

**THE PRODUCTION OF PHOSPHATE FERTILIZERS WITH A DEFICIENCY OF
SULFURIC ACID**

by

RAYMOND CHARLES RICHARDSON

B. S., University of Colorado, 1954

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

**KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE**

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INTRODUCTION

Ordinary or normal superphosphate is prepared by the reaction of sulfuric acid on ground phosphate rock. This results primarily in the formation of calcium phosphate salts and calcium sulphate, and in addition, products due to the presence of impurities in the rock. The reaction of sulfuric acid on apatite, the phosphatic mineral in phosphate rock, is very vigorous, but the mixing period is of short duration and the reactions are incomplete. The acid slurry is discharged from the mixer into a den, where several batches are held until the mass solidifies or "sets up." This solid mass is cut out of the den and held in large piles where the reactions go to completion over a period of approximately four weeks. When phosphate rock is treated with sufficient sulfuric acid, monocalcium phosphate is the primary phosphatic salt formed. If less sulfuric acid is used, the resulting product is a mixture of monocalcium phosphate and unreacted phosphate rock. Concentrated superphosphate is made by the reaction of phosphoric acid on phosphate rock in a similar manner.

Both monocalcium phosphate, $\text{CaH}_4(\text{PO}_4)_2$, and dicalcium phosphate, CaHPO_4 , are generally recognized as being agronomically available forms of P_2O_5 , whereas tricalcium phosphate and mineral apatites are unavailable unless converted to other forms. If it were possible to acidulate phosphate rock so as to form dicalcium phosphate a considerable saving in the amount of acid used could be realized. In addition to the saving in raw material costs, the product would be a neutral and substantially acid free material produced without the necessity of an extended curing

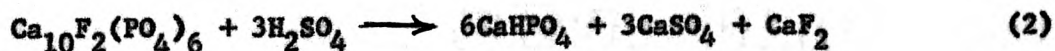
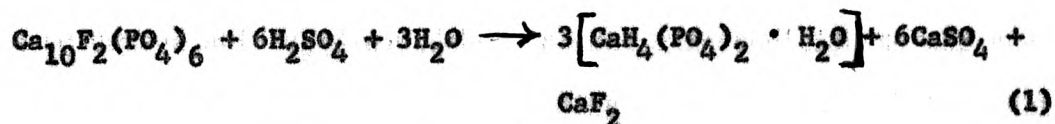
period. The reduction of sulfur reserves coupled with the increasing costs of sulfuric acid makes this process appear very attractive.

The main purpose of this investigation was to determine what variables affected the formation of dicalcium phosphate from phosphate rock and to determine the extent to which these variables influence the final product.

Phosphate is generally found as the mineral, apatite, plus impurities. The mineral does not have the simple form of tricalcium phosphate but is a complex compound usually found as fluorapatite, $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$, or hydroxy apatite, $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$, the fluorapatite being the more common form.

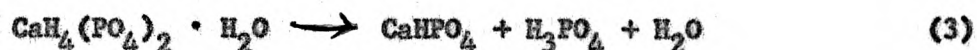
In the acidulation of phosphate rock the sulfuric acid acts not only on the tricalcium phosphate but also upon the calcium fluoride in the apatite molecule and upon any impurities such as organic matter, iron and aluminum compounds, and calcium and magnesium carbonates. All of these side reactions result in the use of additional acid without contributing to the plant food content.

Theoretically the formation of dicalcium phosphate by direct acidulation of phosphate rock with sulfuric acid would require only half as much acid to produce a unit of available phosphorus pentoxide as the formation of monocalcium phosphate. This is demonstrated by the following equations:

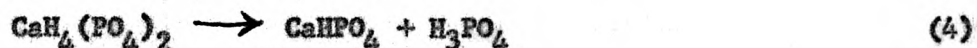


When sulfuric acid is used to produce superphosphate, the theoretical acidulation ratio according to equation (1) is 2 moles of acid per mole of phosphorus pentoxide derived from rock phosphate (or available P_2O_5 in the product). In practice somewhat more acid is used--about 2.6 moles of acid per mole of rock P_2O_5 --because of the side reactions that take place between the acid 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 only be 1 mole of acid per mole of rock phosphorus pentoxide (or available P_2O_5 in the product).

The primary reaction in the proposed process is the hydrolysis of monocalcium phosphate monohydrate to dicalcium phosphate and phosphoric acid according to the equation:

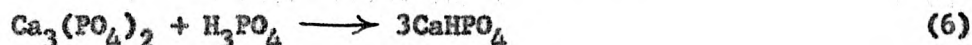
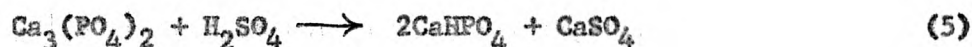


At higher temperatures the monocalcium phosphate monohydrate may lose one molecule of water, forming anhydrous monocalcium phosphate. Then the hydrolysis reaction may be represented by the equation:



The phosphoric acid liberated is free to react with any undecomposed mineral phosphate. Under the usual conditions of acidulation, monocalcium phosphate monohydrate is formed.

The secondary reaction involves the action of sulfuric acid or the liberated phosphoric acid on unreacted apatite or tricalcium phosphate according to the following equations:



The result of these reactions would be the formation of dicalcium phosphate.

Whenever a tendency for spontaneous change exists, work can be obtained from the process if a suitable mechanism is provided. The maximum useful work becomes available only when the process is reversible, i.e., under conditions of balanced forces. In a process which occurs reversibly at constant temperature and pressure, the useful work is equal to the decrease in free energy, ΔG , of the system. Therefore, since the free energy always decreases in any spontaneous process, it can be used as a criteria to tell whether or not an imagined process will or will not take place. The reaction becomes more advantageous as the value of the free energy change becomes larger negatively, and it is less promising if the free energy change is positive. Dodge (7) stated that when the free energy change is larger than +10 Kcal at 25°C, the reaction is very unfavorable.

Since the necessary thermodynamic data was not available, the value of the free energy change for the acidulation of phosphate rock at any given temperature could not be computed. However, the free energy change under standard conditions of temperature and pressure, 25°C, and 1 atm, is useful for estimating the thermodynamic feasibility.

The thermodynamic properties of monocalcium phosphate, dicalcium phosphate, and other compounds as reported by Latimer (15) are given in Table 1. The phosphate is represented by its main constituent, tricalcium phosphate.

Table 1. Thermodynamic data at standard state (25°C, one atm)

Compound	Form	ΔH_f° Enthalpy of formation Kcal/g-mole	ΔG_f° Free Energy of formation Kcal/g-mole	ΔS_f° Entropy of formation Entropy units
Tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$	Crystalline	-988.9	-932.0	56.4
Monocalcium phosphate monohydrate, $\text{CaH}_2(\text{PO}_4) \cdot \text{H}_2\text{O}$	Crystalline	-821.49	-733.52	49.7
Anhydrous monocalcium phosphate, CaHPO_4	Crystalline precipitated	-744.4	-672	45.3
Dicalcium phosphate CaHPO_4	Crystalline	-435.2	-401.5	21
Calcium sulphate CaSO_4	Crystalline Anhydrite	-342.42	-315.56	25.5
Phosphoric acid H_3PO_4	Aqua	-308.2	-274.2	42.1
Sulfuric acid H_2SO_4	Aqua	-216.90	-177.34	4.1
Water, H_2O	Liquid	- 68.32	- 56.69	16.92

The standard free energy changes, using the data given in Table 1, for the hydrolysis of monocalcium phosphate to dicalcium phosphate by reactions 3 and 4, are +1.13 Kcal and -3.7 Kcal, respectively. For the secondary reactions, in which dicalcium phosphate is formed by the action of the mineral acids on tricalcium phosphate, the standard free energy changes are -9.22 Kcal and +1.7 Kcal, respectively. Although the estimated free energy changes for the reactions are not entirely favorable, with the exception of reaction (3), the reactions do appear

to be feasible. The formation of dicalcium phosphate from the action of sulfuric acid on tricalcium phosphate, equation (5), appears to be very favorable.

The reactions that accompany the formation of normal or concentrated superphosphate are well known and have been discussed at length by Waggaman (25) and others. Since the free energy change for these reactions are, in general, much higher they will compete to the disadvantage of the formation of dicalcium phosphate. Also, in the acidulation of phosphate rock there is a considerable amount of calcium sulfate formed (one mole for each two moles of dicalcium phosphate formed and two moles per mole of monocalcium phosphate formed) as well as salts of other metals. These compounds are relatively unsatisfactory for use as plant food and also have a tendency to coat the solid particles decreasing the efficiency of the normal reaction.

Feng (10) developed a process for making a suitable phosphate fertilizer by acidulating phosphate rock with an amount of sulfuric acid which was only slightly in excess of that theoretically necessary to convert all the P_2O_5 in the rock to dicalcium phosphate. The sulfuric acid and phosphate rock were reacted at $90^\circ C$ and atmospheric pressure. The partially acidulated mass was then dried for 24 hours at $105^\circ C$. A predetermined quantity of water was added to small portions of the partially acidulated material and further reacted at superatmospheric pressures and elevated temperatures. A maximum conversion of 82 percent of the total P_2O_5 present to the citrate soluble form (dicalcium phosphate) was reported.

This investigation originally undertook to modify the process to a continuous or one step operation using approximately the optimum conditions reported by Feng.

LITERATURE REVIEW

Ober and Wight (18) suggested a process in which a predetermined quantity of finely divided phosphate rock and another material having a potential fertilizer value and sulfuric acid were mixed together in a confined space. The mass was digested while agitated under super-atmospheric pressures and elevated temperatures. The digestion was continued for a period of time sufficient to effect a substantial conversion of the unavailable phosphate and the material having a potential fertilizer value into available fertilizers, and then the pressure was released and the product dried.

Later work by Ober and Wight (19) indicated that the reaction between the phosphate rock and acid could be accelerated by setting up a vacuum or partial vacuum in an autoclave. These investigators also noted a quick drop in pressure was accompanied by a drop in temperature when superatmospheric pressures were employed. Tests indicated that when a generated pressure of ninety pounds in the container was reduced to atmospheric pressure, there was a simultaneous drop in temperature of 30°C. This release in pressure and cooling also initiated and accelerated crystallization of the mass. However, there appeared to be no effort made in the early investigations to determine the forms or proportions of the different calcium phosphates.

Seyfried (22) suggested a process in which phosphate rock was digested with H_2SO_4 of 25-40 percent strength in a quantity of 1-5 percent in excess of the amount calculated to liberate the P_2O_5 content of the rock as H_3PO_4 ; the resulting solution of H_2SO_4 and H_3PO_4 was filtered. Sufficient ground phosphate rock was added to react with the H_2SO_4 present, to precipitate the dissolved $CaSO_4$, and to utilize 30-50 percent of the acidity of the H_3PO_4 present to form monocalcium phosphate. Lime was then added to the solution to form dicalcium phosphate.

Shoeld (23) patented a process which consisted of reacting phosphate rock and a strong liquid acid, such as H_2SO_4 , in a confined zone while heated by the intermittent introduction of steam, to decrease the partial pressure of the permanent gases and increase the partial pressure of the steam while maintaining the material under superatmospheric pressure.

A process developed by Miller (17) consisted of circulating concentrated H_3PO_4 containing dissolved $CaH_4(PO_4)_2$ over phosphate rock at 75-125°C to dissolve the rock. The solution was cooled to 25°C to crystallize a portion of the dissolved $CaH_4(PO_4)_2$. The crystals were separated and the solution was reheated. The cycle was then repeated. The solid $CaH_4(PO_4)_2$ which was separated was hydrolyzed at 100°C to form $CaHPO_4$ and H_3PO_4 ; the latter was returned to the circulating solution. No mention was made of the degree of conversion to the dicalcium form.

Zbnorick (26) patented a process which comprised mixing ground phosphate rock and concentrated phosphoric acid and autoclaving, giving a product containing at least 90 percent of its total phosphorus content

in available forms; the available forms were distributed between monocalcium and dicalcium phosphates. No more than 50 percent of the quantity of phosphoric acid theoretically necessary to convert all the calcium in the phosphate rock to monocalcium phosphate was used. This reaction was allowed to proceed at 130°C and pressures greater than 25 pounds per square inch gauge.

The moisture contents of the mixes were adjusted to approximately 12, 9, and 6 percent and the last step of the procedure consisted of vaporizing and withdrawing moisture from the heated mixture to a product moisture of approximately 7.4, 4, and 2 percent respectively. These operating conditions gave a product containing over 50 percent of its available phosphorus pentoxide content in the form of dicalcium phosphate. When the moisture content of the mixture exceeded 12 percent, no useful result was obtained. The reaction time allowed ranged from 13 to 35 minutes.

Fatel (20) described a process in which Kossier rock phosphate and trichinopoly phosphatic nodules from Egypt were digested with HCl and neutralized with lime to obtain dicalcium phosphate. A saving of 28 percent in consumption of HCl was reported. Siegfried (24) also reported a similar process using wet rock and gases containing 10-20 percent HCl at 100-150°C with subsequent liming to form dicalcium phosphate.

Gadre (12) described a process for semi-acidulating phosphates. With half the amount of acid required in the manufacture of super-phosphate, 75-80 percent of the total P_2O_5 of the rock was converted to available phosphate; and with 3/4 of the amount of acid required, 90

percent was made available. Heating the acidulated mixture before curing had no effect when H_2SO_4 was used, but with HCl it helped the formation of $CaHPO_4$. The optimum curing period with H_2SO_4 was three weeks, while with HCl it was two weeks.

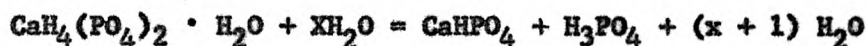
Gerhard, and others (13) reported a process for the manufacture of dicalcium phosphate by bringing together acidic solutions containing calcium, fluorine and H_3PO_4 with a neutralizing agent in an acid medium whose pH is held between 1.5 and 2.5 (preferentially 2.0). The precipitate consisted of dicalcium phosphate mixed with CaF_2 and represented a fertilizer of very high citrate solubility.

A Dutch patent (6) reported a very similar process. $CaHPO_4$ was formed by neutralizing acidic, fluorine containing solutions (obtained by digesting raw phosphate with HNO_3 and separating the precipitate from the solution) to a pH of 1.0-2.5. This prevented the formation of a layer of $[Ca_3(PO_4)_2] \cdot CaF_2$ upon the $CaHPO_4$ particles which would have greatly decreased the citrate solubility of the product.

Boullé (3) studied the dehydration of secondary calcium phosphate. A graph of differential loss of weight on heating $CaHPO_4 \cdot 2H_2O$ plotted against temperature showed breaks at $115^\circ C$ and $132^\circ C$. The substance present between these temperatures was partially dehydrated and was difficult to weigh with precision. X-ray diffraction showed the structure of $CaHPO_4$. The dehydration was completed near $132^\circ C$, but the structure underwent no change. Curves from the thermogravimetric analysis showed several changes of slope, and the general shape was independent of the speed of heating. The formation of $CaHPO_4$ was essentially complete by $255^\circ C$. There was a slow loss of 5 percent of the water with the

beginning of the formation of $\text{Ca}_2\text{P}_2\text{O}_7$ from 225° to 395°C . The formation of $\text{Ca}_2\text{P}_2\text{O}_7$ proceeded rapidly from 395° to 450°C . X-ray spectra confirmed this interpretation. X-ray spectra of samples removed between 133° and 207°C showed the presence of both $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and CaHPO_4 , but the intensities of the lines were greater than would be expected from the loss in weight. When the thermogravimetric analyses were done in a humid atmosphere, the weight loss began at 110°C and proceeded rapidly to 150°C . The loss that corresponded to the formation of $\text{Ca}_2\text{P}_2\text{O}_7$ began about 300°C . The first step in the dehydration was the loss of some water with little change in the crystal lattice. The second step was the lattice conversion, some water having been left in the voids. The humidity of the surroundings was important in initiating the second step.

Elmore and Farr (9) showed that the degree of hydrolysis of monocalcium phosphate monohydrate to phosphoric acid and dicalcium phosphate was a maximum at 100°C in a saturated solution containing 78 percent monocalcium phosphate monohydrate and 22 percent water, but that a conversion almost as high could be achieved in more dilute solutions. The equation proposed by them is:



Increasing the ratio of salt to water increased the acidity of the resultant solution and also the proportion of solid phase to liquid phase in the equilibrium mixture. The maximum conversion was attained when the solution reached an acidity sufficient to prevent further hydrolysis of the monocalcium phosphate monohydrate. Beyond this point

further addition of monocalcium phosphate to a fixed quantity of water merely increased the quantity of solid monocalcium phosphate monohydrate without changing the quantity of dicalcium phosphate. The percentage of total input of monocalcium phosphate that reacted decreased asymptotically.

