Dicalcium Phosphate Fertilizer by Treatment of Phosphate Rock with Mineral Acids
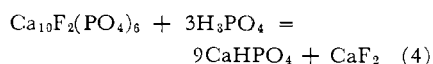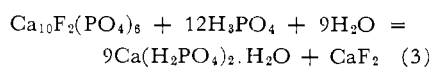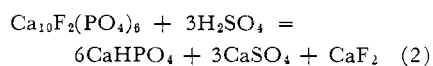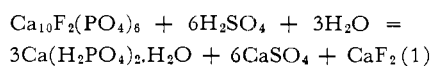
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A process in which phosphate rock is made to react with mineral acids to produce a fertilizer containing primarily dicalcium phosphate consists of refluxing a mixture of phosphate rock, water, and acid, followed by heating in an open container to 130° to 185° C. Conversion to dicalcium phosphate in the product may be increased by adding water and repeating the refluxing and heating steps. When phosphoric acid is used, the acidulation required to produce the new product is only about 50% of that required for production of triple superphosphate, based on the phosphorus pentoxide content of the phosphate rock, or about 75% based on the available phosphorus pentoxide content of the product. When sulfuric acid is used, somewhat higher acidulation ratios are required because of the interfering action of the calcium sulfate. The water-soluble phosphorus pentoxide content of the product may be varied from a small to a large proportion of the total by conditions of treatment.

THE POTENTIAL ADVANTAGES of a process in which dicalcium phosphate fertilizer could be produced by direct acidulation of phosphate rock with mineral acids have long been recognized and much research has been directed toward discovery of such a process. However, previous investigators have not found practical conditions under which dicalcium phosphate could be prepared by direct acidulation of phosphate rock.

Theoretically the formation of dicalcium phosphate by direct acidulation of phosphate rock with either sulfuric or phosphoric acid would require only half as much acid to produce a unit of available phosphorus pentoxide as formation of monocalcium phosphate, the principal component of superphosphates. This is illustrated by the following equations:

$$Ca_{10}F_2(PO_4)_6 + 6H_2SO_4 + 3H_2O =$$
$$3Ca(H_2PO_4)_2.H_2O + 6CaSO_4 + CaF_2 \quad (1)$$

$$Ca_{10}F_2(PO_4)_6 + 3H_2SO_4 =$$
$$6CaHPO_4 + 3CaSO_4 + CaF_2 \quad (2)$$

$$Ca_{10}F_2(PO_4)_6 + 12H_3PO_4 + 9H_2O =$$
$$9Ca(H_2PO_4)_2.H_2O + CaF_2 \quad (3)$$

$$Ca_{10}F_2(PO_4)_6 + 3H_3PO_4 =$$
$$9CaHPO_4 + CaF_2 \quad (4)$$

Reactions 1 and 3 take place in the manufacture of normal and triple superphosphate, respectively. Reactions 2 and 4 do not occur appreciably under ordinary conditions of acidulation.

When sulfuric acid is used to produce

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normal superphosphate, the theoretical acidulation ratio according to Equation 1 is 2 moles of acid per mole of phosphorus pentoxide derived from rock phosphate (or available phosphorus pentoxide in the product). In practice somewhat more acid is used—about 2.6 moles of acid per mole of rock phosphorus pentoxide—because of side reactions that take place between the acid and calcium carbonate, calcium fluoride, iron and aluminum compounds, and other constituents of the rock. If sulfuric acid could be made to produce dicalcium phosphate according to Equation 2, the theoretical acidulation ratio would be only 1 mole of acid per mole of rock phosphorus pentoxide (or available phosphorus pentoxide in the product).

When phosphoric acid is used to produce triple superphosphate, the theoretical acidulation ratio according to Equation 3 is 2 moles of acid phosphorus pentoxide per mole of rock phosphorus pentoxide or $2/3$ mole of acid phosphorus pentoxide per mole of available phosphorus pentoxide in the product. In practice about 2.3 moles of acid phosphorus pentoxide per mole of rock phosphorus pentoxide is used because of side reactions. If phosphoric acid could be made to produce dicalcium phosphate according to Equation 4, the theoretical acidulation ratio would be only 0.5 mole of acid phosphorus pentoxide per mole of rock phosphorus pentoxide or 0.33 mole of acid phosphorus pentoxide per mole of available phosphorus pentoxide in the product.

One significant advantage of a direct acidulation process for dicalcium phosphate fertilizer, in addition to savings in acid requirements, would be that the nation's sulfur reserves would be greatly extended, as the fertilizer industry is a major consumer of sulfuric acid, which is required for normal superphosphate manufacture and indirectly for triple superphosphate manufacture.

Previous Investigations

Many previous investigators (4-6) have concluded that dicalcium phosphate cannot be formed by treatment of phosphate rock with mineral acids. Elmore and Farr (3) studied the hydrolysis of monocalcium phosphate according to the following equation:

$$Ca(H_2PO_4)_2.H_2O + xH_2O =$$
$$CaHPO_4 + H_3PO_4 + (x + 1)H_2O \quad (5)$$
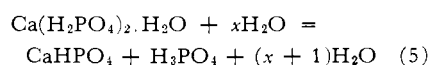
with the objective of utilizing the phosphoric acid formed by this reaction to react with phosphate rock and thereby achieving a substantial conversion to dicalcium phosphate. It was not found possible to do this except by separation of the dicalcium phosphate from the dilute phosphoric acid by filtration, followed by concentration of the acid and reaction with phosphate rock (6). Zbornik (7) patented a process in which phosphate rock, phosphoric acid, and water were autoclaved at about 100 pounds per square inch and 200° C. to produce a dicalcium phosphate product, but the process has never been adopted commercially because it requires high pressure operation.

