered it necessary to wash corn and tobacco leaves with dilute acid prior to iron determination, and Jacobson and Oertli (3) washed sunflower leaves with 2% Dreft detergent solution for the same purpose. Nicholas, Lloyd-Jones, and Fisher (6) studied methods of removing surface contamination from tomato tops and showed that immersion of fresh tissue in a detergent (0.37% Teepol) or in detergent and then 0.25*N* hydrochloric acid, followed by distilled water rinsing, removed iron contaminant from leaf surfaces without causing loss of potassium, phosphorus, manganese, or internal iron (tagged with iron-59).

This paper describes studies designed to obtain additional information, for three herbaceous species, on the efficiency of procedures for removing contamination with manganese, copper, zinc, and molybdenum as well as iron. This information is of consequence because of increasing recognition of the need for reliable chemical analyses in order to assess potential micronutrient deficiencies in annual crops where the analytical hazard from soil and spray residue contamination is large.

Because of the nature of the foliar sample—usually small and easily bruised leaves—it did not appear that procedures

recommended for cleaning surfaces of tree leaves would be generally applicable. Smith, Reuther, and Specht (7) and others have recommended either scrubbing citrus leaves with a fiber-bristled hand brush or wiping with moistened clean cloth, and Jacobsen (2) rubbed pear leaves with the fingers in 0.3*N* hydrochloric acid. These procedures would be time-consuming when applied to tissues such as grasses or tomato leaves and also subject to the risk of damaging the tissue and permitting leakage of ions from the interior. Therefore, the procedure of Nicholas *et al.* (6), of simply immersing and agitating the samples in the washing and rinsing solutions, was studied to determine whether surface contamination could be removed from the species under consideration.

The question of whether elements are leached from within plant materials is usually raised when decontamination by washing is suggested. In a recent review of foliar leaching, Tukey, Tukey, and Wittwer (8) presented data which show that the continuous leaching of plant leaves with distilled water for periods up to 24 hours results in the loss of appreciable quantities of some absorbed nutrients. However, their data show that the leaching losses are a direct function of time, and that losses to be expected even in 2 hours' leaching from detached leaves appear to be 5% or less, depending upon the element and plant species studied. Their results therefore support the conclusions of

Nicholas *et al.* (6) and of the authors (as will be shown) that there is negligible hazard of leaching losses during washing procedures of short duration (2 minutes in this study).

Materials and Methods

The three species used—sugar beet, rye, and tomato—represent a variety of leaf types. The plants were cultured on nutrient solutions according to the procedure of Johnson *et al.* (4) in a relatively dust-free greenhouse (filtered ventilating air and concrete floor), and were about 2 months old when contaminated with dust or spray. Six 18-liter containers of nutrient solutions were provided for each species. For tomato and sugar beet, six plants were grown in each container; for rye there were 18 plants per container.

Within each species, plants were randomized among containers just before application of contaminants. This precaution to minimize the effects of possible variation between culture solutions was perhaps unnecessary, as the media were carefully made up and growth for a given species was visibly uniform.

Contamination Treatments

The plants of two containers of each species were retained uncontaminated as controls. Those of two other containers were sprayed with a Bordeaux-type spray containing 1 gram per liter