The maximum conversion increased with increasing temperature provided a corresponding decrease was made in the ratio of water to salt. At 25°C, 50.7°C, 75°C and 100°C maximum conversions of 56.5, 67.5, 74.0 and 79 percent were obtained for monocalcium phosphate monohydrate containing 51.5, 41.5, 33, and 26 percent moisture respectively. A plot of the common logarithm of the maximum conversion in percent against the reciprocal of the absolute temperature gave sensibly a straight line with a slope of 223 between 25°C and 100°C.

Larson (16) found that prolonged heating of monocalcium phosphate monohydrate at 100°C caused a loss in weight equivalent to 0.96 molecule of water per molecule of phosphate (variation from one molecule within limit of error) showing that the molecule of water is lost at a lower temperature than is reported by some investigators, and that the anhydrous salt is quite stable when heated for long periods of time at this temperature. It was also stable when heated for five-hour period over a temperature range of 103 to 153°C. The water loss was higher at higher temperatures being nearly equivalent to 2.5 molecules of water at 200 to 205°C for ten weeks. This loss was accounted for by the formation of a mixture of calcium meta-phosphate and pyro-phosphate.

Since all samples were to be analyzed for phosphate content using the colorimeter method, the possibility of any interference in the

formation or permanency of the color ion was investigated. Ellis (8) reported on the repression of the color development caused by the fluoride ion in the $(\text{NH}_4)_2\text{MoO}_4\text{-HCl}$ solution and reported:

1. Ammonium fluoride represses color development even when present in small concentrations (0.03N).
2. Ammonium fluoride represses color development more as the acid increases.
3. Color repression is greater for greater concentrations of phosphorus.

Since the mineral apatite does contain appreciable amounts of fluoride and hydrochloric acid was used in digesting the samples, this effect could cause some scattering of the data. After the reactions are completed the fluoride will be tied up, generally, in four different compounds. First, a certain portion of the rock will remain unreacted. Any fluoride in the apatite will be essentially insoluble and will not interfere with the color formation. Secondly, a certain portion of the fluoride will be reacted with the water present to form hydrofluoric acid. Since the process suggested utilizes moderately high temperatures and pressures and the system must be vented to remove the product, any of the hydrofluoric acid in the gases will be passed out of the system. Thirdly, a portion of the fluoride will react with the silica or calcium present to form hydrofluosilicate and calcium fluoride, respectively. Both of these compounds are relatively insoluble. These factors combine to reduce the possibility of any color repression. The colorimetric determinations were made according to the method developed by Bridger, and others (4). This method has been shown to give comparable results to the methods of the Association of Official Agricultural Chemists(2).

Frey and Byè (11) reported on the kinetics and mechanisms of the reaction of phosphoric acid on tricalcium phosphate. The system was studied by calorimetric measurements, by microscopic examination of solid phases, and by chemical analysis of the phases. At between 20° and 40°C the reaction of the $\text{Ca}_3(\text{PO}_4)_2$ with H_3PO_4 was rapid, proceeding in a few minutes. Reaction masses composed of 30 percent Ca_3PO_4 and 70 percent phosphoric acid, containing either 12 percent or 20 percent P_2O_5 , produced dicalcium phosphate. If the acid concentration was 36.4 percent P_2O_5 , however, monocalcium phosphate was produced. In the absence of centers for crystallization the acid phosphates obtained were metastable for several days to several months. The CaHPO_4 was found to have less tendency to change from the anhydride to the hydrate than did the $\text{CaH}_4(\text{PO}_4)_2$.

Krasnov (14) also described the kinetics of the solution of apatite in saturated solutions in the system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$. The rate of solution of apatite was studied at 40°, 75°, and 100°C in solutions saturated with CaHPO_4 , $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, and $\text{CaH}_4(\text{PO}_4)_2$. In solutions saturated with CaHPO_4 , the rate of solution slowed down to zero with the deposition on the undissolved apatite of a layer of reaction product, 1-60 μ thick. In solutions saturated with $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, the layer thickness sufficient to stop the solution was determined to be 40 to 100 microns. In solutions saturated with $\text{CaH}_4(\text{PO}_4)_2$ no impermeable layer was formed, but the solution rate decreased with time. The initial solution rate at 40°C in solutions saturated with $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ increased with the liquid-phase P_2O_5 concentration.

A different approach to producing dicalcium phosphate fertilizer was reported by Bridger, and others (5). This process consisted of

reacting phosphate rock with mineral acids by refluxing the mixture (water is added in controlled amounts) followed by heating in an open container to 130° to 185°C. The conversion to dicalcium phosphate in the product was increased by adding water and repeating the refluxing and heating steps. When phosphoric acid was used, the acidulation required to produce the product was only about 50 percent of that required for production of triple superphosphate, based on the P_2O_5 content of the phosphate rock, or about 25 percent based on the available P_2O_5 content of the product. When sulfuric acid was used, somewhat higher acidulation ratios were required because of the interferring action of the calcium sulfate. The water-soluble P_2O_5 content of the product was varied from a small to a large proportion of the total by varying the conditions of treatment.

MATERIALS AND METHODS

Materials

The phosphate rock used was Florida land pebble ground to 65.67 percent through 100 mesh and 57.4 percent through 200 mesh. This rock contained 35.1 percent P_2O_5 which is equivalent to 76.6 percent bone phosphate of lime (on a dry basis). The screen analysis and chemical composition are reported in Table 2.

Analytical grade sulfuric acid was used for the acidulation of all samples. The 95 percent (65° Baume) acid was diluted with distilled water to approximately the desired concentration and cooled to room temperature. The exact concentration was determined by the specific gravity method.

Table 2. Screen and chemical analysis of Florida land pebble phosphate rock

Components	Percent	Screen Analysis	
		U.S. Std. Mesh	Percent
P ₂ O ₅	35.10		
CaO	49.64		
Fe ₂ O ₃	0.86	+ 70	7.77
Al ₂ O ₃	1.22	- 70 + 100	16.66
F	4.12	- 100 + 140	7.92
CO ₂	1.48	- 140 + 200	10.35
H ₂ O	0.95	- 200	57.40

Nitric and hydrochloric acids of analytical reagent grade were used to prepare the samples for analysis. Other reagents necessary for the preparation of the solutions used in analyzing samples were crystalline citric acid, ammonium vanadate (meta), 81 percent ammonium molybdate, and ammonium hydroxide (28-29 percent NH₃).

Experimental Methods

Three different processes were tried. The first used a longitudinal rotating batch reactor which was heated externally by a direct gas flame. The second method used was based on the procedure previously developed by Feng (10) and consisted of two steps. The first step was the acidulation of phosphate rock in an open autoclave with less acid than that required for complete conversion to monocalcium phosphate. The second step consisted of heating the solid mass from the first step, after adding water to a predetermined moisture content, in a closed, stirred autoclave. The third method used a small temperature controlled

stainless steel autoclave in which a small amount of material (20 to 40 grams) did not require mixing to effect the complete reaction.

The stoichiometric quantity of sulfuric acid needed to produce dicalcium phosphate from the Florida land pebble whose composition is given in Table 1 was computed as follows:

Basis: 100 grams phosphate rock (35.1 g. P_2O_5)

Weight of H_2SO_4 needed for conversion of all phosphate to $CaHPO_4$

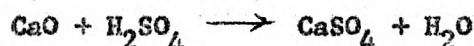


$$\frac{35.1 \times 3 \times 98}{142 \times 3} = 24.2 \text{ grams } H_2SO_4$$

Weight of CaO not in apatite:

$$49.64 - \frac{35.1 \times 10 \times 56}{142 \times 3} = 49.64 - 46.2 = 3.44 \text{ gram}$$

Weight of H_2SO_4 used for excess CaO:



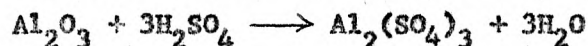
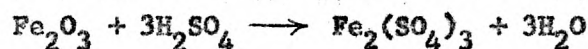
$$\frac{3.44}{56} \times 98 = 6.02 \text{ grams of } H_2SO_4$$

Weight of H_2SO_4 used for CaF_2 :



$$\frac{78 \times 35.1}{3 \times 142} \times \frac{98}{78} = 8.07 \text{ grams of } H_2SO_4$$

Weight of H_2SO_4 used for Fe_2O_3 and Al_2O_3 :



$$\frac{0.86 \times 98 \times 3}{159.7} + \frac{1.22 \times 98 \times 3}{101.96} = 5.11 \text{ grams of } H_2SO_4$$

Total sulfuric acid required = 24.2 + 6.02 + 8.07 + 5.11 =

43.4 grams of 100 percent H_2SO_4

The amount of acid used is generally expressed as an acidulation ratio, which is defined as the ratio of the weight of 100 percent sulfuric acid used to the weight of P_2O_5 in the phosphate rock acidulated. In industrial practice, the acidulation ratio is usually about 1.7 to 1.8 depending on the rock used. The acidulation ratio will be used hereafter to express the extent of acidulation of all samples.

Since phosphate rock contains other materials which also react with the sulfuric acid, the calculated requirement is only an approximation. To allow for this contingency, the smallest amount of acid used was 50 grams per 100 grams of phosphate rock. This quantity of acid gave an acidulation ratio of 1.42, which should be sufficient to produce dicalcium phosphate.

Rotary Reactor. The reactor was constructed of six-inch, schedule 40, black iron pipe. A ten-inch flange was welded to each end of the pipe leaving the full cross section open. Each flange had a blank companion flange which was gasketed and held in place by four $\frac{1}{2}$ -inch bolts to make a pressure-tight reactor. All flanges were machined and trued.

Short pieces of one-inch, schedule 40, black iron pipe were welded into the center of each outside flange. These extensions held the pressure gauge, thermometer well, and a pressure relief valve. The construction of this autoclave shell is described in Plate I.

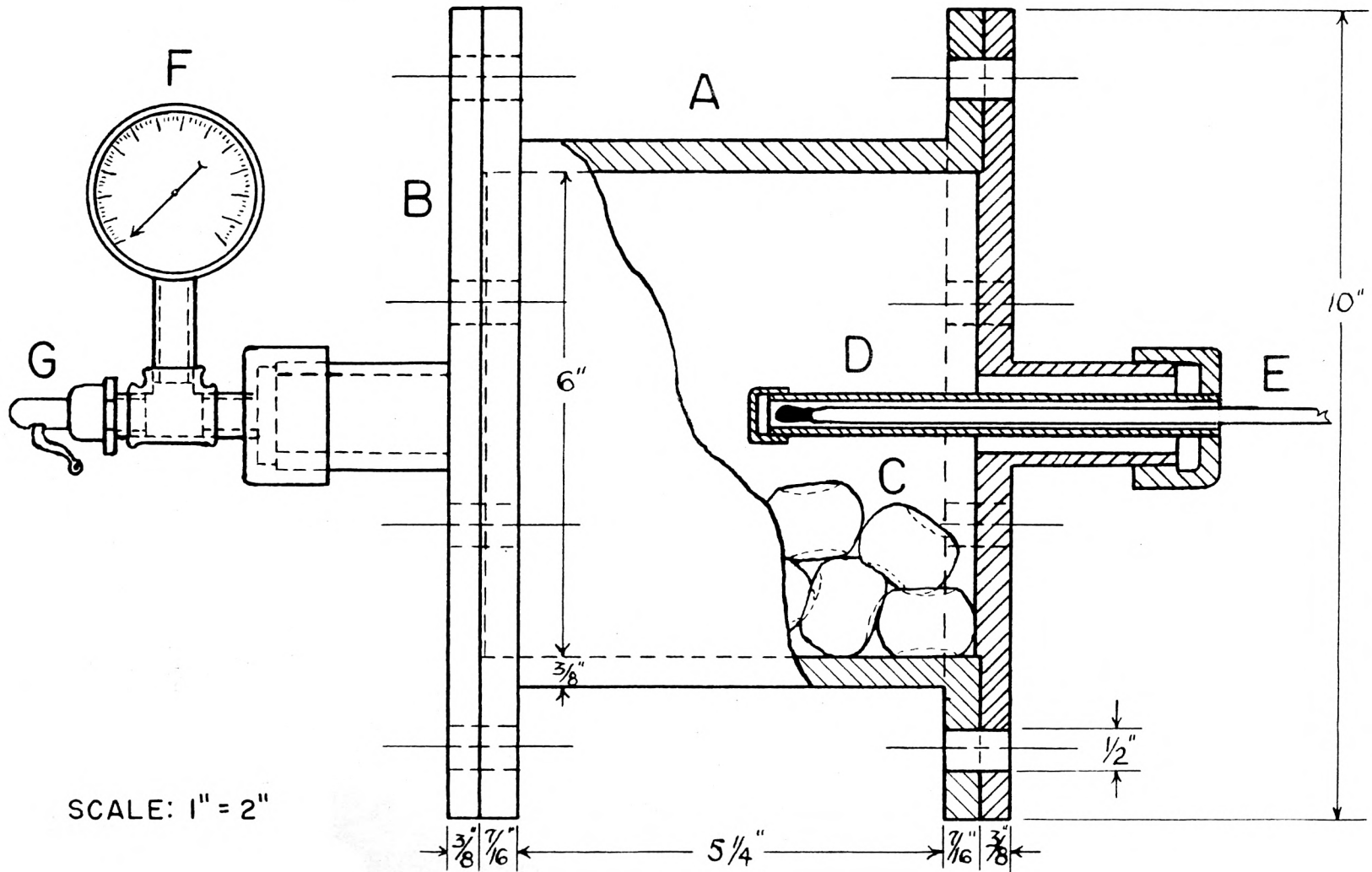
The reactor was rotated by means of a set of rollers driven by a $\frac{1}{3}$ h.p. Reeves Vari-Speed Motodrive motor connected to a speed reducer by a V-belt drive.

EXPLANATION OF PLATE I

Drawing of Rotary Autoclave

- A. Reactor shell
- B. Machined flange with welded, centered
1 inch by 3 inch standard nipple
- C. One inch diameter steel balls
- D. One-half inch standard stainless steel
thermometer well
- E. Mercury thermometer
- F. Pressure gauge
- G. Pressure relief valve

PLATE I



Three hundred grams of phosphate rock and a predetermined quantity of sulfuric acid were charged to the preheated autoclave. The cover was secured pressure-tight. The shell was rotated at approximately 11 r.p.m. and mixing was provided by steel balls approximately 1-inch in diameter or stainless steel rods $\frac{1}{4}$ -inch by $5\frac{1}{2}$ inches and $\frac{3}{8}$ -inch by $5\frac{1}{2}$ inches. A gas flame was used to bring the reacting mass to a specified temperature, after which the temperature was maintained constant by adjusting the flame. Reaction times of 5 to 40 minutes were used, after which the heat source was removed and the mixture allowed to mix an additional 10 minutes. The material was then removed from the shell as a mix of semi-dry solid spherical particles. The samples were dried and cooled for 24 hours at room temperature, then ground to a finely divided powder before analyzing. Samples that were used to determine the effect of curing time were stored the required time in a constant humidity chamber at 100°F and 25 percent relative humidity.