Exploratory Experiments

A large number of exploratory experiments were carried out in attempts to dis-

cover conditions under which dicalcium phosphate could be formed by direct reaction between phosphate rock and phosphoric or sulfuric acid. Because monocalcium phosphate is usually the first product of reaction between phosphate rock and either acid, studies were also made to discover conditions under which reactions could be effected between monocalcium phosphate and phosphate rock. Conditions were explored under which monocalcium phosphate would be hydrolyzed according to Reaction 5 to a large extent and new conditions were then imposed to promote reaction between the phosphate rock and phosphoric acid according to Equation 3. It is seen that if Reactions 5 and 3 could be made to take place alternately or simultaneously, substantially complete conversion of the phosphorus pentoxide in phosphate rock to dicalcium phosphate could be effected, the net result of which would be substantially equivalent to Reaction 4.

A procedure was evolved by which this can be carried out.

1. Mixing phosphate rock with monocalcium phosphate and water, or with phosphoric or sulfuric acid and water, in a proportion such as to convert only part of the phosphate rock into monocalcium phosphate.
2. Heating the mixture at or near its boiling point (usually about 110° C.) under reflux, so as to promote hydrolysis of the monocalcium phosphate in the mixture to dicalcium phosphate and phosphoric acid.
3. Heating the mixture without reflux in an open container to a temperature of at least 130° C. and preferably 185° C., under which conditions the acid formed by the hydrolysis is concentrated and reacts with the phosphate rock. The product from this heating is a dry mass consisting largely of dicalcium phosphate and small proportions of monocalcium phosphate and rock phosphate.
4. Grinding the product from step 3, rewetting with water, and repeating steps 2 and 3, thereby converting the unreacted monocalcium phosphate and phosphate

rock from step 3 largely into dicalcium phosphate. The entire cycle may be repeated as many times as desired, with a smaller degree of conversion taking place each time, but in practice, the conversion attained with only one or two cycles is probably sufficient from an economical point of view.

After the general procedure had been established, experiments were carried out to determine the optimum conditions.

Materials and Procedure

A Florida phosphate rock was used which had the following percentage composition on a dry basis.

P_2O_5	33.2
Citrate-insoluble P_2O_5	29.4
CaO	47.8
MgO	0.4
Al_2O_3	1.3
Fe_2O_3	1.1
SiO_2	9.1
F	3.80

The screen analysis (per cent) of the phosphate rock was as follows:

+60 mesh	0.3
−60 +100	10.3
−100 +150	11.4
−150 +200	22.8
−200 +325	43.5
−325	11.7

c.p. monocalcium phosphate monohydrate containing 56.0% phosphorus pentoxide, and c.p. grades of phosphoric and sulfuric acids were used.

Procedure Phosphate rock, water, and monocalcium phosphate monohydrate, superphosphate, or acid were mixed in a 250- or 300-ml. Erlenmeyer flask, which was then fitted with a reflux condenser and a stainless steel mixer, the shaft of which extended through the condenser. The flask was then placed in an oil bath heated by either an electric hot plate or gas flame. The oil bath was maintained at a tem-

perature sufficient to cause gentle boiling of the mixture in the flask; the oil bath temperature was generally 120° to 125° C. and the boiling temperature of the mixture was usually 110° to 115° C. The mixer was operated at a moderate speed. Most of the mixtures varied in consistency from very thick slurries to pasty masses at room temperature, but on heating they became thin slurries which were easily agitated.

After completion of the refluxing, the condenser was removed and the open flask was placed in a second oil bath heated to the desired conversion temperature. Agitation during the conversion step was not used for most of the experiments, because the slurry soon became too thick to be mixed by the laboratory mixer. When the temperature of the material approached the desired conversion temperature, the heat input to the bath was reduced; otherwise the flask temperature would exceed the bath temperature by as much as 20° C. because of the exothermic reaction in this step. The material was held at the desired conversion temperature for a specified period, then was removed, allowed to cool, and ground in a Micro-Samplmill with a screen having herringbone slots of 0.013-inch opening. A typical particle size of the product after grinding was as follows (per cent):

+60 mesh	1
−60 +100	14
−100 +150	15
−150 +200	25
−200 +325	40
−325	5

In subsequent cycles, the ground product was brought back to the same free water content as the initial mixture, and the hydrolysis and conversion steps were repeated.

The samples were analyzed according to the procedures of the Association of Official Agricultural Chemists (1), except that the colorimetric procedure of Bridger, Boylan, and Markey (2) was used for determination of phosphorus pentoxide in the final solutions. The procedure was checked frequently against a Bureau of Standards phosphate rock sample.

