THE PRODUCTION OF DI-CALCIUM PHOSPHATE BY THE DIRECT
ACIDULATION OF PHOSPHATE ROCK

by

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TABLE OF CONTENTS

INTRODUCTION

The great bulk of superphosphate fertilizer is manufactured today by acidulating phosphate rock with sulfuric acid. The purpose of acidulating phosphate rock is to convert the phosphate in the mineral, apatite, into forms which are available to plants. Both mono-calcium phosphate and di-calcium phosphate are considered to be available. When phosphate rock is treated with sufficient sulfuric acid, mono-calcium phosphate is formed. However, if less sulfuric acid is added, mono-calcium phosphate and undecomposed phosphate rock result.

Were it possible to conduct the acidulation of phosphate rock in such a manner that di-calcium phosphate would be produced instead of mono-calcium phosphate, less sulfuric acid would be required. Beside this economy of acidulating agent, another advantage would be the production of a neutral and highly desirable fertilizer. Forecasts of greatly increased needs for fertilizers coupled with depletion of sulfur reserves have resulted in an active interest in new processes that require less sulfuric acid.

The main object of the present investigation was to find a method of acidulating phosphate rock which would produce primarily di-calcium phosphate and therefore use less acid.

Phosphate rock consists of the mineral, apatite, $Ca_{10}F_2(PO_4)_6$, plus impurities, hence the sulfuric acid added not only acts upon the phosphate of lime but upon calcium fluoride tied up in the apatite molecule and directly or indirectly upon such impurities as organic matter, iron and aluminum compounds, and carbonates of

lime and magnesium, all of which consume a certain amount of acid.

During acidulation the apatite molecule is broken down, and for the purpose of this research a series of reactions between H_2SO_4, $Ca_3(PO_4)_2$, and CaF_2 may be considered to occur. Tri-calcium phosphate treated with sulfuric acid is converted into a mixture of calcium sulfate and hydrated mono-calcium phosphate. These two compounds are the chief constituents of ordinary superphosphate. The reaction may be represented as follows:

$$Ca_3(PO)_2 + 2H_2SO_4 + H_2O \longrightarrow 2CaSO_4 + CaH_4(PO_4)_2 \cdot H_2O$$

Superphosphate made with sulfuric acid of 70 per cent concentration appears to be a more or less self-drying product. The heat of reaction is sufficient to drive off most of the excess water; however, it is generally believed that a considerable quantity of water remains combined as water of hydration.

Both temperature and acid concentration have an important effect on the form of calcium sulfate in superphosphate. Low temperature and dilute acid favor the formation of gypsum ($CaSO_4 \cdot 2H_2O$) but in the acid concentration range from 65 to 75 per cent H_2SO_4, where the heat of reaction is not dissipated by artificial cooling, the water of hydration is driven off, so that anhydrite ($CaSO_4$) is the form of calcium sulfate in the final product.

If less sulfuric acid is added to the phosphate rock than that required, instead of the formation of dicalcium phosphate, a mixture of mono-calcium phosphate and tri-calcium phosphate is obtained. The purpose of this research was to find a method of producing di-calcium phosphate by a reaction such as the following:

$$Ca_3(PO_4)_2 + H_2SO_4 + 2H_2O \longrightarrow CaSO_4 + 2CaHPO_4 \cdot 2H_2O$$
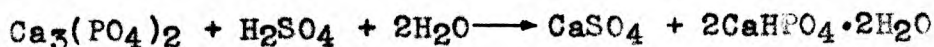
This reaction is very difficult to attain. The final product nearly always consists of a mixture of water-soluble mono-calcium phosphate and residual or undecomposed phosphate rock. Mono-calcium phosphate has rather weak acidic properties and does not readily react with fluoraptite. Hence phosphate rock so treated always contains a high percentage of undecomposed phosphate rock even after it has stood for a long time.

Calcium fluoride, which is present in phosphate rock, combined with tri-calcium phosphate in the apatite molecule, $Ca_{10}F_2(PO_4)_6$, reacts with sulfuric acid thus:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

The hydrofluoric acid, HF, reacts with the silica present in the rock thus:

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$

The silicon tetrafluoride is decomposed by water to form silica and hydrofluosilicate, thus:

$$3SiF_4 + 2H_2O \longrightarrow SiO_2 + 2H_2SiF_6$$
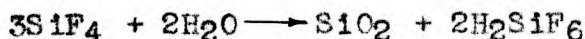
When sulfuric acid containing only 70 per cent H_2SO_4 is used to decompose phosphate rock, only about 25 per cent of the fluorine is evolved, the balance remaining in the superphosphate.