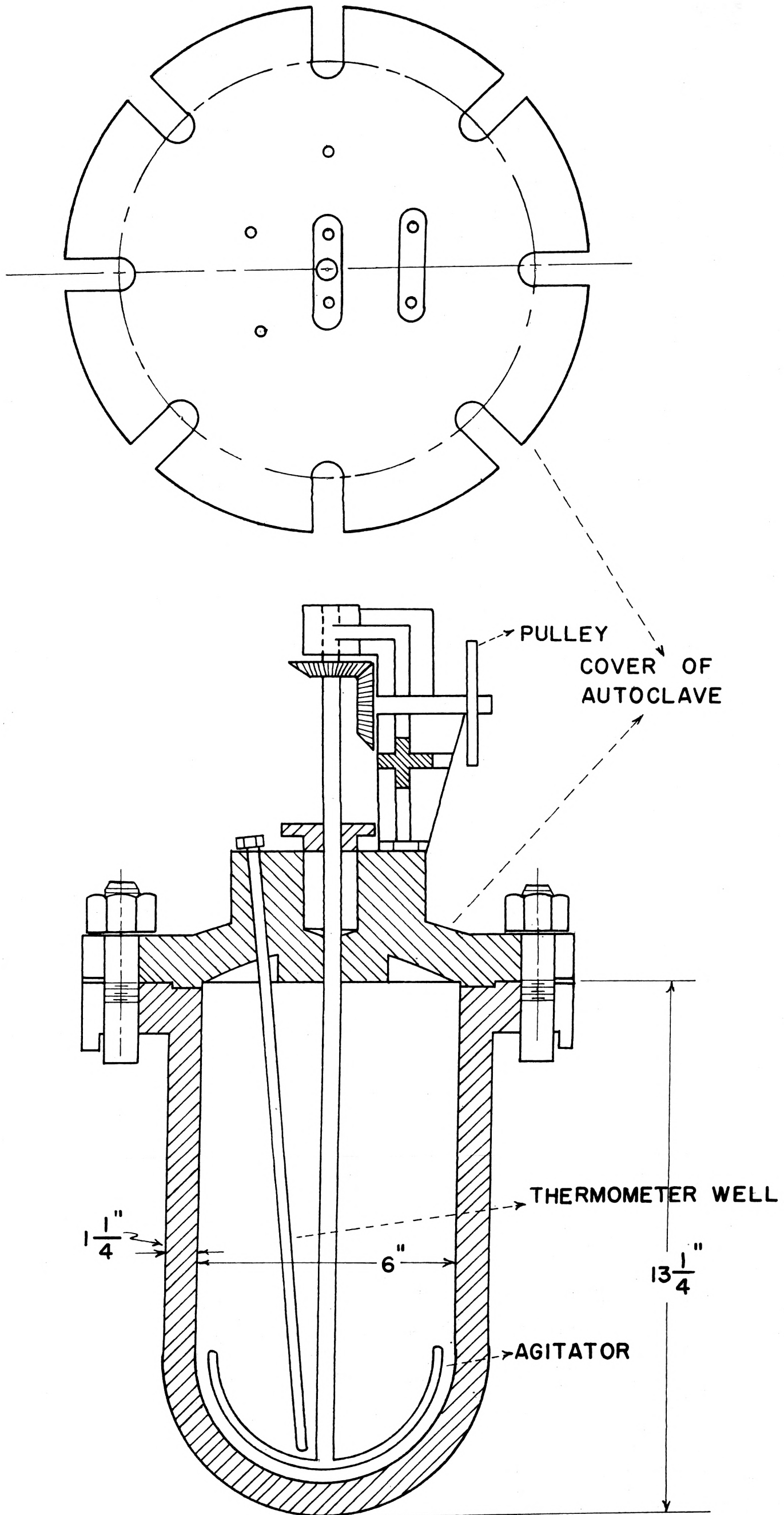
Two Step Autoclave Process. A small laboratory agitated cast steel autoclave of two quart capacity was used. This autoclave was six inches in diameter and 12 inches in length and was secured with a cover which was held in place by eight one-inch bolts. The details of the construction are shown in Plate II.

The cover had a raised ring which fitted into the groove in the top of the autoclave, and the thermometer well was screwed through the cover. The autoclave rested on a ring which supported the edge of the flange, and was heated by natural gas burned inside a cylindrical sheet metal case. The bottom of the autoclave was above the gas ring.

EXPLANATION OF PLATE II

**Drawing of the Autoclave Used in the Two
Step Autoclave Process.**

PLATE II



The agitator shaft passed through the center of the cover and was driven at 30 r.p.m. by a V-belt drive from a $\frac{1}{2}$ h.p. electric motor. The agitator blade was of the anchor type. The cover was also provided with a pressure gauge and a gas escape valve.

The second step of the process utilized a small stainless steel autoclave. This autoclave was constructed of a 1-inch by 6-inch piece of pipe threaded on both ends. One end of the reactor was capped with a stainless steel cap while the other end was fitted with a straight tee. At right angles to the reactor a valve was installed by which the internal pressure could be released. The top part of the tee was provided with a male reducer through which a thermocouple and well ($\frac{1}{2}$ -inch stainless steel pipe) was placed.

The reactor was heated by placing it in a cylindrical metal sheath 1 $\frac{3}{4}$ inch in diameter by 5 $\frac{1}{8}$ inches long wrapped in nichrome heating wire. The reactor sheath was fitted with asbestos insulation 4 $\frac{3}{4}$ inch in diameter by 7 inches long reinforced by three $\frac{3}{8}$ -inch metal bands. The amount of external heat was controlled by a powerstat and the heating current measured by an ammeter. The temperature of the reacting material was determined by the use of an iron-constantan thermocouple in combination with a Leeds and Northrup potentiometer. A description of the reactor is provided by Plate III.

The procedure used was based on that outlined by Feng (10). The process was conducted in two steps. In the first step the phosphate rock was reacted with sulfuric acid in the stirred autoclave at atmospheric pressure, then removed, dried, and ground. In the second step portions of this acidulated mass were further reacted in the small

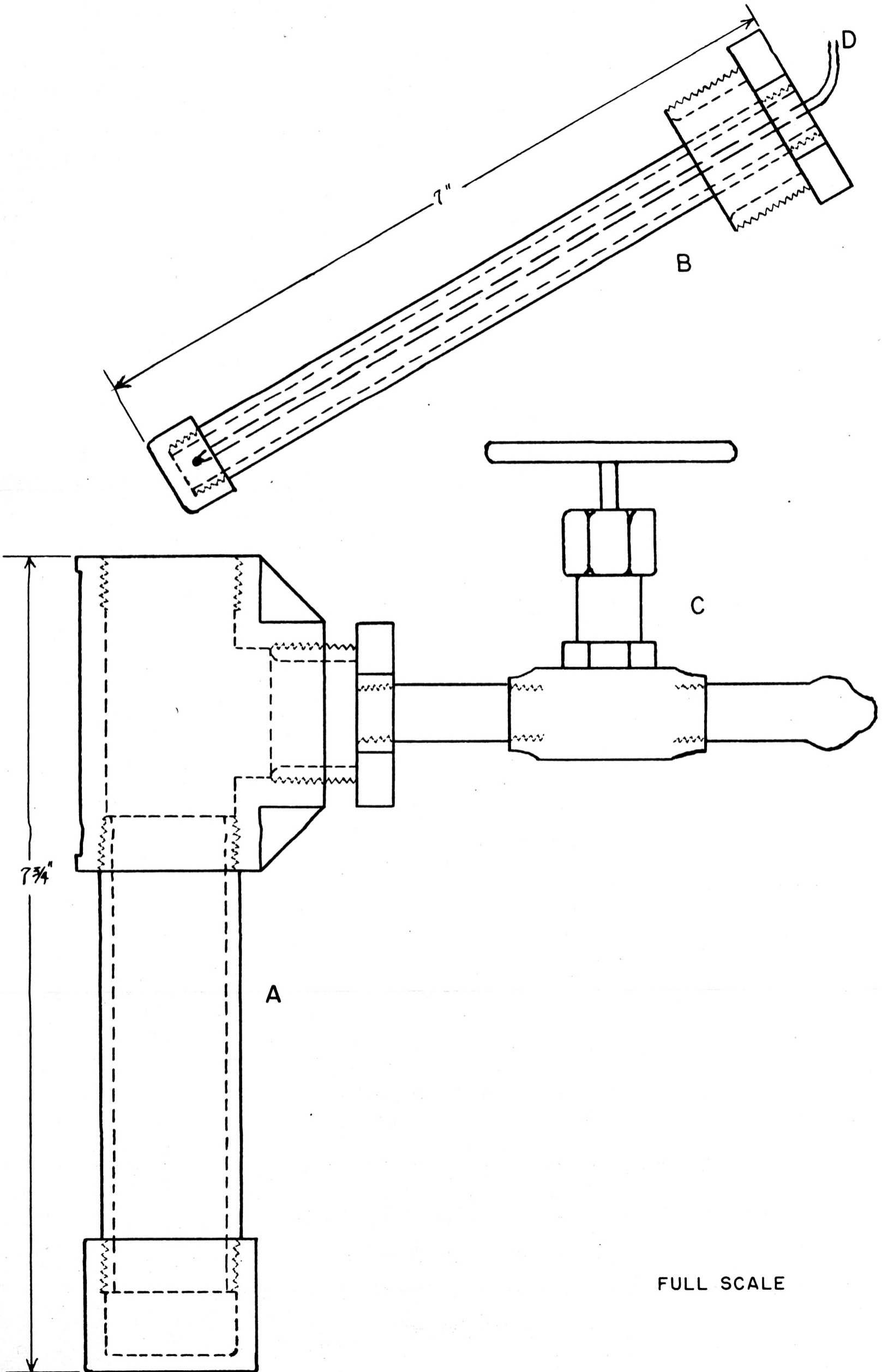
EXPLANATION OF PLATE III

Drawing of Autoclave Used in the Single Step Autoclave Process

All Stainless Steel Construction

- A. Standard 1-inch by $4\frac{1}{2}$ inches nipple with cap and straight tee.**
- B. Standard $\frac{1}{2}$ -inch nipple with cap and bushing.**
- C. Needle valve.**
- D. Iron-constantan thermocouple.**

PLATE III



FULL SCALE

electrically heated autoclave under varying conditions of temperature, pressure, and moisture content.

In the first step three separate batches of 800 grams of the phosphate rock were reacted with 400 grams of 100 percent sulfuric acid supplied as 71.2 percent acid. This quantity of acid corresponds to the value previously calculated to be sufficient for the formation of dicalcium phosphate, giving an acidulation ratio of 1.42. These mixtures of phosphate rock and acid were reacted for 30 minutes in the stirred autoclave. The temperature was maintained at 90°C and the pressure was atmospheric. The reaction was incomplete; the mass contained some free acid at this stage and was sticky and difficult to handle. The product was then dried at 80°C for 24 hours before use. Each batch was ground to pass a 40 mesh screen before re-autoclaving. The analysis of these mixtures is given in Table 3.

Table 3. Chemical analyses of partially acidulated rock, dried at 80°C for 24 hours

	Run No. 1		Run No. 2		Run No. 3	
	After	Drying	Before	After	Before	After
Acidulation Ratio	1.42		1.42	--	1.41	--
Total P ₂ O ₅ , %	23.61		23.79	25.23	22.80	24.57
Water Soluble						
P ₂ O ₅ , %	12.83		14.24	11.81	15.37	12.76
Citrate Soluble						
P ₂ O ₅ , %	2.46		1.55	3.53	1.13	3.63
Citrate Insoluble						
P ₂ O ₅ , %	8.32		8.00	9.89	6.30	8.17
Product Moisture, %	2.96		--	0.64	--	0.91
Conversion to						
Available P ₂ O ₅ , %	64.8		66.4	60.8	72.4	66.7
Conversion to Citrate						
Soluble P ₂ O ₅ , %	10.4		6.51	13.9	4.96	14.8

Single Step Autoclave Process. The small electrically heated, stainless steel reactor previously described and shown in Plate III was used to react a mixture of phosphate rock and sulfuric acid in a one step procedure. The purpose of these experimental runs was to investigate a wider range of the variables affecting the conversion, and the extent to which the degree of conversion (to available forms of phosphate) was affected by the operating variables.

Twenty-five grams of the phosphate rock described in Table 2 were mixed thoroughly with a predetermined amount of sulfuric acid (varying concentrations were also used) in a mortar and then placed in the preheated reactor to be autoclaved at the required temperature. The total reaction time at a constant temperature was 45 minutes. After this time had elapsed the product was removed from the reactor, dried 24 hours at room conditions, ground to a finely divided powder, cured for one week in a closed container at room conditions and finally analyzed for total P_2O_5 , citrate insoluble P_2O_5 , and water soluble P_2O_5 .

Analytical Methods

Sampling. All samples were cured at room temperature for one week or were cured from 4 weeks to 52 weeks in the constant humidity chamber at 100°F and 25 percent relative humidity. The samples were then ground to pass through a standard 35 mesh sieve. The grinding was done as rapidly as possible to avoid any extensive loss or gain in moisture. The ground samples were mixed thoroughly and preserved in tightly stoppered bottles.

Moisture Determination. Approximately two grams of the sample were placed into a regular weighing bottle that had been weighed to four

place accuracy. The sample was dried in an oven at 100°C for exactly five hours and then placed in a desiccator to cool and then reweighed to the same fourth place accuracy.

Total Phosphoric Acid. The colorimetric method of Bridger, and others (4) was used for all P_2O_5 determinations. The extractions were carried out by the methods of the Association of Official Agricultural Chemists (2). For total P_2O_5 determinations one gram of the sample was weighed and placed in a 250 ml volumetric flask with 30 ml of nitric acid and 7 ml of hydrochloric acid. The volumetric flask with solution was heated on a hot plate until the evolution of brown fumes stopped. The solution was cooled to room temperature and diluted with distilled water to volume. The solution was filtered using standard filters (no suction) and collected in a 250 ml receiving flask for colorimetry.

A one ml aliquot of the above extract was pipetted directly to a 100 ml volumetric flask. This aliquot of the phosphate solution was selected to contain approximately two mg of phosphorus pentoxide. Twenty-five ml of the standard color solution was added, and the resulting solution was diluted with distilled water to volume. The phosphorus pentoxide content of this aliquot was determined colorimetrically from a calibration curve previously determined by using samples of phosphate rock analyzed by the National Bureau of Standards.

Water Soluble Phosphoric Acid. One gram of the sample was placed on a nine cm Whatman No. 5 filter paper on a Buchner funnel and washed with successive small portions of distilled water until the filtrate was approximately 250 ml. Each portion of wash water was allowed to

pass through the filter before more was added. A small amount of suction was applied to insure that the washing would be complete within one hour. The filtrate was transferred from the suction flask to a 500 ml volumetric flask, washing with small aliquots of water and then diluted to the mark. If the filtrate was turbid, one to two ml of nitric acid was added, and the resulting solution mixed thoroughly.

After the final dilution, four ml of the solution was pipetted directly to a 100 ml volumetric flask, 25 ml of the standard color solution was added, and the phosphorus pentoxide content of the sample determined colorimetrically.

Citrate Insoluble Phosphoric Acid. The acidulated sample, after the water-soluble P_2O_5 was washed out, was transferred (filter and residue) to a 250 ml flask containing 100 ml of ammonium citrate (neutral) solution previously heated to 65°C in a constant temperature water bath. The flask was closed tightly with a smooth rubber stopper and shaken vigorously until the filter paper was reduced to a pulp. The pressure was relieved by momentarily removing the stopper. The flask was returned to the bath, stoppered loosely to prevent evaporation. The contents of the flask were maintained at exactly 65°C and the level of the water in the bath was kept above that of the citrate solution in the flask. The flask was shaken every five minutes. After exactly one hour had expired from the time the filter and residue were introduced, the flask was removed from the bath, and the contents were immediately filtered as rapidly as possible through Whatman filter paper No. 5 on a Buchner filter with suction. The residue was washed with water at 65°C until the volume of the filtrate was approximately 350 ml, allowing

time for thorough draining before new portions of water were added. However, the filter paper was not allowed to go completely dry or the pulp fines would clog the pores of the paper and eliminate the filter action. If the sample gave a cloudy filtrate, the residue was washed with a solution of ammonium nitrate. The filter paper and residue were transferred to a 250 ml volumetric flask and treated with aqua regia in the same manner as for the total P_2O_5 determination.

Four ml of the filtered solution were pipetted directly to a 100 ml volumetric flask. This aliquot was diluted with approximately 50 ml of distilled water and twenty-five ml of color solution added, and the resulting solution diluted to volume with distilled water. The P_2O_5 content was determined from the standard calibration curve and the colorimeter reading.

Citrate Soluble Phosphoric Acid. The citrate soluble P_2O_5 was determined by difference between the total P_2O_5 and the sum of the water soluble and citrate insoluble P_2O_5 .

EXPERIMENTAL RESULTS

Rotary Reactor

Effect of Initial Moisture Content. The initial moisture content of the charge was determined by the quantity of free moisture available in the phosphate rock and sulfuric acid and was reported as percent, wet basis. This method was used because the compounds formed in the final product may be hydrated or mixtures of anhydrous and hydrated salt. This meant that the pressure of the system was not always a direct result of the actual moisture present. Also, the initial moisture

content was easily reproducible for any number of samples by adjusting the strength of the acid used.

A set of experimental runs was made at 278-280°F while the initial moisture content was varied between 2 and 12 percent. The results of these runs are shown in Table 4.

Table 4. Effect of initial moisture content on the conversion of phosphate to available forms of superphosphates made in the rotary reactor at an acidulation ratio of 1.42 and a temperature of 278°F.