Reaction of Phosphate Rock with Monocalcium Phosphate Monohydrate

A series of experiments was carried out to determine the optimum conditions for reaction between phosphate rock and monocalcium phosphate monohydrate. In these experiments the proportion of monocalcium phosphate monohydrate was expressed as an equivalent acidulation ratio of acid phosphorus pentoxide to rock phosphorus pentoxide. In calculating this ratio it was assumed that two thirds of the phosphorus pentoxide in the

Table I. Effect of Water Content of Hydrolysis Mixture on Reaction of Phosphate Rock and Monocalcium Phosphate Monohydrate[a]

| % Free Water | % P_2O_5 in Product | | | | % P_2O_5 Availability |
	Total	Citrate-insol.	Avail.	Water-soluble	
Untreated mixture[b]	47.9	8.7	39.2	31.8	82.0
0	51.0	11.0	40.0	32.0	78.5
1.6	51.0	6.9	43.1	32.3	84.6
7.3	51.8	1.8	50.0	19.7	96.5
14.3	52.6	1.2	51.4	18.8	97.7
18.9	51.0	2.2	48.8	16.6	95.7
24.7	52.2	2.1	50.1	13.1	96.0
42.1	51.6	3.5	48.1	15.5	93.2

[a] Acidulation ratio, 1.0 mole acid P_2O_5/mole rock P_2O_5; hydrolysis time, 30 min.; conversion temperature, 185° C.; conversion time, 30 min.
[b] No free water.

monocalcium phosphate monohydrate was acid phosphorus pentoxide and one third was rock phosphorus pentoxide, as required by Equation 3. As an example of the calculation, when 50 grams of phosphate rock and 88.5 grams of monocalcium phosphate monohydrate were used, the acidulation ratio was 1.0, calculated as follows:

$$\text{Acidulation ratio} = \frac{(0.667)\,(88.5)\,(0.560)}{(0.333)(88.5)(0.560) + (50)(0.332)} = 1.0$$

Effect of Hydrolysis Time
Experiments were made in which the hydrolysis time was varied from 0 to 2 hours. The hydrolysis time was considered to be time at boiling and did not include preheating time, which was usually 15 to 20 minutes for a conversion temperature of 130° C.

When hydrolysis was omitted entirely, the increase in conversion to available phosphorus pentoxide was less than half that achieved with 15-minute hydrolysis time. Some hydrolysis took place during the preheating and conversion step, but a definite advantage was achieved by holding the mixture at its boiling point for at least 15 minutes.

When the hydrolysis time was increased to 1 or 2 hours, the improvement in conversion was less than 1%. It was concluded that a 15-minute hydrolysis time was sufficient to achieve high conversion and that greater times were not warranted.

Effect of Water Content
The data of Elmore and Farr (3) show that the hydrolysis of monocalcium phosphate monohydrate to phosphoric acid and dicalcium phosphate (Equation 5) is at a maximum at 100° C. in a saturated solution containing 78% monocalcium phosphate monohydrate and 22% water, but that almost as high conversion can be achieved in considerably more dilute solutions. In the present work approximately the same proportion of free water to monocalcium phosphate monohydrate was usually used, but almost as good results could be obtained with smaller proportions. It was found that only sufficient water to produce a slurry at the boiling temperature was needed to promote the hydrolysis. It is desirable to use the least amount of water consistent with good conversion, as the expense of removing the water in the conversion step will thereby be reduced.

Table I shows the results of experiments made with various proportions of free water. These experiments were at an acidulation ratio of 1.0 pound of acid phosphorus pentoxide per pound of rock phosphorus pentoxide (1.77 pounds of monocalcium phosphate monohydrate per pound of phosphate rock). A 30-minute hydrolysis time, a conversion temperature of 185° C., and a conversion time of 30 minutes were used.

When no free water was used, no conversion to available phosphorus pentoxide was achieved; in fact, there was a slight decrease in conversion. With the lowest percentage of free water used (1.6%), the mixture appeared to be dry and little agglomeration took place, but a slight improvement in conversion resulted. With the next highest percentage of free water (7.3%), a thick paste and high conversion resulted. With all the other proportions of water, thin slurries resulted. Maximum conversion was achieved at about 14% free water, but the effect of water proportion was not great over a wide range (from 7.3 to 42.1%). The water-soluble phosphorus pentoxide content of the products decreased at the higher free water contents, presumably because of the greater time of heating to the conversion temperature.

Effect of Conversion Temperature
A series of experiments was made with an acidulation ratio of 1.0 pound of acid phosphorus pentoxide per pound of rock phosphorus pentoxide (1.77 pounds of monocalcium phosphate monohydrate per pound of phosphate rock). A hydrolysis time of 15 minutes and a conversion time of 30 minutes were used.

The results are shown in Table II and Figure 1. Maximum conversion to available phosphorus pentoxide (98.2%) was achieved at a conversion temperature of 185° C. However, over a temperature range from 155° to 245° C., conversions of 95% or higher were achieved. The water-soluble phosphorus pentoxide content of the products, however, decreased rapidly over this temperature range, and it would therefore be possible to produce products having large or small proportions of their phosphorus pentoxide in the water-soluble form as desired. For example, a product having half of its available phosphorus pentoxide in the water-soluble form could be made at a conversion temperature of 147° C. with a conversion of 94%, and a product having 25% of its available phosphorus pentoxide in a water-soluble form could be made at a conversion temperature of 173° C. with a conversion of 98%.