The reaction between sulfuric acid and the iron contained in phosphate rock is not known, but the iron is probably distributed between the sulfate and the phosphate. The reaction may be represented as follows:

$$2FePO_4 + 3H_2SO_4 + H_2O \longrightarrow Fe_2(SO_4)_3 + 2H_3PO_4$$
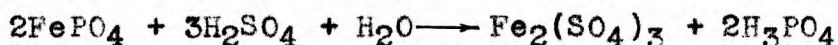
This reaction is more or less reversible and in the presence of water hydrated iron phosphate is formed thus:

$$Fe_2(SO_4)_3 + 2H_3PO_4 + 4H_2O \longrightarrow 2FePO_4 \cdot 2H_2O + 3H_2SO_4$$
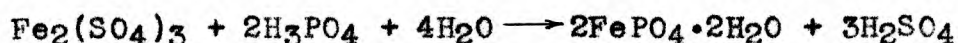
Hydrated iron phosphate may be converted into the anhydrous, and even less soluble, condition by reacting with anhydrous calcium sulfate, the latter compound being converted into gypsum as follows:

$$FePO_4 \cdot 2H_2O + CaSO_4 \longrightarrow CaSO_4 \cdot 2H_2O + FePO_4$$

The reaction between sulfuric acid and aluminum in phosphate rock is similar to that of iron.

Sulfuric acid acts upon calcium or magnesium carbonate to form magnesium sulfate or calcium sulfate, water and carbon dioxide.

$$H_2SO_4 + MgCO_3 \longrightarrow MgSO_4 + CO_2 + H_2O$$

$$H_2SO_4 + CaCO_3 \longrightarrow CaCO_4 + CO_2 + H_2O$$
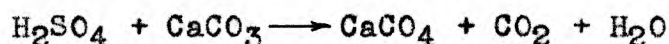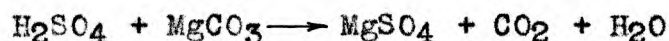
From the value of the free energy change for any reaction the chemical equilibrium constant and therefore the thermodynamic feasibility of the reaction can be computed. The reaction becomes more promising as the value of the free energy change becomes more negative. The reaction becomes less favorable if the free energy change is positive. When it is larger than 10 kilocalories at 25° C., the reaction is very unfavorable. Because of the lack of necessary thermodynamic data, the value of the free energy change for the acidulation of phosphate rock at any given temperature is impossible to compute. The value of the free energy change under standard conditions of temperature and pressure
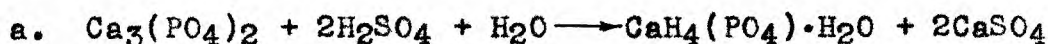
is a good measure of the thermodynamic feasibility, however, and will be computed in the following.

The thermodynamic properties of tri-calcium phosphate, mono-calcium phosphate, di-calcium phosphate and other compounds are summarized in Table 1, which is taken from Latimer (7).

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

Compound	Form	ΔH^o_f Kcal./g-mole	ΔF^o_f Kcal./g-mole	ΔS^o_f Entropy units
$Ca_3(PO_4)_2$	Crystalline	-929.7	-932	57.6
$Ca(H_2PO_4)_2$	Crystalline Precipitated	-744.4	-672	45.3
$Ca(H_2PO_4)_2H_2O$	Crystalline	-821.49	-733.52	49.7
$CaHPO_4$	Crystalline	-434.70	-403.14	28.0
$CaHPO_4 \cdot 2H_2O$	Crystalline	-575.72	-516.52	46.7
H_3PO_4	Aqua	-308.2	-274.2	42.1
H_2SO_4	Aqua	-216.90	-177.34	4.1
$CaSO_4 \cdot 2H_2O$	Crystalline	-483.06	-429.19	46.36
$CaSO_4$	Crystalline Anhydrite	-342.42	-315.56	25.5
H_2O	Liquid	- 68.32	- 56.69	16.92

The free energy changes at standard conditions, ΔF^o, for the reactions of most interest in the acidulation of phosphate rock are computed as follows:

a. $Ca_3(PO_4)_2 + 2H_2SO_4 + H_2O \longrightarrow CaH_4(PO_4) \cdot H_2O + 2CaSO_4$

$\Delta F^o = (-733.52) + 2(-315.6) - (-932) - 2(-177.34) - (-56.69) = -21.37$ Kcal.

b. $Ca_3(PO_4)_2 + 2H_2SO_4 + 5H_2O \longrightarrow CaH_4(PO_4)_2 \cdot H_2O + 2CaSO_4 \cdot 2H_2O$