Initial Moisture Content, percent	2.4	3.9	6.16	11.7
Total P ₂ O ₅ , %	23.39	23.46	23.00	22.15
Water Soluble P ₂ O ₅ , %	14.12	15.21	15.01	14.59
Citrate Soluble P ₂ O ₅ , %	1.96	1.83	2.81	2.84
Citrate Insoluble P ₂ O ₅ , %	7.31	6.42	5.18	4.72
Conversion to Available P ₂ O ₅ , %	68.9	72.6	77.4	78.7
Conversion to Citrate Soluble P ₂ O ₅ , %	8.4	7.8	12.2	13.42

Effect of Temperature. The results of the investigations of Elmore and Farr (9) and Larson (16) indicated that heating monocalcium phosphate would increase the conversion of monocalcium phosphate to dicalcium phosphate. Therefore a series of experimental runs was made, using two initial moisture content levels of 11.7 and 3.9 percent, at temperatures between 200° and 350°F. For each run 300 grams of phosphate rock and the required amounts of sulfuric acid and water were charged to the rotary autoclave. The acidulation ratio was fixed as close to 1.42 as possible for all samples. Each experimental run was allowed to react at a predetermined temperature for thirty minutes.

Mixing was provided by stainless steel rods or steel balls which were placed in the reaction chamber before the material was charged. The results of these experimental runs are given in Table 5,

Effect of Reaction Time. Three hundred grams of phosphate rock and 207 grams of 71.6 percent sulfuric acid were charged to the rotary autoclave giving an acidulation ratio of 1.41, and the reaction was allowed to proceed at 295°F for reaction times of 5, 20, 30 and 40 minutes. The results of these runs are reported in Table 6.

Effect of Curing Time. Three hundred grams of phosphate rock and 207 grams of 71.6 percent sulfuric acid were charged to the rotary autoclave and reacted at 250°, 280°, and 285°F. The samples were analyzed as made (after curing for one week in a closed container at room conditions) and again after curing four additional weeks in an open container at 100°F and 25 percent relative humidity. The results of this test are reported in Table 7.

Two Step Autoclave Process

Effect of Initial Moisture Content. Forty grams of the partially acidulated rock were mixed with varying amounts of water and autoclaved in the small stainless steel reactor previously described. The reactor was preheated before the materials were added, and the reaction time allowed was 45 minutes. Two series of experimental runs were made at temperature levels of 230° and 280°F. The results of these runs are shown in Table 8.

Effect of Temperature. Two series of runs were made using initial moisture content levels of 8.26 and 2.9 percent. Forty grams of the

Table 5. Effect of temperature on the conversion of phosphate to available forms for superphosphates made in the rotary reactor at an acidulation ratio of 1.42.

Temperature, °F	213	215	229	254	278	282	292	295	310
Initial moisture content, %	11.6	3.9	11.7	11.7	11.7	3.9	11.7	3.9	11.7
Total P ₂ O ₅ , %	22.19	22.78	24.10	22.08	22.15	23.46	22.16	22.72	22.48
Water Soluble P ₂ O ₅ , %	14.36	14.45	15.31	14.04	14.59	15.21	14.21	13.35	13.85
Citrate Soluble P ₂ O ₅ , %	2.06	1.70	3.08	3.17	2.84	1.83	3.00	2.47	2.54
Citrate Insoluble P ₂ O ₅ , %	5.77	6.63	5.71	4.87	4.72	6.42	4.95	6.90	6.09
Conversion to Available P ₂ O ₅ , %	74.0	70.8	76.3	78.0	78.7	72.6	77.8	69.7	72.5
Conversion to Citrate Soluble P ₂ O ₅ , %	9.3	7.46	12.8	14.4	13.4	7.8	13.6	10.9	11.3

Table 6. Effect of reaction time on the conversion of phosphate to available forms for superphosphates made in the rotary reactor at an acidulation ratio of 1.42 and a temperature range of 292°-295°F and an initial moisture content of 11.7 percent.

Reaction time, minutes	5	20	30	45
Total P ₂ O ₅ , %	23.00	22.66	22.16	22.73
Water Soluble P ₂ O ₅ , %	14.25	14.57	14.21	14.79
Citrate Soluble P ₂ O ₅ , %	2.14	2.59	3.00	2.82
Citrate Insoluble P ₂ O ₅ , %	6.61	5.50	4.95	5.12
Conversion to Available P ₂ O ₅ , %	71.2	75.6	77.8	77.5
Conversion to Citrate Soluble P ₂ O ₅ , %	9.3	11.4	13.6	12.4

Table 7. Effect of curing time on the conversion of phosphate to available forms for superphosphates made in the rotary reactor.

Temperature, °F	278		285		293	
	1 ¹	4 ²	1 ¹	4 ²	1 ¹	4 ²
Curing time, weeks						
Initial Moisture Content, %	11.7	--	11.7	--	11.7	--
Total P ₂ O ₅ , %	22.15	22.81	22.66	22.60	22.73	22.81
Water Soluble P ₂ O ₅ , %	14.59	14.27	14.57	14.42	14.79	14.55
Citrate Soluble P ₂ O ₅ , %	2.84	3.30	2.59	3.02	2.82	3.52
Citrate Insoluble P ₂ O ₅ , %	4.72	5.24	5.50	5.16	5.12	4.74
Conversion to Available P ₂ O ₅ , %	78.7	77.0	75.6	77.2	77.5	79.1
Conversion to Citrate Soluble P ₂ O ₅ , %	12.8	14.5	11.4	13.35	12.4	15.4
Acidulation Ratio	1.42	--	1.42	--	1.43	--

¹ Cured in a closed container at room conditions.

² Cured at 100°F and 25 percent relative humidity.

Table 8. Effect of initial moisture content on the conversion of phosphate to available forms for superphosphates made by the two step autoclave process at an acidulation ratio of 1.42.

Initial moisture content, %	0.64		0.91		2.9		5.64		8.26		10.7
	230	280	230	280	230	280	230	280	230	280	280
Temperature, °F											
Total P ₂ O ₅ , %	24.58	25.16	23.61	23.04	24.72	23.92	23.43	24.36	23.42	24.03	23.52
Water Soluble P ₂ O ₅ , %	13.48	13.44	14.33	13.33	15.92	15.10	15.45	15.52	15.60	15.51	14.98
Citrate Soluble P ₂ O ₅ , %	1.93	2.33	2.35	2.76	2.08	1.12	1.37	1.74	1.12	1.88	1.77
Citrate Insoluble P ₂ O ₅ , %	9.17	9.39	6.93	6.95	6.72	7.70	6.61	6.90	6.70	6.64	6.77
Conversion to Available P ₂ O ₅ , %	62.7	62.7	70.6	69.8	72.9	67.8	71.2	71.7	71.5	72.4	71.3
Conversion to Citrate Soluble P ₂ O ₅ , %	7.85	9.26	9.96	11.98	8.41	4.68	5.84	7.96	4.78	7.81	7.85

partially acidulated rock and a predetermined quantity of water were mixed in the preheated stainless steel reactor and reacted for 30 minutes at temperatures between 200° and 350°F. At the end of the reaction time the gases were vented, and the product was dried and cured before analyzing. The results of these runs are reported in Table 9.

Effect of Reaction Time. The effect of reaction time was studied by reacting 40 grams of partially acidulated rock with enough water added to bring the initial moisture content to 10.7 percent at a temperature of 285°F for varying amounts of time. The results are shown in Table 10.

Effect of Curing Time. Forty grams of the partially acidulated rock, adjusted to an initial moisture content of 8.26 percent, were reacted at 230°F. The sample was analyzed as made and then analyzed again after a 52 week period. The results of this test are reported in Table 11.

Effect of Re-Autoclaving. Bridger, and others (5) described a method for the formation of dicalcium phosphate by refluxing a mixture of sulfuric acid (or other mineral acids) and phosphate rock with further heating in an open container. The conversion to dicalcium phosphate was increased by repeating the refluxing and heating steps. This seemed to indicate that re-autoclaving should have a favorable effect on the formation of dicalcium phosphate. To test this theory, 40 gram samples of partially acidulated rock were autoclaved for 45 minutes at an initial moisture content of nine percent at three different temperatures. These samples were analyzed as made and the product moisture determined. The moisture content of each sample was brought

Table 9. Effect of temperature on the conversion of phosphate to available forms for superphosphates made by the two step autoclave process at an acidulation ratio of 1.42.

Temperature, °F	230	230	230	250	275	278	280	284	287	306
Initial Moisture Content, %	0.64	2.9	8.26	0.64	2.9	8.26	0.64	2.9	8.26	0.64
Total P ₂ O ₅ , %	24.58	23.92	23.42	24.40	23.41	24.03	25.16	25.50	24.47	24.70
Water Soluble P ₂ O ₅ , %	13.48	15.10	15.60	13.71	12.50	15.51	13.44	13.66	14.41	12.80
Citrate Soluble P ₂ O ₅ , %	1.93	1.12	1.12	1.80	3.64	1.88	2.33	2.74	1.81	2.28
Citrate Insoluble P ₂ O ₅ , %	9.17	7.70	6.70	8.89	7.27	6.64	9.39	9.10	8.25	9.62
Conversion to Available P ₂ O ₅ , %	62.7	67.8	71.5	63.6	69.0	72.4	62.7	64.3	66.4	61.0
Conversion to Citrate Soluble P ₂ O ₅ , %	7.85	4.68	4.78	7.37	15.58	7.81	9.26	10.75	7.39	9.22

Table 10. Effect of reaction time on the conversion of phosphate to available forms for superphosphates made by the two step autoclave process at an acidulation ratio of 1.42 and a temperature range of 280°-285°F.

Reaction time, minutes	20	45
Initial Moisture Content, %	10.7	10.7
Total P ₂ O ₅ , %	24.38	23.52
Water Soluble P ₂ O ₅ , %	14.21	14.98
Citrate Soluble P ₂ O ₅ , %	1.89	1.77
Citrate Insoluble P ₂ O ₅ , %	8.28	6.77
Conversion to Available P ₂ O ₅ , %	66.6	71.3
Conversion to Citrate Soluble P ₂ O ₅ , %	7.76	7.85

Table 11. Effect of curing time on the conversion of phosphate to available forms for superphosphates made by the two step autoclave process at an acidulation ratio of 1.42, a temperature of 230°F and an initial moisture content of 8.26%.

Curing time	As made	52 weeks
Total P ₂ O ₅ , %	23.42	23.96
Water Soluble P ₂ O ₅ , %	15.60	16.40
Citrate Soluble P ₂ O ₅ , %	1.12	1.52
Citrate Insoluble P ₂ O ₅ , %	6.70	6.04
Conversion to Available P ₂ O ₅ , %	71.5	75.0
Conversion to Citrate Soluble P ₂ O ₅ , %	4.78	6.35

to its initial value by the addition of the required quantity of distilled water, and each sample was re-autoclaved for 45 minutes at the original autoclaving temperature. The product moisture of each of the re-autoclaved samples was determined. The analyses are reported in Table 12.

Single Step Autoclave Process

Effect of Initial Moisture Content. Twenty-five grams of phosphate rock and approximately 50 grams of 100 percent sulfuric acid per 100 grams of rock were pre-mixed in a mortar and charged to the stainless steel reactor. The acid was supplied as 71.2, 83.86, and 96 percent sulfuric acid depending on the desired initial moisture content. A range of moisture concentrations from 2 to 18.0 percent were used with two temperature levels of 220° and 300°F. The results of these runs are shown in Table 13.

Effect of Temperature. Twenty-five grams of phosphate rock and 12.9 grams of 96 percent sulfuric acid were pre-mixed in a mortar with additional water to furnish the desired initial moisture content and charged to the preheated reactor. Three temperature levels of 220°, 260°, and 300°F were used for initial moisture contents of approximately 7 and 13 percent. The reaction time used was 45 minutes. The results are reported in Table 14.

Effect of Reaction Time. Three experimental runs were made at an initial moisture content of 12.5 percent and a reaction temperature range of 300° to 310°F. Each charge to the preheated reactor consisted of 25 grams of phosphate rock and 17.5 grams of 71.2 percent sulfuric

Table 12. Effect of re-autoclaving on the conversion of phosphate to available forms for superphosphates made by the two step autoclave process at an acidulation ratio of 1.42.

Temperature, °F	First Autoclaving					Second Autoclaving				
	230	275	285	300	300	230	275	285	300	300
Initial Moisture Content, %	8.9	8.8	8.8	6.6	12.6	8.9	9.0	8.7	6.6	12.6
Total P ₂ O ₅ , %	23.52	23.57	23.60	23.58	21.76	24.37	24.87	24.56	25.27	23.95
Water Soluble P ₂ O ₅ , %	15.18	15.44	14.20	15.12	16.04	14.90	12.24	11.15	8.32	13.20
Citrate Soluble P ₂ O ₅ , %	2.58	2.38	2.09	1.20	0.68	3.43	7.20	6.78	9.79	6.20
Citrate Insoluble P ₂ O ₅ , %	5.76	5.75	7.31	7.26	5.04	6.04	5.43	6.63	7.16	4.55
Conversion to Available P ₂ O ₅ , %	75.4	75.7	69.0	69.2	77.5	75.5	78.2	73.1	71.7	81.0
Conversion to Citrate Soluble P ₂ O ₅ , %	11.0	10.1	8.85	5.1	3.13	14.1	28.9	27.6	38.7	25.9
Product Moisture, %	2.13	1.92	2.17	--	--	2.27	2.0	2.27	--	--

Table 13. Effect of initial moisture content on the conversion of phosphate to available forms for superphosphates made by the single step autoclave process at an acidulation ratio of 1.42.

Initial Moisture Content, %	2.0	6.6	6.8	12.5	13.0	13.1	18.0
Temperature, °F	300	220	300	220	300	220	300
Total P ₂ O ₅ , %	23.47	24.00	23.58	23.42	24.07	23.24	22.53
Water Soluble P ₂ O ₅ , %	15.13	15.01	15.12	15.85	15.56	16.24	15.00
Citrate Soluble P ₂ O ₅ , %	0.29	1.70	1.20	0.86	1.44	1.06	2.35
Citrate Insoluble P ₂ O ₅ , %	8.05	7.29	7.26	6.71	7.07	5.94	5.18
Conversion to Available P ₂ O ₅ , %	65.7	69.5	69.2	71.5	70.5	74.4	77.0
Conversion to Citrate Soluble P ₂ O ₅ , %	1.24	7.08	5.1	3.67	5.99	4.56	10.4

Table 14. Effect of temperature on the conversion of phosphate to available forms for superphosphates made by the single step autoclave process at an acidulation ratio of 1.42.

Temperature, °F	220		260		300	
Initial Moisture Content, %	6.8	13.0	7.1	12.7	6.8	12.5
Total P ₂ O ₅ , %	23.42	23.24	22.00	22.28	23.58	24.07
Water Soluble P ₂ O ₅ , %	15.85	16.24	15.12	15.16	15.12	15.56
Citrate Soluble P ₂ O ₅ , %	0.86	1.06	1.08	1.49	1.20	1.44
Citrate Insoluble P ₂ O ₅ , %	6.71	5.94	5.80	5.63	7.26	7.07
Conversion to Available P ₂ O ₅ , %	71.5	74.4	73.6	74.7	69.2	70.5
Conversion to Citrate Soluble P ₂ O ₅ , %	3.67	4.56	4.9	6.7	5.1	5.99

acid. Reaction times of 20, 45, and 60 minutes were used. The results are given in Table 15.

Table 15. Effect of reaction time on the conversion of phosphate to available forms for superphosphates made by the single step autoclave process at an acidulation ratio of 1.42 and a temperature range of 300-310°F.

Reaction time, minutes	20	45	60
Initial Moisture Content, %	12.5	13	13
Total P ₂ O ₅ , %	24.32	23.22	22.53
Water Soluble P ₂ O ₅ , %	16.44	15.61	15.00
Citrate Soluble P ₂ O ₅ , %	0.75	2.16	2.35
Citrate Insoluble P ₂ O ₅ , %	7.13	5.45	5.18
Conversion to Available P ₂ O ₅ , %	70.5	76.5	77.0
Conversion to Citrate Soluble P ₂ O ₅ , %	3.08	9.3	10.4

Effect of Curing Time. Twenty-five grams of phosphate rock were mixed with 20 grams of 71.2 percent sulfuric acid and reacted at 220°F for 45 minutes. This quantity of acid gave an acidulation ratio of 1.62. The sample was analyzed as made and again after a 16-week period for curing during which the sample was stored in a constant humidity cabinet at 100°F and 25 percent relative humidity. The analyses are given in Table 16.

Table 16. Effect of curing time on the conversion of phosphate to available forms for superphosphates made by the single step autoclave process at an acidulation ratio of 1.62 and a temperature of 220°F.

Analysis	As Made	16 Weeks
Initial Moisture Content, %	13.3	--
Total P ₂ O ₅ , %	21.80	22.22
Water Soluble P ₂ O ₅ , %	17.24	18.30
Citrate Soluble P ₂ O ₅ , %	1.42	1.62
Citrate Insoluble P ₂ O ₅ , %	3.14	2.30
Conversion to Available P ₂ O ₅ , %	85.5	89.6
Conversion to Citrate Soluble P ₂ O ₅ , %	6.51	7.3

Effect of Acidulation Ratio. Twenty-five grams of phosphate rock and a predetermined quantity of sulfuric acid were charged to the stainless steel reactor. A series of experimental runs was made at two temperature levels of 220° and 300°F. Runs were made for varying initial moisture contents at a fixed acidulation ratio. The acidulation ratio was varied from 1.4 to 1.93. The results are shown in Table 17.