Effect of Conversion Time
Conversion time was varied in a series of runs in which conversion temperature was 185° C. (Table III). The time required for the hydrolyzed mixture to reach conver-

Table II. Effect of Conversion Temperature on Reaction of Phosphate Rock and Monocalcium Phosphate Monohydrate^a

| Conversion Temp., °C. | % P$_2$O$_5$ in Product | | | | % P$_2$O$_5$ Avail-ability | % F | % F Loss |
	Total	Citrate-insol.	Avail.	Water-soluble			
Untreated mixture^b	47.9	8.7	39.2	31.8	82.0	1.37^c	...
115	48.0	5.9	42.1	31.7	88.0	...	...
125	49.8	4.4	45.4	30.7	91.1	1.14	14
135	49.3	4.6	44.7	26.5	90.8	0.65	54
145	51.0	3.5	47.5	25.1	93.1	1.09	25
155	51.4	3.2	48.2	23.2	93.8	0.87	41
165	52.8	1.6	51.2	...	97.0	0.64	57
175	53.7	1.4	52.3	12.0	97.4	0.68	56
185	53.5	1.0	52.5	11.2	98.2	0.75	51
195	53.9	1.2	52.7	7.4	98.0	0.69	55
205	52.2	1.4	50.8	7.0	97.4	0.57	62
215	53.4	1.6	51.8	4.4	97.1	0.80	48
225	53.4	1.8	51.6	5.4	96.9	0.76	50
258	53.0	3.2	49.8	4.8	94.0	...	...

^{a} Equivalent acidulation ratio, 1.0 mole acid P$_2$O$_5$/mole rock P$_2$O$_5$; free water content during hydrolysis, 14%; hydrolysis time, 15 min.; conversion time, 30 min.
^{b} Before addition of free water.
^{c} Calculated from fluorine content of rock.

Table III. Effect of Conversion Time on Reaction of Phosphate Rock and Monocalcium Phosphate Monohydrate^a

| Conversion Time, Min. | % P$_2$O$_5$ in Product | | | | % P$_2$O$_5$ Availability |
	Total	Citrate-insol.	Avail.	Water-soluble	
0	51.4	1.8	49.6	23.6	96.8
10	51.4	1.8	49.6	21.2	96.8
30	52.5	1.5	51.0	19.8	97.2
60	52.4	1.3	51.1	18.9	97.7
180	53.4	1.5	51.9	15.5	97.3

^{a} Acidulation ratio, 1.0 mole acid P$_2$O$_5$/mole rock P$_2$O$_5$; hydrolysis time, 30 min.; free water content during hydrolysis, 14%; conversion temperature, 185° C.
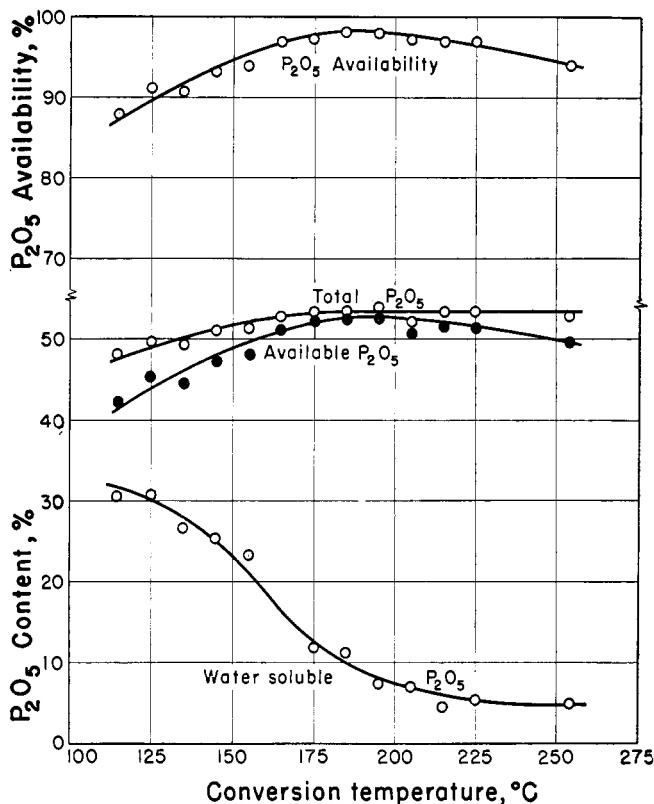
Figure 1. Effect of conversion temperature in treatment of phosphate rock and monocalcium phosphate
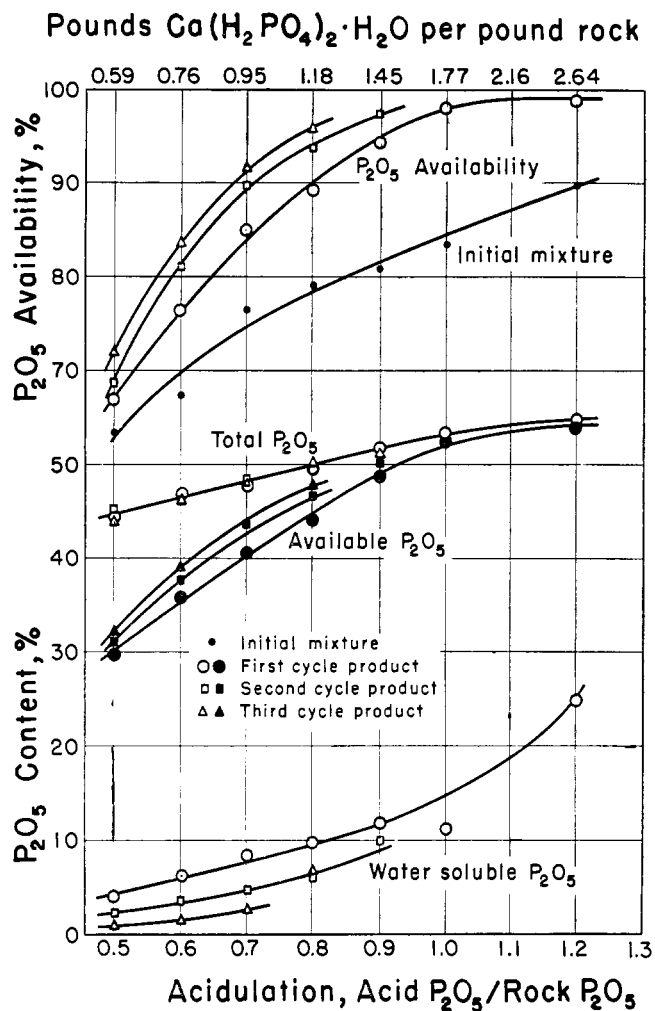Acidulation ratio 1.0