Effect of the Addition of Hydrochloric Acid. Patel (20) and Gadre (12), as well as other investigators, have used hydrochloric acid under various conditions to form a product consisting of dicalcium phosphate or mixtures including dicalcium phosphate. It was reasonable, therefore, to expect that the addition of small amounts of hydrochloric acid would enhance the formation of the dicalcium phosphate.

A set of three runs was made at an initial moisture content of 12.2 percent and at temperatures of 220, 250, and 300°F. For each sample, 25 grams of phosphate rock were mixed with 14.6 grams of 83.86 percent sulfuric acid, 2.7 grams of 37 percent hydrochloric acid, and one gram of water. The mixture was placed in the preheated stainless steel reactor and reacted for 45 minutes. The results of these runs are given in Table 18.

Table 17. Effect of acidulation ratio on the conversion of phosphate to available forms for superphosphates made by the single step autoclave process.

Acidulation Ratio	Temperature °F	Initial	Total	Water Soluble	Citrate Soluble	Citrate Insoluble	Conversion to Available	
		Moisture Content, %	P ₂ O ₅ , %	P ₂ O ₅ , %	P ₂ O ₅ , %	P ₂ O ₅ , %	P ₂ O ₅ , %	Soluble P ₂ O ₅ , %
1.41 - 1.42	220	2.00	23.47	15.13	0.29	8.05	65.7	1.24
		6.8	23.42	15.85	0.86	6.71	71.5	3.67
		13.0	23.24	16.24	1.06	5.94	74.4	4.56
	300	17.9	23.70	14.26	2.52	6.92	70.7	10.6
		1.97	24.00	15.01	1.70	7.29	69.5	7.08
		6.6	23.58	15.12	1.20	7.26	69.2	5.1
		12.5	24.07	15.56	1.44	7.07	70.5	5.99
1.60 - 1.62	220	2.09	22.32	15.59	0.21	6.52	70.9	0.94
		2.09	22.18	16.18	0.41	5.59	74.7	1.85
		11.3	23.12	17.15	1.63	4.34	81.2	7.05
		13.3	21.80	17.24	1.42	3.14	85.5	6.56
	300	2.07	22.61	15.21	0.93	6.47	71.5	4.11
		7.00	22.99	15.74	1.42	5.83	74.5	6.17
		13.1	22.72	16.25	1.43	5.04	77.8	6.29
		13.3	22.70	16.36	1.76	4.58	79.9	7.75
1.80 - 1.81	220	2.18	21.38	15.01	0.48	5.89	72.5	2.24
		14.1	20.50	17.28	0.15	3.07	85.1	0.73
	300	2.17	20.51	14.84	0.67	5.00	75.6	3.27
1.91	300	7.7	20.14	16.80	0.97	2.37	85.3	4.82
		14.5	20.63	17.66	0.95	2.02	90.3	4.6

Table 18. Effect of the addition of HCl on the conversion of phosphate to available forms for superphosphates made by the single step autoclave process at an acidulation ratio of 1.55.¹

Temperature, °F	: 220		: 260		: 300	
HCl added, grams of 37% acid per 25 grams of phosphate rock	none	2.7	none	2.7	none	2.7
Initial Moisture Content, %	13.0	12.5	12.7	12.5	12.5	12.5
Total P ₂ O ₅ , %	23.24	21.81	22.28	22.52	24.07	23.01
Water Soluble P ₂ O ₅ , %	16.24	15.08	15.16	14.42	15.56	14.56
Citrate Soluble P ₂ O ₅ , %	1.06	2.09	1.49	2.52	1.44	2.57
Citrate Insoluble P ₂ O ₅ , %	5.94	4.64	5.63	5.58	7.07	5.88
Conversion to Available P ₂ O ₅ , %	74.4	82.5	74.7	75.2	70.5	74.5
Conversion to Citrate Soluble P ₂ O ₅ , %	4.56	9.58	6.7	11.2	5.99	11.2

¹ Equivalent to grams of 100% H₂SO₄ per gram of P₂O₅ in phosphate rock.

Chemical Reaction of Monocalcium Phosphate Monohydrate and Tricalcium Phosphate. To further investigate the proposed reactions, analytical reagent grade monocalcium phosphate monohydrate and tricalcium phosphate were reacted together. This method was used to study the effect of the reactions without any of the interfering or competing reactions which occur with phosphate rock.

Three tests were made. The first test consisted of charging 100 grams of monocalcium phosphate monohydrate, 40 grams of tricalcium phosphate, and five grams of distilled water to the autoclave described in Plate II. The mixture was reacted, under pressure, for 30 minutes at 214°F. The second test consisted of a charge of the same proportions of reagents which was placed in the autoclave and reacted, under pressure, for 30 minutes at 286°F. The third test consisted of placing a mixture of 20 grams of monocalcium phosphate monohydrate, eight grams of tricalcium phosphate, and one gram of distilled water in an oven maintained

at 135°F for 24 hours. The results of these tests are given in

Table 19.

Table 19. Effect of temperature on the chemical reaction of monocalcium phosphate monohydrate and tricalcium phosphate.

Temperature, °F	: 135	: 214	: 286
Reaction time, minutes	1440	30	30
Total P ₂ O ₅ , %	50.66	51.19	51.07
Water Soluble P ₂ O ₅ , %	23.29	24.35	21.30
Citrate Soluble P ₂ O ₅ , %	27.27	26.74	28.17
Citrate Insoluble P ₂ O ₅ , %	0.10	0.10	1.60
Conversion to Available P ₂ O ₅ , %	99.8	99.8	96.9
Conversion to Citrate Soluble P ₂ O ₅ , %	53.7	53.2	55.0

DISCUSSION OF RESULTS

Although some of the reactions occurring in the manufacture of superphosphate are well known, the structure and identity of the compounds actually formed are not entirely known. It is generally accepted that monocalcium phosphate monohydrate is almost entirely water soluble; dicalcium phosphate is not water soluble, but is soluble in a neutral ammonium citrate solution; tricalcium phosphate and mineral apatite are neither water soluble nor citrate soluble. The results reported here are given in terms of water soluble, citrate soluble, and citrate insoluble (which infers water insoluble) phosphorus pentoxide content. The term, total P₂O₅ content, refers to all the phosphorus as P₂O₅ in the sample regardless of its actual form or composition. Since the water soluble P₂O₅ content consists almost entirely of all the monocalcium phosphate monohydrate, the terms water soluble and monocalcium phosphate monohydrate are used interchangeably. Also the citrate soluble P₂O₅ as analyzed in the sample consists almost

entirely of dicalcium phosphate and the terms citrate soluble and dicalcium phosphate are used interchangeably.

Since only the water soluble and citrate soluble phosphates are considered agronomically available, the fraction of the total phosphate present in these forms in the final product is a measure of the efficiency of the process. The conversion, or degree of conversion, therefore, is defined here as the percent of the total P_2O_5 content of the product that is water soluble, citrate soluble, or a combination of these two forms of phosphate.

Increasing the initial moisture content of the phosphate rock and sulfuric acid mixture gave an increase in the degree of conversion to all available forms. Although the conversion to both available P_2O_5 and citrate soluble P_2O_5 followed this trend, the maximum conversion for both forms did not occur at the same moisture content in most cases. For the two step autoclave process, the maximum conversion to available P_2O_5 occurred at moisture contents of 4 to 8 percent while the maximum conversion to citrate soluble P_2O_5 occurred at moisture contents of 0.5 to 3 percent. The effect of high moistures in the reaction mixture was to decrease the formation of dicalcium phosphate or citrate soluble material as shown in Fig. 1. At higher temperature levels increasing the moisture caused an increase in total available P_2O_5 content and also an increase in the formation of citrate soluble P_2O_5 . However, the effect of increasing the moisture above 4 percent was small. The maximum conversion to citrate soluble P_2O_5 , 15.58 percent, occurred at a reaction temperature of 275°F and 2.9 percent moisture. The effect of drying the reaction mixture for a 24 hour period in the first step of the process was to increase the formation of dicalcium phosphate. This

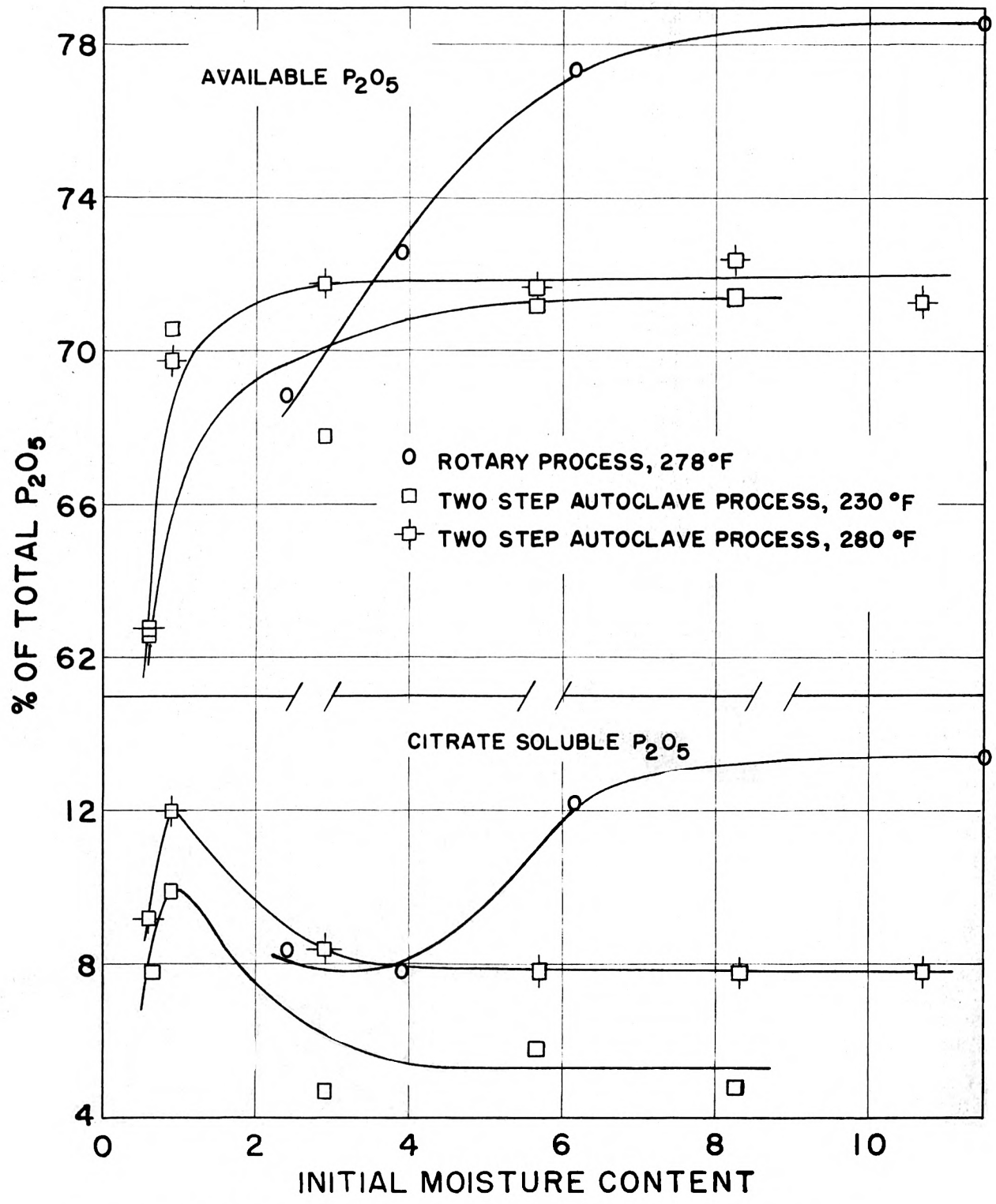


Fig. 1. Effect of initial moisture content on the conversion of phosphate to available forms for superphosphates made at an acidulation ratio of 1.42.

effect can be seen from the data shown in Table 3. As a result further increase in conversion to dicalcium phosphate in the autoclave step was not large.

Superphosphates made by the rotary process and single step process gave higher conversions than those made by the two step autoclave process as shown in Fig. 1 and Fig. 2. The maximum conversion to dicalcium phosphate or citrate soluble P_2O_5 was 10 to 14 percent at moisture contents of 11 to 13 percent. For the same reaction temperature increasing the moisture content appeared to be favorable to the formation of dicalcium phosphate, and the total conversion to available P_2O_5 also increased. The maximum conversion to available P_2O_5 was 78.7 percent using the rotary process and a reaction temperature of 278°F and a moisture content of 11.7 percent. The maximum conversion obtained in superphosphate made by the single step autoclave process was 77 percent at a reaction temperature of 300°F and a moisture content of 13.1 percent. Since the acidulation ratio was fixed at 1.42, the quantity of monocalcium phosphate formed should have been substantially constant. Therefore, decreasing the initial moisture content effectively increased the proportion of this salt to water. Elmore and Farr (9) found that increasing the proportion of monocalcium phosphate to water in the system, $CaO-P_2O_5-H_2O$ increased the conversion of monocalcium phosphate up to a certain maximum concentration. These data appear to follow this trend, but the maximum conversion to dicalcium phosphate does not occur at the same moisture content for all the processes.

There was a trend to higher conversions when the reaction was completed in a single step which seems to indicate that the hydrolysis

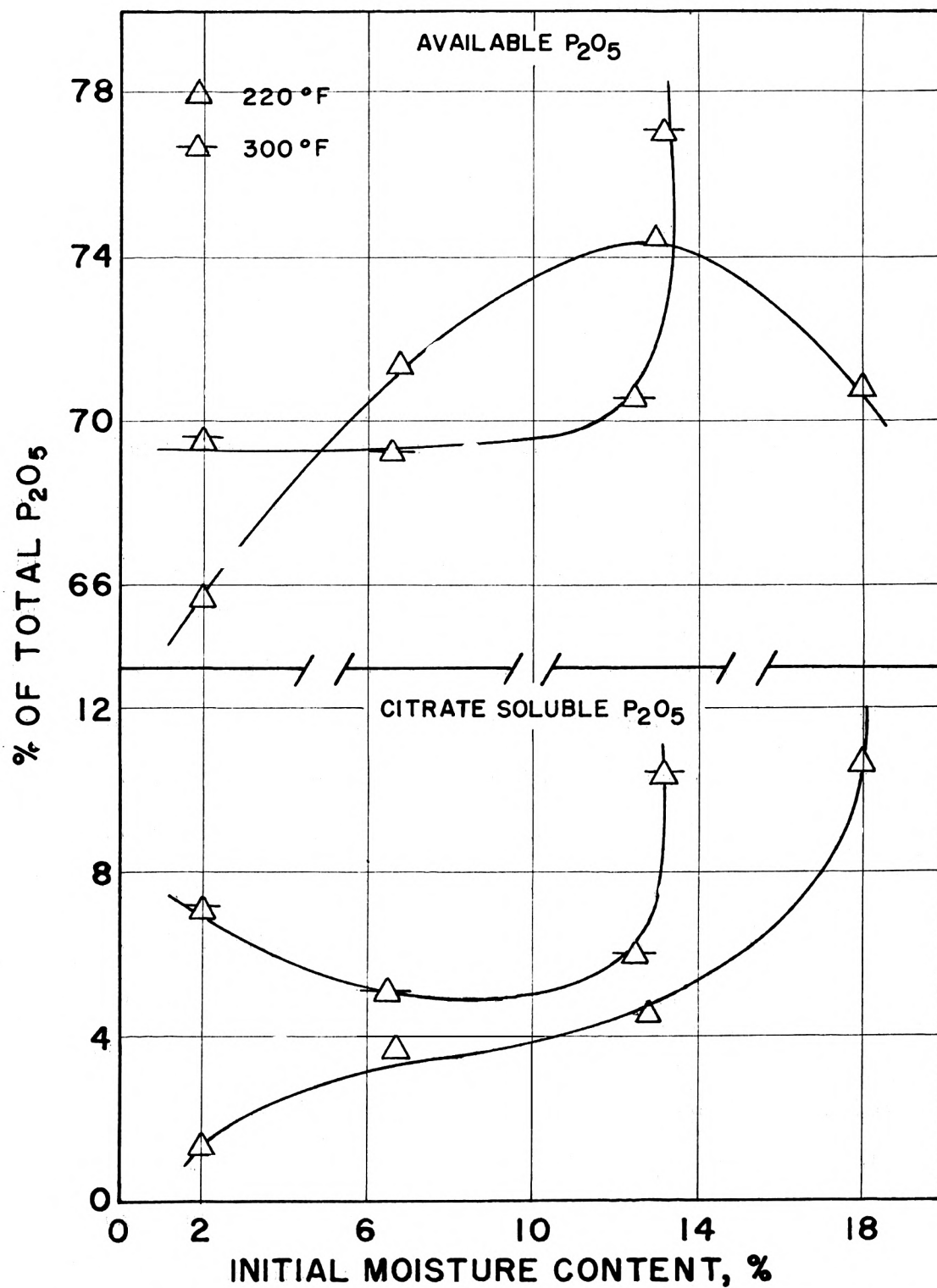
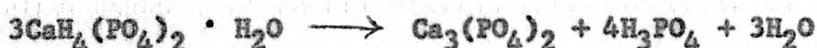


Fig. 2. Effect of initial moisture content on the conversion of phosphate to available forms for superphosphates by the single step auto-clave process at an acidulation ratio of 1.42.

of monocalcium phosphate is easier to accomplish than that of monocalcium phosphate monohydrate, which is not stable at the higher temperatures. It is also apparent that higher temperatures increased the conversion of P_2O_5 to available forms, but were not particularly favorable to the formation of dicalcium phosphate in the two step process.

Increasing the reaction temperature for a constant moisture content increased the conversion to available P_2O_5 content of superphosphates made by all three processes. As the temperature increased, the conversion passed through a maximum. This maximum conversion occurred in a temperature range of 270° to $285^\circ F$ for the range of moisture contents studied. The interrelationship of moisture and temperature in increasing the conversion to both citrate soluble and available forms of P_2O_5 is shown in Figs. 3, 4, and 5. At higher moisture levels the maximum conversion was increased and also shifted to higher temperatures.

The rotary process was the most efficient of the three processes, giving a maximum conversion to available P_2O_5 of 78.7 percent using a reaction temperature of $278^\circ F$ and an initial moisture content of 11.7 percent. The rotary process and the two step autoclave process gave similar conversions to dicalcium phosphate as may be seen from Fig. 4 and Fig. 5. This maximum conversion to dicalcium phosphate occurred at a moisture content of 2.9 percent in superphosphates made by the two step autoclave process and at a moisture content of 11.7 percent using the rotary process. At temperatures higher than $310^\circ F$ the reverse reaction of monocalcium phosphate to tricalcium phosphate became effective. This reaction is given by:



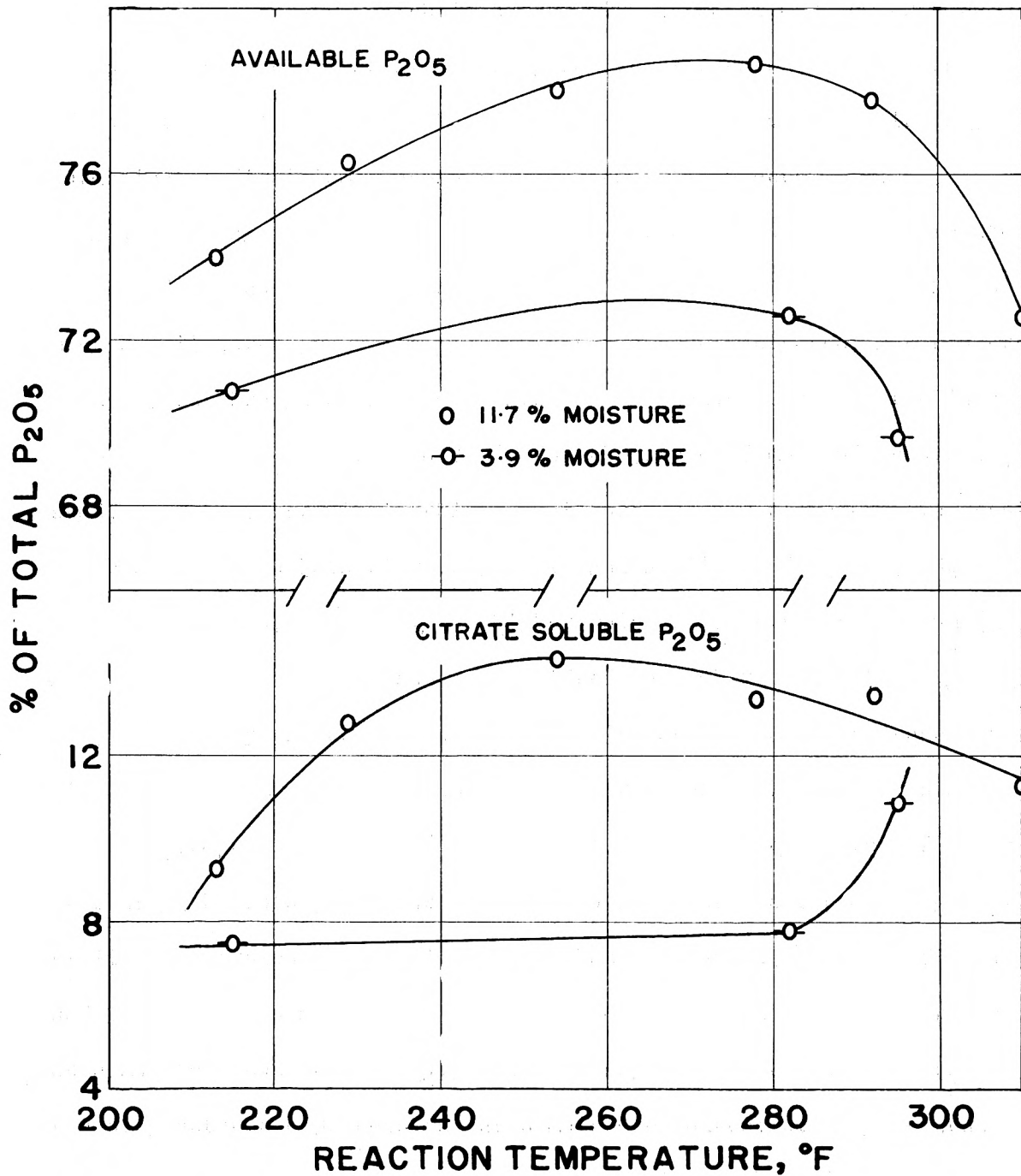


Fig. 3. Effect of temperature on the conversion of phosphate to available forms for superphosphates made by the rotary process at an acidulation ratio of 1.42 and varying initial moistures.

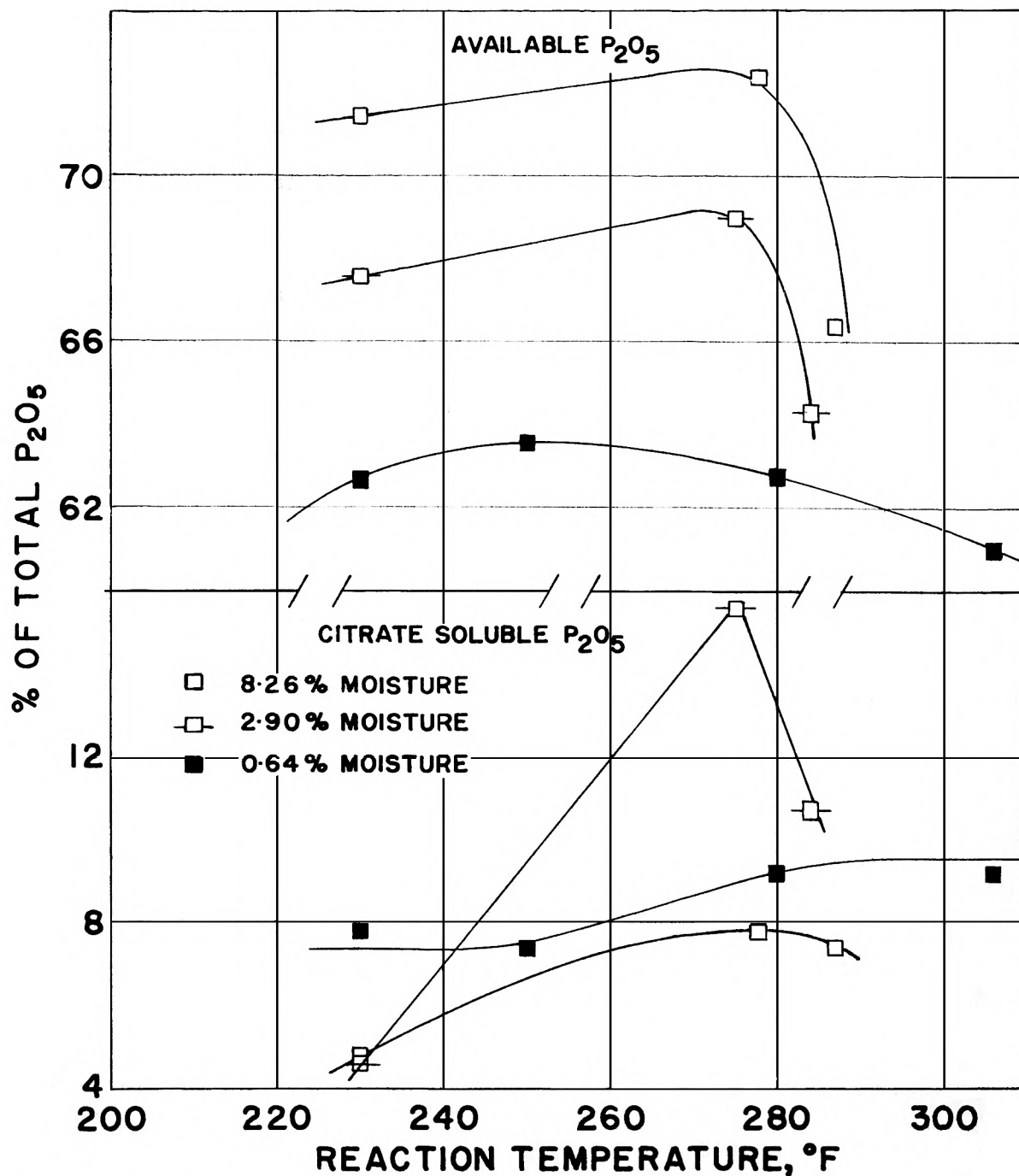


Fig. 4. Effect of temperature on the conversion of phosphate to available forms for superphosphates made by the two step autoclave process at an acidulation ratio of 1.42 and varying initial moistures.

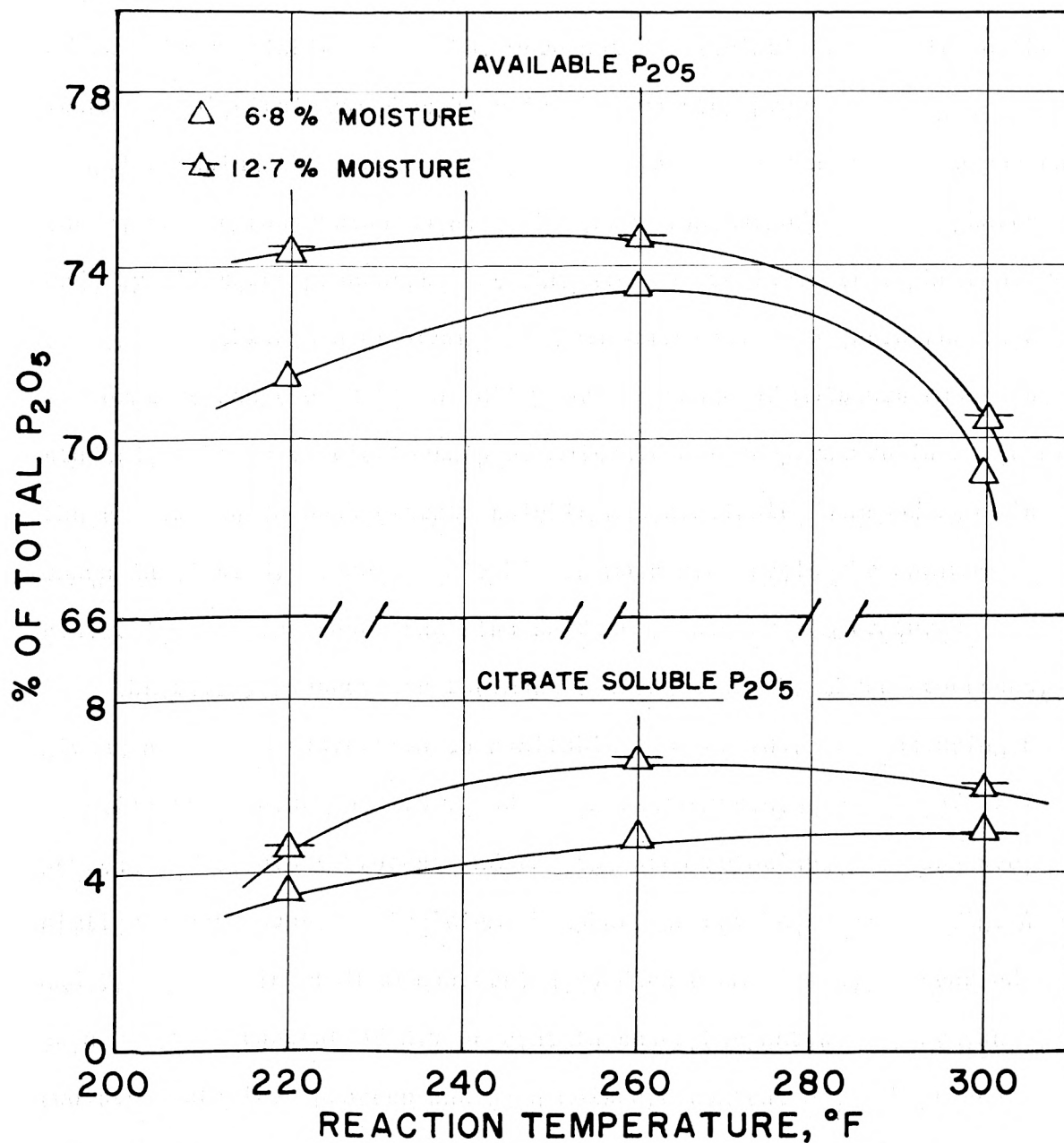


Fig. 5. Effect of temperature on the conversion of phosphate to available forms for superphosphates made by the single step autoclave process at an acidulation ratio of 1.42.

Longer reaction times increased the total conversion to all available forms of P_2O_5 and also increased the conversion to dicalcium phosphate as can be seen from the data shown in Fig. 6. A reaction time of 25 to 30 minutes appeared to be sufficient time for the rotary process, whereas 30 to 60 minutes was more favorable for the two step and the single step autoclave processes.

Curing periods of four weeks and less had a small effect on conversion of P_2O_5 to available forms. This effect was higher for low acidulation ratios. Over longer periods of time the increase was less noticeable as can be seen from the data in Fig. 7. The hydrolysis reaction probably continued to a small degree for several weeks after the samples were autoclaved. The following symbols were used to identify the curves in Fig. 7:

- O Superphosphate made in the rotary reactor at an acidulation ratio of 1.42, a reaction temperature of 278°F and an initial moisture content of 11.7 percent.
- Superphosphate made in the rotary reactor at an acidulation ratio of 1.42, a reaction temperature of 285°F and an initial moisture content of 11.7 percent.
- Superphosphate made in the rotary reactor at an acidulation ratio of 1.42, a reaction temperature of 293°F and an initial moisture content of 11.7 percent.
- Superphosphate made in the two step autoclave process at an acidulation ratio of 1.42, a reaction temperature of 230°F and an initial moisture content of 8.26 percent.
- △ Superphosphate made in the single step autoclave process at an acidulation ratio of 1.62, a reaction temperature of 220°F and an initial moisture content of 13.3 percent.

Increasing the acidulation ratio increased the degree of conversion to available forms, as would be expected. The degree of conversion to both available P_2O_5 and citrate soluble P_2O_5 was higher for the lower temperature levels and larger initial moisture contents as shown in Figs. 8 and 9.