Figure 2. Effect of acidulation ratio in treatment of phosphate rock with monocalcium phosphate ▶
Conversion temperature 185 °C.

Pounds Ca(H₂PO₄)₂·H₂O per pound rock

Acidulation, Acid P₂O₅/Rock P₂O₅

sion temperature was 80 minutes. Additional time at this temperature improved conversion only very slightly, but significantly decreased the water-soluble phosphorus pentoxide content and increased total and available phosphorus pentoxide content, apparently through dehydration. Conversion time is therefore another means of controlling the proportion of water-soluble phosphorus pentoxide in the product.

Effect of Acidulation Ratio Experiments were made with various proportions of monocalcium phosphate monohydrate and rock; a hydrolysis time of 1 hour, a conversion temperature of 185° C., and a conversion time of 30 minutes were used. The free water content of the hydrolysis mixture ranged from 12.4 to 19.6%, the largest proportion being used at the lowest acidulation ratio.

The results are shown in Figure 2. For a single cycle the conversion to available phosphorus pentoxide decreases sharply at acidulation ratios lower than 1.0 mole of acid phosphorus pentoxide per mole of rock phosphorus pentoxide. However, second cycle product having a conversion of 97.3% was obtained at an acidulation ratio of 0.9 and third cycle product having a conversion

of 95.8% was achieved at an acidulation ratio of 0.8. Further cycles would probably have increased the conversion slightly but not enough to be of practical interest. It appears that high conversions cannot be attained at still lower acidulation ratios approaching the theoretical limit of 0.5; this is doubtless due to consumption of some of the acid by the rock impurities and to the small proportion of residual monocalcium phosphate monohydrate.

As expected, the water-soluble phosphorus pentoxide content of the products decreased with decreasing acidulation ratio and with each cycle of treatment. The proportion of available phosphorus pentoxide in the water-soluble form can thus be controlled by the acidulation ratio as well as by conversion time and temperature.

Reaction of Phosphate Rock with Superphosphates

As normal and triple superphosphates are the cheapest sources of monocalcium phosphate monohydrate, experiments were made in which these materials were made to react with phosphate rock by the above process.

The first series of experiments was

carried out with a triple superphosphate made in the laboratory by mixing some of the phosphate rock with 74% c.p. phosphoric acid at an acidulation ratio of 2.3 moles of acid phosphorus pentoxide per mole of rock phosphorus pentoxide and curing at room temperature until the moisture content of the product was 1.6%. This triple superphosphate was then mixed with various proportions of phosphate rock and subjected to treatments in which a 30-minute hydrolysis time, a 185° C. conversion temperature, and a 30-minute conversion time were used. The results are shown in Table IV. To achieve high conversion (94%) in a single cycle, it was necessary to use an acidulation ratio of 1.2 moles of acid phosphorus pentoxide per mole of rock phosphorus pentoxide. When an acidulation ratio of 1.1 was used, the same conversion could be obtained by using two cycles. The necessity for higher acidulation ratios than in the experiments with pure monocalcium phosphate was due to the additional impurities from the triple superphosphate. The water-soluble phosphorus pentoxide contents of the products were lower than when pure monocalcium phosphate was used.

In another series of experiments, a commercial triple superphosphate made

with wet-process phosphoric acid was used in various proportions. In calculating acidulation ratio, it was assumed that the superphosphate had been made with an acidulation ratio of 2.3 moles of acid phosphorus pentoxide per mole of rock phosphorus pentoxide. In these experiments a hydrolysis time of 15 minutes, a conversion time of 30 minutes, and a conversion temperature of 130° C. were used (Table IV).