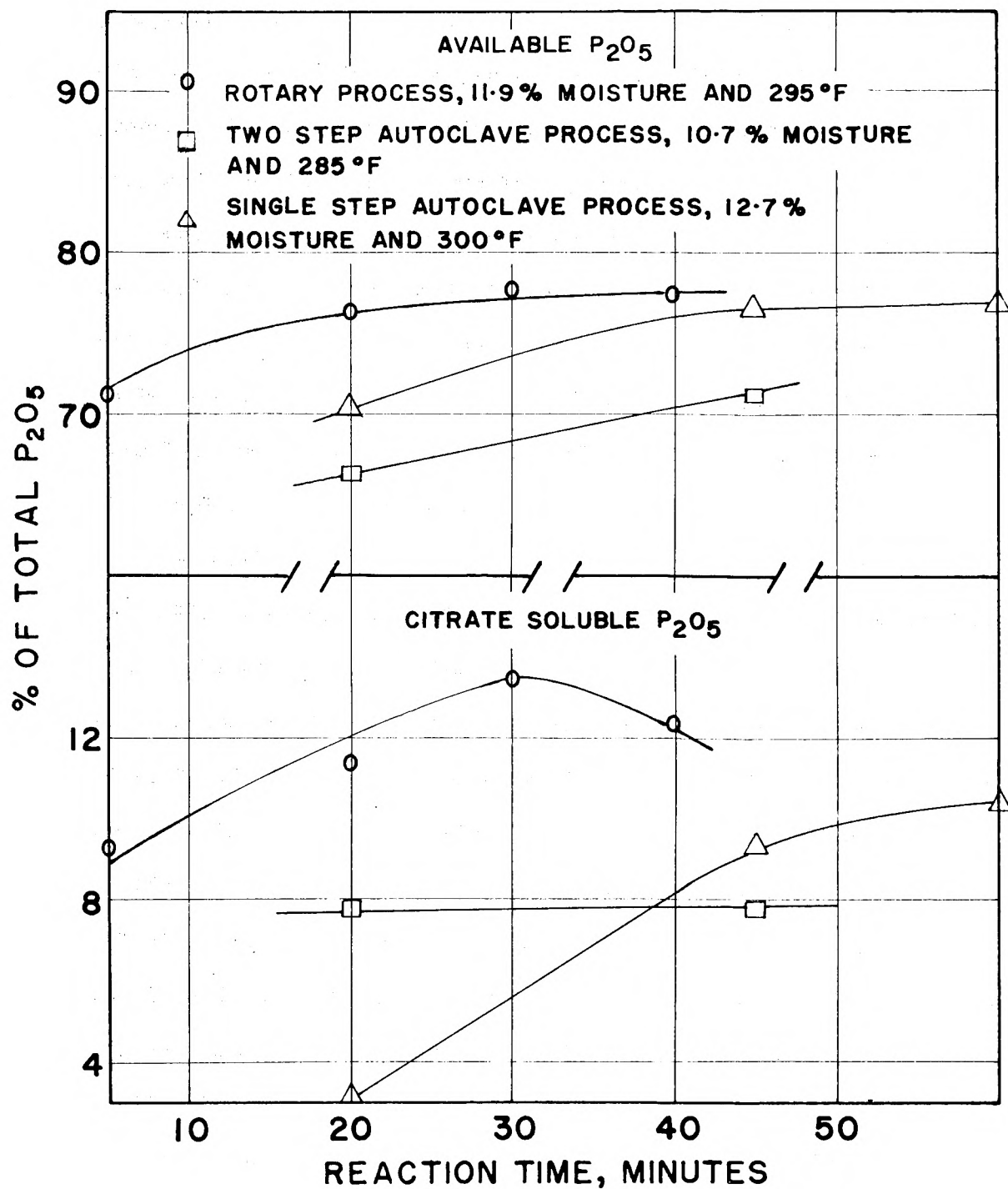


Fig. 6. Effect of reaction time on the conversion of phosphate to available forms for superphosphates made at an acidulation ratio of 1.42.

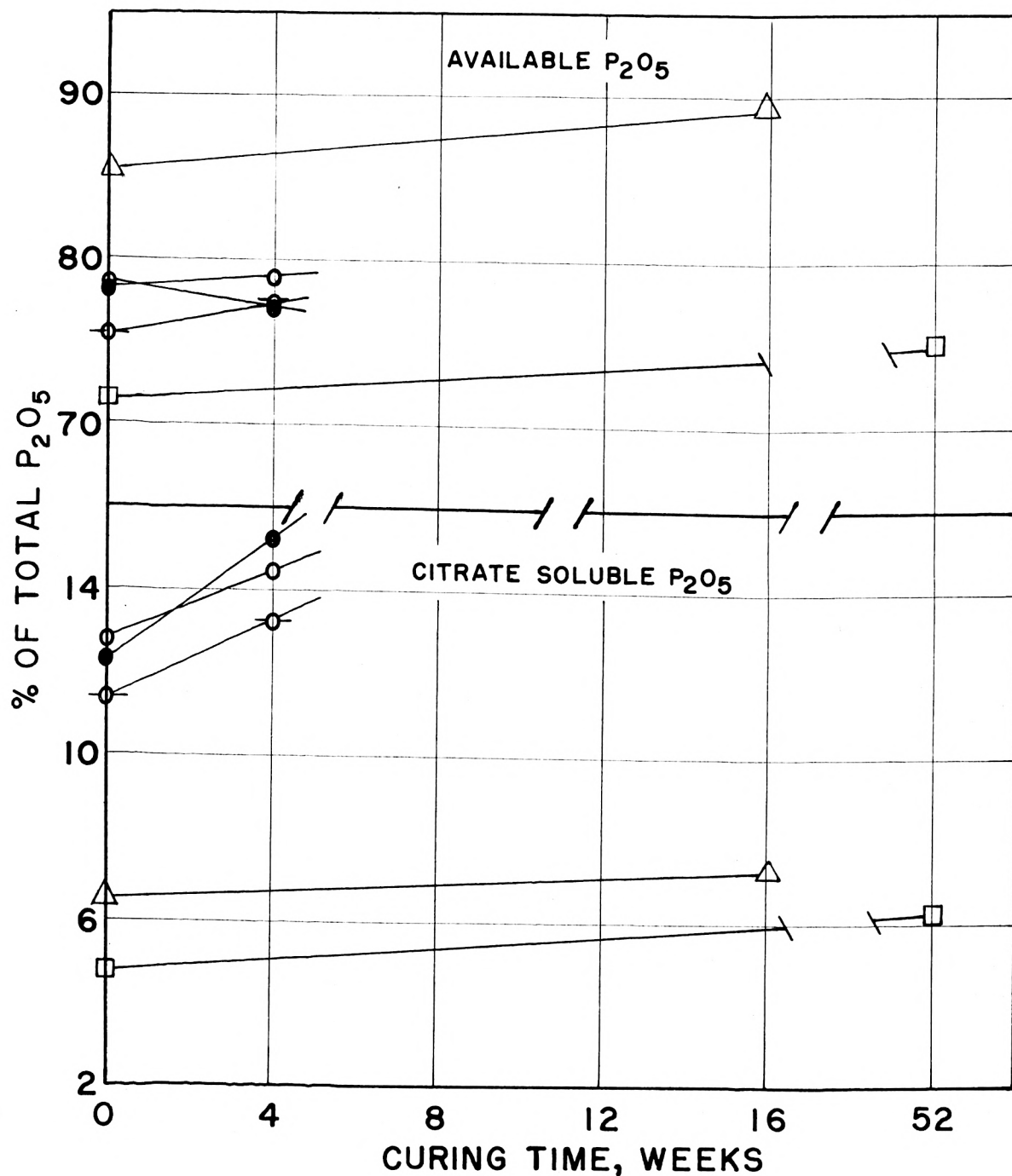


Fig. 7. Effect of curing time on the conversion of phosphate to available forms for superphosphate.

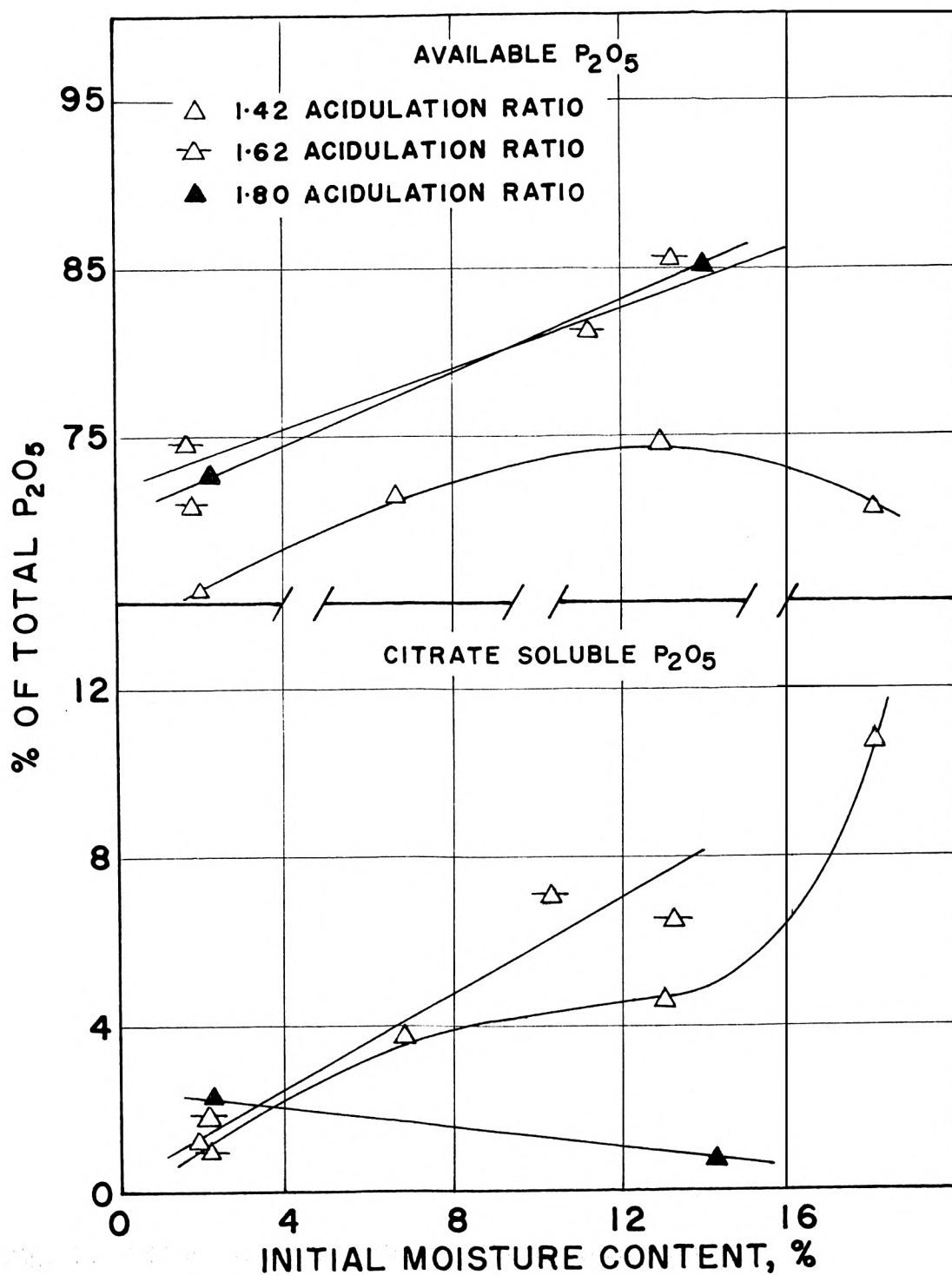


Fig. 8. Effect of acidulation ratio on the conversion of phosphate to available forms for superphosphates made by the single step autoclave process at a temperature of 220°F.

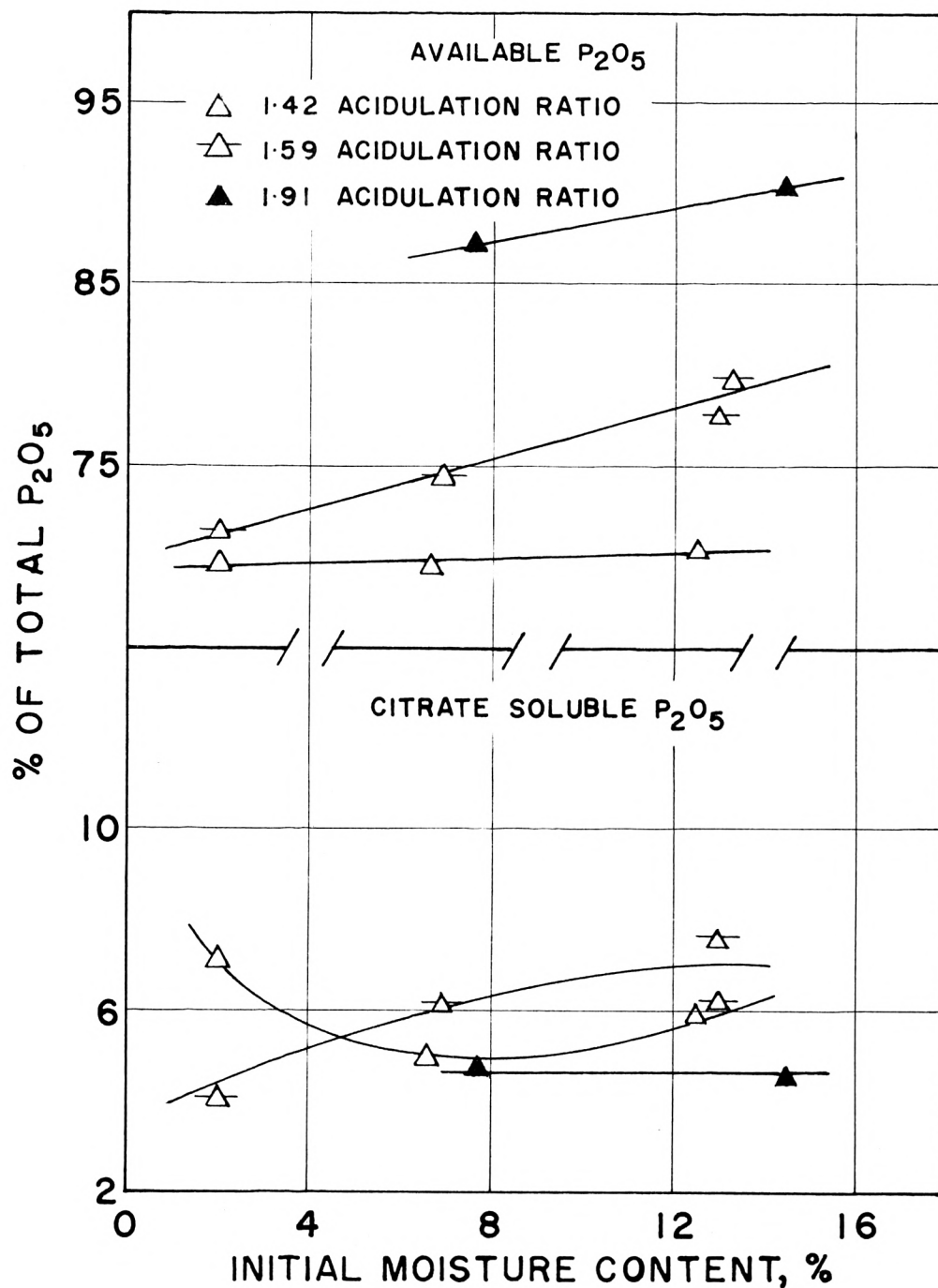


Fig. 9. Effect of acidulation ratio on the conversion of phosphate to available forms for superphosphates made by the single step autoclave process at a temperature of 300°F.

A considerable portion of insoluble P_2O_5 was present, but this is a normal condition due to the fact that all of the free (sulfuric) acid does not react at once. Generally, for the higher acidulation ratios, a curing time of two to four weeks was needed to complete the reaction. At 300°F, the formation of dicalcium phosphate was not enhanced by higher acidulation ratios as was expected from the equilibrium conditions. However, at 220°F a favorable condition for the formation of dicalcium phosphate existed for acidulation ratios as high as 1.62.

The effect of re-autoclaving was to increase considerably the formation of dicalcium phosphate. As shown in Table 12 and Fig. 10, the amount of dicalcium phosphate, or citrate soluble P_2O_5 , was almost tripled in each trial. Three runs at the nine percent initial moisture content level were made at 230°, 275°, and 285°F. Since the water soluble P_2O_5 , or monocalcium phosphate, decreased as well as the tricalcium phosphate, it appears that the hydrolysis reaction was accelerated. The product moistures are also given with the chemical analysis. It would appear that several autoclaving steps in sequence would have a more favorable effect than an extended period of one autoclaving. The increase in total available P_2O_5 varied from 0.1 to 4.1 percent at 230° and 285°F, respectively. The increase in dicalcium phosphate or citrate soluble P_2O_5 varied from 3.1 to 18.75 percent corresponding to 230° and 285°F, respectively.

Hydrochloric acid was added to the phosphate rock-sulfuric acid mixture before autoclaving so that the mixture of acids gave an acidulation ratio corresponding to 1.55. Two series of three runs were made at a moisture content of 12.2 percent and at reaction temperatures of 220°, 260°, and 300°F. One series of samples was autoclaved using

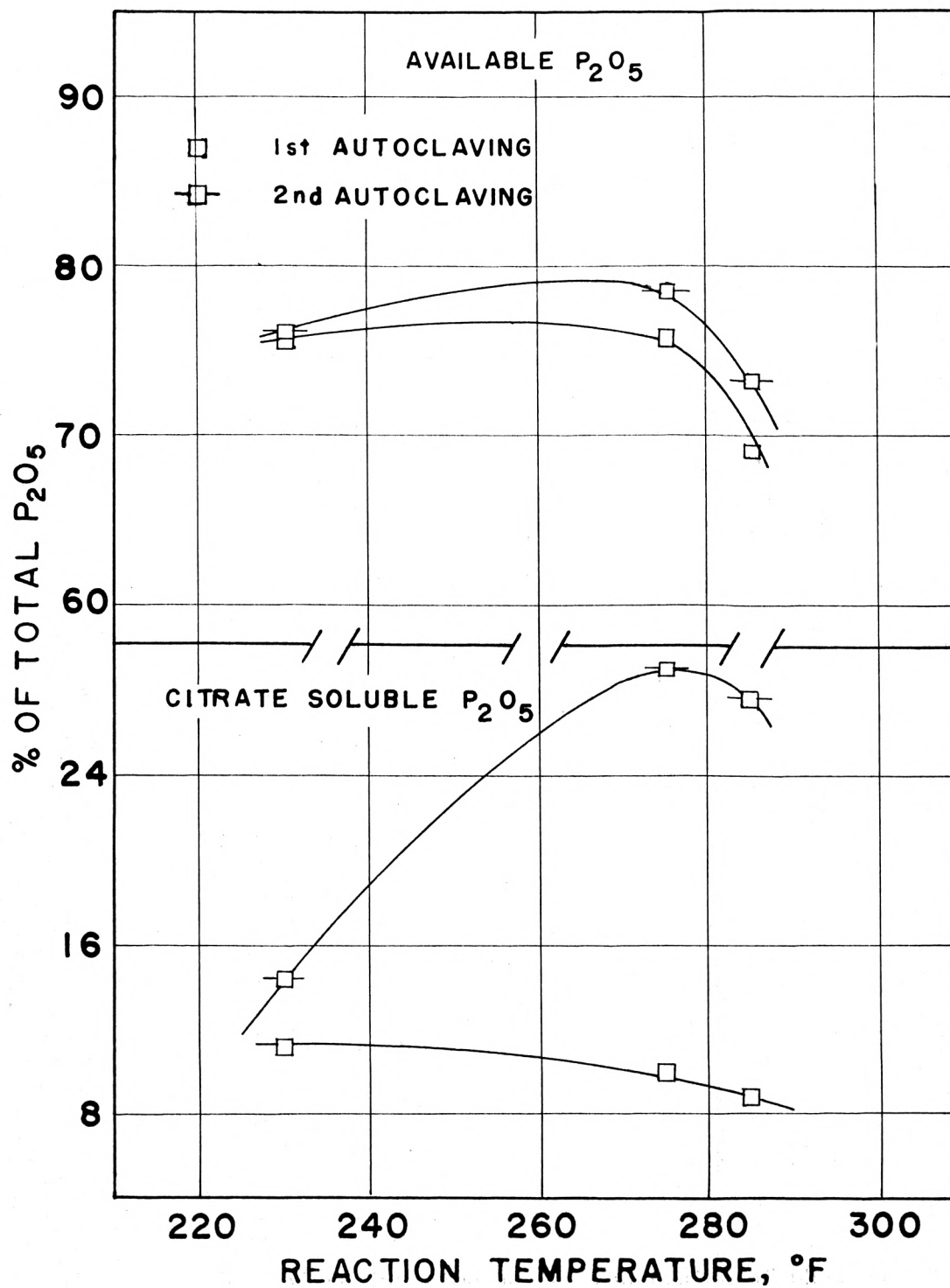


Fig. 10. Effect of re-autoclaving on the conversion of phosphate to available forms for superphosphates made by the two step autoclave process at an initial moisture of 9%.

only sulfuric acid and an acidulation ratio of 1.42. Each of the three runs made with the hydrochloric-sulfuric acid mixture gave an increase in the formation of dicalcium phosphate as well as an increase in the total available P_2O_5 , as the data in Fig. 11 shows.

Comparing the runs made with hydrochloric acid and samples made at an acidulation ratio of 1.59 showed that the total available P_2O_5 contents are similar but that conversion to dicalcium phosphate was greater when hydrochloric acid was added. At a reaction temperature of 220°F (13 percent moisture), adding hydrochloric acid gave a conversion to available P_2O_5 of 82.5 percent and a conversion to citrate soluble P_2O_5 of 9.58 percent which corresponded to 85.5 percent and 6.52 percent conversion to total available and citrate soluble P_2O_5 , respectively, in superphosphates made at an acidulation ratio of 1.59. When a reaction temperature of 300°F (13 percent moisture) was used, adding hydrochloric acid gave a conversion to available P_2O_5 of 74.5 percent and a conversion to citrate soluble P_2O_5 of 11.2 percent which corresponded to a conversion of 79.9 percent and 7.05 percent to total available and citrate soluble P_2O_5 , respectively, in superphosphates made at an acidulation ratio of 1.59.

Chemically pure monocalcium phosphate monohydrate and tricalcium phosphate were reacted at atmospheric pressure and 185°F for 24 hours. A mixture of these reagents was also reacted for 30 minutes at 214° and 286°F at 15 and 23 pounds per square inch gauge, respectively. In all these cases almost complete conversion to available forms of phosphate were obtained. The conversion to available P_2O_5 was 99.8 percent except in the case of the reaction at 286°F which gave a conversion of 96.9 percent. The theoretical P_2O_5 content of the mixture was calculated to

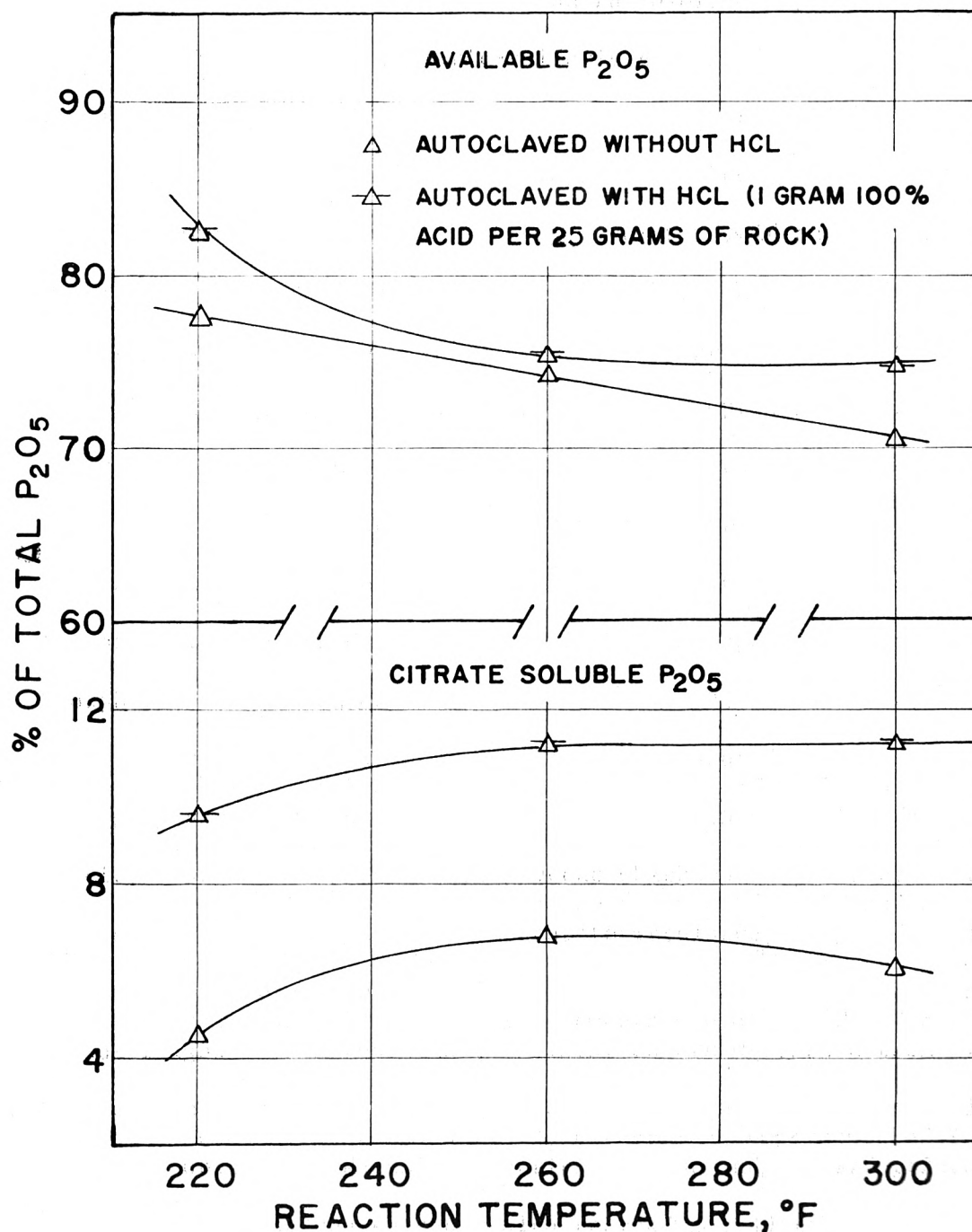


Fig. 11. Effect of addition of HCl on the conversion of phosphate to available forms for superphosphates made by the single step autoclave process at an initial moisture of 12.5% and an acidulation ratio of 1.42 (based on sulfuric acid used).

be 53 percent which agreed closely with the analysis of the products.

If the hydrolysis of monocalcium phosphate monohydrate were complete, the theoretical citrate soluble P_2O_5 content would have been 20 percent while the analyses gave values of 26.74 to 28.17 percent. These figures indicate that a small amount of the monocalcium phosphate monohydrate is converted to dicalcium phosphate or other citrate soluble forms. These data also indicated that, in the absence of inert material and competing reactions, the hydrolysis of monocalcium phosphate is easily attained.

CONCLUSIONS

The original purpose in continuing the investigation, which was to develop a suitable method for making superphosphate using a deficiency of sulfuric acid, still appears to be a valid goal. However, the two step autoclave process, which was based on the work done by Feng, did not give comparable conversions to total available P_2O_5 and citrate soluble P_2O_5 that were obtained by that investigator. Feng reported a maximum conversion to dicalcium phosphate of 81.3 percent compared to 15.58 percent obtained using the two step autoclave process. The results indicate that the conditions under which the partial acidulation step is performed is critical to this process.

The results of the three methods investigated indicate that the rotary process has the most value as a potential commercial process. This process has the advantage of requiring a single operation in charging the autoclave and should be easily adaptable to continuous operation. Since mechanical agitation is necessary, a rotating shell with a fixed agitator has some advantage. Also, the product from the

rotary process was in the form of moist spherical lumps which could be further processed easily to make a dry granular material. This type of product has considerable commercial advantage.

Since the hydrolysis of monocalcium phosphate was almost complete when reagent grade monocalcium phosphate monohydrate and tricalcium phosphate were reacted in the absence of phosphate rock and sulfuric acid, it appears that the presence of calcium sulphate in the products from the acidulation of phosphate rock with sulfuric acid may be the cause of the poor conversions found. It is possible that thin layers of calcium sulphate precipitated onto the surface of the rock particles and made them impervious to further action of mineral acids.

Two possible areas of investigation are suggested. First, the effect of the addition, before autoclaving, of surface active agents which will enhance the solid-liquid reaction and increase the penetrating ability of the acid, should be studied. Second, the effect of various mixing or stirring methods should be investigated to determine a device which will break up the layer of inert material thereby increasing the conversion.

Since the interrelation of the moisture content and reaction temperature was such that the maximum conversion was shifted to lower temperatures as the moisture content was decreased, an improvement in the mechanical apparatus is suggested. The rotary reactor should be made, as a continuous unit, so that the material passes through three or more reaction zones. These reaction zones could be maintained at successively lower temperatures to give the maximum conversion as the moisture content of the reaction mass is continuously decreased.

Although no economic study was made, it appears that the conversion should be approximately 95 percent to overcome the cost of operation of pressure equipment in order to compete with existing commercial operations which manufacture normal superphosphates and similar products. The results obtained were not sufficient to determine if these conditions are possible, but they do indicate further investigation is worthwhile.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. William H. Honstead for his assistance and guidance in carrying out this study.

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THE PRODUCTION OF PHOSPHATE FERTILIZERS WITH A DEFICIENCY OF
SULFURIC ACID

by

RAYMOND CHARLES RICHARDSON

B. S., University of Colorado, 1954

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

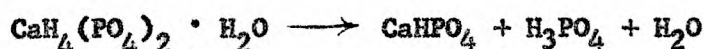
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1958

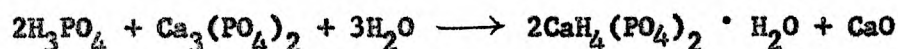
Sulfuric acid was reacted with the mineral apatite to convert the phosphate in the apatite into forms which were available to plants. Monocalcium phosphate, which is water soluble, and dicalcium phosphate, which is soluble in neutral ammonium citrate solutions, are considered to be available. The mineral apatite and sulfuric acid were reacted under pressure and at moderate temperatures that would favor the following reaction:



The amount of acid required to produce this phosphate would be only about 75 percent of that necessary to produce normal superphosphate, based on the total P_2O_5 content of the phosphate rock. In the commercial manufacture of normal superphosphate, the reaction of sulfuric acid on the phosphate in mineral apatite gives almost entirely monocalcium phosphate monohydrate. A large portion of the dicalcium phosphate formed by these processes was the result of the hydrolysis of monocalcium phosphate monohydrate according to the reaction:



The phosphoric acid liberated as a result of this reaction was then free to react further with the phosphate in the apatite to give monocalcium phosphate by the following reaction:



The proposed reactions appeared to be thermodynamically feasible, as indicated by the free energy calculations. The equilibrium system, $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$, was also investigated.

Three processes, a rotary process, a two step autoclave process, and a single step autoclave process were used to produce a superphosphate which would contain substantial amounts of dicalcium phosphate. A mixture of phosphate rock and sulfuric acid, corresponding to an acidulation ratio of 1.42, which contained 0.64 to 18 percent moisture was autoclaved for periods of 5 to 60 minutes under its own pressure using reaction temperatures of 213° to 310°F. The effect of curing time on the conversion to dicalcium phosphate was also investigated. The single step process was also used to determine the effect of autoclaving phosphate rock-sulfuric acid mixtures using higher acidulation ratios (1.59 to 1.91) and to determine the effect of the addition of a small amount of hydrochloric acid (equivalent to an acidulation ratio of 1.55) on the conversion to dicalcium phosphate. The effect of re-autoclaving on the conversion to dicalcium phosphate was investigated using the two step autoclave process.

The conversion to dicalcium phosphate in superphosphates made by the three processes did not compare favorably with those obtained by several other investigators. The results indicate that the conditions under which the partial acidulation step in the two step autoclave process is performed is critical to this process. The maximum conversion was obtained using the two step autoclave process and re-autoclaving the first product. The material was re-autoclaved under the same initial conditions using a moisture content of 6.6 percent and a reaction temperature of 300°F to give a conversion to dicalcium phosphate of 38.7 percent, or a citrate soluble P_2O_5 content of 9.78 percent. The conversion to total available P_2O_5 was 71.7 percent, or a total available P_2O_5 content of 18.11 percent.

For a single autoclaving, the rotary process gave consistently higher conversions for both total available and citrate soluble P_2O_5 . The maximum conversion to dicalcium phosphate, 13.42 percent, was obtained at a reaction temperature of 278°F and an initial moisture content of 11.7 percent. These reaction conditions also gave the highest conversion to available P_2O_5 , 78.7 percent.

The results of the three methods investigated indicated that the rotary process had the most value as a potential commercial process. In addition to easy operation it has the advantage of being adaptable to continuous operation. The product from this process was of such condition that it could be easily processed further to give a dry granular material, which would make it commercially attractive. A suggested mechanical improvement in this method was a modification to a continuous unit which should be so constructed that the material passes through three or more reaction zones at successively lower temperatures to give maximum conversion as the moisture of the reaction mass is continuously decreased.

The effect of addition, before autoclaving, of surface active agents which will benefit the solid-liquid reaction should be investigated. A conversion of approximately 95 percent is necessary to make the process commercially attractive.