It is not possible to compare these results precisely with those from the monocalcium phosphate monohydrate and laboratory triple superphosphate experiments as there is some uncertainty about the exact acidulation ratio. However, the results demonstrate that the process is applicable to commercial triple superphosphate made with wet-process acid, which contains sulfuric acid and other impurities. It appears that a product of high phosphorus pentoxide availability can be made at an equivalent acidulation ratio of about 1.2 pounds of acid phosphorus pentoxide per pound of rock phosphorus pentoxide with a two-cycle treatment and with an acidulation ratio of about 1.4 with a one-cycle treatment.

Two series of experiments were made with an experimental normal superphosphate prepared by mixing the phosphate rock with 72% c.p. sulfuric acid in the proportion of 2.6 moles of sulfuric acid per mole of rock phosphorus pentoxide and curing the mixture at room temperature until its moisture content was 7%. Mixtures of the normal superphosphate and phosphate rock in proportions equivalent to 1.6 and 2.1 moles of sulfuric acid per mole of rock phosphorus pentoxide were subjected to several cycles of hydrolysis and conversion. In the first series, the hydrolysis time was 15 minutes, the conversion temperature was 130° C., and the conversion time was 30 minutes. In the second series, the hydrolysis time was 1 hour, the conversion temperature was 185° C., and the conversion time was 30 minutes.

The results are shown in Table V. Although significant conversion was achieved at acidulations lower than those used for normal superphosphate manufacture, several cycles were necessary and higher acidulation ratios were required than with monocalcium phosphate or triple superphosphate. This is doubtless due to the interfering action of the calcium sulfate in the product. Both the total and available phosphorus pentoxide contents of the products were higher than those of the initial normal superphosphate, which is due to the fact that there is less calcium sulfate present.

Reaction of Phosphate Rock with Phosphoric Acid

Experiments were made to determine the conditions under which phosphate rock and phosphoric acid could be used directly in the process. In the first series of these experiments, phosphate rock and phosphoric acid were subjected directly to hydrolysis. A hydrolysis time of 1 hour, a conversion temperature of 185° C. and a conversion time of 30 minutes were used. Acidulation ratios of 0.8, 1.0, and 1.2 pounds of acid phosphorus pentoxide per pound of rock phosphorus pentoxide were used. The results, shown in Table VI, indicate that conversion is not so high after the first cycle as in the experiments with laboratory triple superphosphate, but the second cycle product was about the same. This seemed to indicate that the limiting factor in the first cycle conversion was formation of monocalcium phosphate monohydrate initially from the rock and acid.

Further experiments were made in which the rock and acid were mixed in two steps. In the first step, sufficient rock was added to bring the acidulation

Table IV. Reaction of Triple Superphosphate and Phosphate Rock

Acidulation Ratio		% Free Water[a]	Cycle	% P₂O₅ in Product				% P₂O₅ Availability
Acid P₂O₅ / Rock P₂O₅	Lb. TSP / Lb. rock			Total	Citrate-insol.	Avail.	Water-soluble	
			Laboratory TSP Made with c.p. Acid[b]					
...	...	...	TSP[c]	50.1	0.8	49.3	47.6	98.4
1.0	1.68	20.9	UM[d]	43.8[d]	10.2[d]	33.6[d]	30.6[d]	76.8[d]
			1	48.0	6.6	41.4	10.2	86.2
			2	47.9	4.4	43.5	5.3	90.8
1.1	2.01	20.5	UM[d]	45.0[d]	9.3[d]	35.7[d]	32.5[d]	78.4[d]
			1	49.3	4.9	44.4	9.5	90.0
			2	49.6	2.7	46.9	5.5	94.5
1.2	2.39	20.2	UM[d]	44.8[d]	8.4[d]	36.4[d]	34.0[d]	81.3[d]
			1	49.1	2.9	46.2	13.6	94.0
			2	49.5	2.0	47.5	7.6	96.0
			Commercial TSP Made with Wet-Process Acid[e]					
...	...	...	TSP[f]	45.8	1.0	44.8	42.0	98.0
1.14	2.36	16.5	UM[d]	43.2[d]	8.9[d]	34.3[d]	29.6[d]	79.4[d]
			1	43.8	6.9	36.9	24.1	84.4
			2	45.2	6.5	38.7	19.4	85.7
1.25	2.84	20.6	UM[d]	43.0[d]	6.4[d]	36.6[d]	30.2[d]	85.2[d]
			1	44.6	4.5	40.1	22.4	90.0
			2	45.6	2.4	43.2	16.3	94.6
			3	45.6	1.6	44.0	14.9	96.5
1.38	3.62	15.1	UM[d]	43.6[d]	4.7[d]	38.9[d]	32.4[d]	89.4[d]
			1	46.4	2.9	43.5	24.9	94.0
			2	47.0	1.6	45.4	16.5	96.5
			3	47.0	1.0	46.0	14.0	98.0
1.45	4.06	20.1	UM[d]	43.8[d]	4.3[d]	39.5[d]	33.1[d]	90.1[d]
			1	46.4	2.2	44.2	24.6	95.3
			2	47.0	0.8	46.2	18.2	98.3
			3	47.0	0.5	46.5	16.8	99.0

[a] In hydrolysis mixture; includes water added and moisture content of TSP.
[b] Hydrolysis time, 30 min.; conversion temperature, 185° C.; conversion time, 30 min.
[c] TSP contained 1.6% moisture.
[d] Untreated mixture before addition of free water.
[e] Hydrolysis time, 15 min.; conversion temperature, 130° C.; conversion time, 30 min.
[f] TSP contained 2.3% moisture.

Table V. Reaction of Normal Superphosphate and Phosphate Rock

Acidulation Ratio Moles H₂SO₄ / Mole P₂O₅	Lb. NSP / Lb. rock	% Free Water[a]	Cycle	Total	Citrate-insol.	Avail.	Water-soluble	% P₂O₅ Availability
...	...	...	NSP[b]	20.2	0.3	19.9	18.3	98.6
			Runs with Conversion Temperature of 130° C.[a]					
1.6	2.73	30.3	UM[c]	24.0[c]	7.1[c]	16.9[c]	13.8[c]	70.5[c]
			1	24.9	6.2	18.7	8.5	75.1
			2	25.5	5.0	20.5	4.3	80.5
			3	26.0	4.5	21.5	2.1	82.8
2.1	7.15	30.5	UM[c]	22.2[c]	3.3[c]	18.9[c]	16.6[c]	85.2[c]
			1	22.3	2.5	19.8	15.7	89.0
			2	23.7	2.0	21.7	9.4	91.5
			3	23.7	1.4	22.3	7.9	94.2
			4	23.9	1.4	22.5	6.2	94.2
			Runs with Conversion Temperature of 185° C.[d]					
1.6	2.73	30.3	UM[c]	24.0[c]	7.1[c]	16.9[c]	13.8[c]	70.5[c]
			1	24.7	6.7	18.0	4.0	72.9
			2	25.6	6.4	19.2	3.4	75.0
2.1	7.15	30.5	UM[c]	22.2[c]	3.3[c]	18.9[c]	16.6[c]	85.2[c]
			1	23.2	2.3	20.9	6.6	90.2
			2	24.6	2.2	22.4	4.6	91.1

[a] Hydrolysis time, 15 min.; conversion time, 30 min.
[b] Normal superphosphate contained 7.0% moisture.
[c] Untreated mixture before addition of free water.
[d] Hydrolysis time, 1 hour; conversion time, 30 min.

ratio to 2.3 pounds of acid phosphorus pentoxide per pound of rock phosphorus pentoxide. The mixture was hydrolyzed for 1.5 hours, the remainder of the rock was added, and the conversion step was carried out at a temperature of 185° C. and a time of 30 minutes. It was thought that by this procedure the rock added after hydrolysis might be more reactive, as its surface would be free of precipitated dicalcium phosphate. However, the results of these experiments, which are not shown in detail, were not significantly different from those in which all the rock was added at the same time.

In the next series of experiments, various precuring times were used between mixing of rock, water, and acid, and hydrolysis. The precuring was carried out at room temperature in closed flasks. The results, which are not shown in detail, indicated that a 2-day precuring period was sufficient to give products equivalent to those made from the laboratory triple superphosphate. Products were made by this procedure at three different acidu-

Table VI. Reaction of Phosphoric Acid and Phosphate Rock

Acidulation Ratio Acid P₂O₅ / Rock P₂O₅	Lb. H₃PO₄ / Lb. rock	% Free Water[a]	Cycle	Total	Citrate-insoluble	Available	Water-soluble	% P₂O₅ Availability
			Direct Hydrolysis Procedure[b]					
0.8	0.367	20.1	1	45.2	11.6	33.6	6.1	73.4
			2	46.5	9.6	36.9	3.6	79.4
1.0	0.459	19.0	1	46.6	8.6	38.0	10.5	81.5
			2	48.2	4.3	43.9	5.8	89.2
1.2	0.550	18.1	1	49.8	4.7	45.1	13.2	92.6
			2	49.0	1.2	47.8	9.0	97.6
			2-Day Precuring Procedure[c]					
1.0	0.459	19.0	1	47.8	6.0	41.8	12.1	87.5
			2	47.9	3.7	44.2	4.5	92.5
1.1	0.505	18.5	1	49.6	6.0	43.6	11.6	88.0
			2	48.5	2.6	45.9	6.0	94.7
1.2	0.550	18.1	1	49.2	5.1	44.1	16.1	89.7
			2	49.0	1.4	47.6	11.5	97.3
			Increased Hydrolysis Time Procedure[d]					
1.0	0.459	19.0	1	46.9	6.4	40.5	11.7	86.4
			2	47.4	2.8	44.6	4.0	94.3
1.1	0.505	18.5	1	47.4	4.9	42.5	14.0	90.0
			2	47.8	1.6	46.5	6.0	96.8
1.2	0.550	18.1	1	49.5	3.0	46.5	10.6	94.0
			2	48.2	0.8	47.4	11.3	98.3

[a] In hydrolysis mixture.
[b] Hydrolysis time, 1 hour; conversion temperature, 185° C.; conversion time, 30 min.
[c] Hydrolysis time, 30 min.; conversion temperature, 185° C.; conversion time, 30 min.
[d] Hydrolysis time, 5 hours for first cycle and 1 hour for second cycle; conversion temperature, 185° C.; conversion time, 30 min.

lations and with two cycles of treatment; the results are shown in Table VI. Except for the first cycle product at an acidulation ratio of 1.2, the products were somewhat higher in conversion than those from the direct hydrolysis procedure.

Another procedure that gave improved results was use of an increased hydrolysis time. A series of experiments was made in which the phosphate rock, phosphoric acid, and water were mixed and immediately subjected to hydrolysis for 5 hours, followed by conversion at 185° C. for 30 minutes. The results, shown in Table VI, indicate improved conversion over the 1-hour direct hydrolysis procedure and the 2-day precuring procedure for both first and second cycle products.

Use of Other Phosphate Rocks

A number of Idaho phosphate rocks of various grades were tried in the process. Each rock was made to react with monocalcium phosphate monohydrate at an acidulation ratio of 1.0 mole of acid phosphorus pentoxide per mole of rock phosphorus pentoxide. A hydrolysis time of 30 minutes, a conversion temperature of 185° C., and a conversion time of 30 minutes were used. The results, shown in Table VII, indicate that all the rocks respond to the treatment.

Properties of Products

Several of the products were subjected to x-ray diffraction analysis. The results show that the products made at a conversion temperature of 185° C. consisted primarily of anhydrous dicalcium phosphate and a small amount of unreacted phosphate rock; monocalcium phosphate was not identified, but there was evidence of amorphous material. Products made at a conversion temperature of 130° C. also contained a small amount of monocalcium phosphate monohydrate. The sample made from commercial triple superphosphate, normal superphosphate, and sulfuric acid contained in addition anhydrous calcium sulfate and a small proportion of calcium sulfate hemihydrate.

Free acid and moisture were determined in a number of products. Moisture was usually in the range 0 to 1%, since the products had been heated to considerably higher temperatures than the 100° C. which is used in the moisture determination. Free acid as determined by the acetone extraction method was very low, usually less than 2%.

Fluorine determinations were made on some of the samples, and some of the results are shown in Table II. In general, about half of the fluorine in the initial raw materials was volatilized in the treatment. This is somewhat more than is usually volatilized in normal or triple superphosphate manufacture, and the potential fluorine recovery would therefore be greater for the new process.

Proposed Continuous Process

The process is adaptable for development to continuous operation. A continuous process would consist of a series of units for continuous mixing, hydrolysis, conversion, and grinding. The product from the first cycle of steps could be rewetted and processed a second time in a separate series of units, or part of it could be recycled to the first series of units. Engineering development will be required, but no inherent difficulties seem to present themselves.

Advantages Considerably less acid is required to convert the phosphorus pentoxide in phosphate rock to an available form than in other processes. When phosphoric acid is used, only about half as much acid based on the rock phosphorus pentoxide, or about three fourths as much based on the available phosphorus pentoxide in the product, is required as by the usual triple superphosphate process. When sulfuric acid is used, the saving is less but significant. Because both sulfuric and phosphoric acids are heavily dependent on elemental sulfur production, the process offers a means of extending sulfur reserves over a considerably longer period.

The product made with phosphoric acid is almost as high in available phosphorus pentoxide concentration as triple superphosphate, and that made with sulfuric acid is higher in available phosphorus pentoxide concentration than normal superphosphate.

No curing of the product is required in the process, whereas in many present processes several weeks of curing are required.

The phosphorus pentoxide content of the product may be either largely water-insoluble or partly water-insoluble and partly water-soluble; the relative proportions of the two forms are controllable by the proportion of monocalcium phosphate or acid used, and by the conversion time and temperature. For some fertilizer applications a product having most of its phosphorus pentoxide water-insoluble is advantageous; for others it is desirable to have some of the phosphorus pentoxide in a water-soluble form.

The physical condition of the product is excellent, as its moisture content and free acid content are very low and it probably can be stored in bags or bulk without caking or bag rot.

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Table VII. Reaction of Idaho Phosphate Rocks with Monocalcium Phosphate[a]

% P2O5 in Phosphate Rock	Cycle	% P2O5 in Product				% P2O5 Availability
		Total	Citrate-insoluble	Available	Water-soluble	
35.3	UM[b]	48.2[b]	7.8[b]	40.4[b]	37.4[b]	83.6[b]
	1	51.4	1.9	49.5	16.2	96.3
31.6	UM[b]	45.7[b]	8.2[b]	37.5[b]	35.0[b]	82.0[b]
	1	50.1	3.2	46.9	12.7	93.5
31.2	UM[b]	45.1[b]	7.8[b]	37.3[b]	35.2[b]	82.7[b]
	1	50.1	3.2	46.9	16.2	93.5
29.7	UM[b]	45.3[b]	8.5[b]	36.8[b]	33.5[b]	81.3[b]
	1	50.5	3.4	47.1	11.7	93.3

[a] Acidulation ratio, 1.0 mole acid P_2O_5/mole rock P_2O_5; hydrolysis time, 30 min.; free water in hydrolysis, 14%; conversion temperature, 185° C.; conversion time, 30 min.
[b] Untreated mixture before addition of free water.