$\Delta F^o = (-733.52) + 2(-429.19) - (-932) - 2(-177.34) - 5(-56.69) = -21.77$ Kcal.

c. $Ca_3(PO_4)_2 + H_2SO_4 + 4H_2O \longrightarrow 2CaHPO_4 \cdot 2H_2O + CaSO_4$
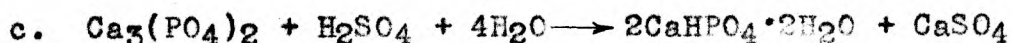
$\Delta F^O = 2(-516.52) + (-315.56) - (-932) - (-177.34) - 4(-56.69) = -12.5$ Kcal.

d. $Ca_3(PO_4)_2 + H_2SO_4 + 6H_2O \longrightarrow 2CaHPO_4 \cdot 2H_2O + CaSO_4 \cdot 2H_2O$
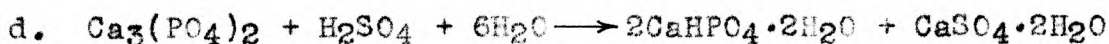
$\Delta F^O = 2(-516.52) + (-429.19) - (-932) - (-177.34) - 6(-56.69) = -12.7$ Kcal.

e. $CaH_4(PO_4) \cdot H_2O + H_2O \longrightarrow CaHPO_4 \cdot 2H_2O + H_3PO_4$
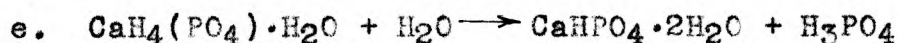
$\Delta F^O = (-516.52) + (-274.2) - (-733.52) - (-56.69)$
$= -0.51$ Kcal.

f. $CaH_4(PO_4) + 2H_2O \longrightarrow CaHPO_4 \cdot 2H_2O + H_3PO_4$
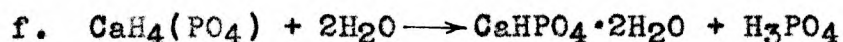
$\Delta F^O = (-516.52) + (-274.2) - (-672) - 2(-56.69)$
$= -5.34$ Kcal.

g. $CaH_4(PO_4)_2 \longrightarrow CaHPO_4 + H_3PO_4$

$\Delta F^O = (-403.14) + (-274.2) - (-672)$
$= -5.34$ Kcal.

h. $Ca(H_2PO_4)_2 \cdot H_2O + xH_2O \longrightarrow CaHPO_4 + H_3PO_4 + (x + 1) H_2O$
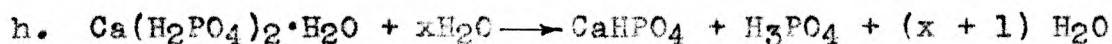
$\Delta F^O = (-403.14) + (-274.2) + (-56.69) - (-733.52)$
$= -0.51$ Kcal.

Since all of the standard free energy changes are negative, all of the reactions are thermodynamically possible. Actually, only reactions (a) and (b) have been attained in acidulating phosphate rock. The reaction (c) appears feasible but the final product of the reaction of sulfuric acid with phosphate rock nearly always consists of a mixture of mono-calcium phosphate and undecomposed phosphate rock.

According to Elmore and Farr (3), mono-calcium phosphate

hydrolyzes according to the equation:

$$CaH_4(PO_4)_2 + xH_2O \longrightarrow CaHPO_4 + H_3PO_4 + (x + 1) H_2O$$
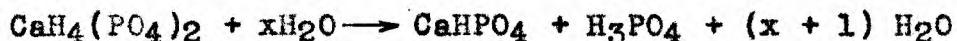
The extent to which mono-calcium phosphate is converted to di-calcium phosphate depends on the amount of water in the system. The optimum ratio of the reactants and the maximum conversion to di-calcium phosphate at four temperatures are given in Table 2 from the work of the above authors.

Table 2. Maximum conversion from mono-calcium phosphate mono-hydrate to di-calcium phosphate.

Temperature $^\circ$ C.	Reactants, $g.H_2O/100$ g. $Ca(H_2PO_4)_2 \cdot H_2O$	Per cent of $Ca(H_2PO_4)_2 \cdot H_2O$ converted to $CaHPO_4$
25	98	57
50.7	62	68
75	42	74
100	28	79

It is obvious that increasing the temperature will increase the conversion from $Ca(H_2PO_4)_2 \cdot H_2O$ to $CaHPO_4$. At temperatures above 108° C., which is its decomposition temperature, mono-calcium phosphate mono-hydrate cannot exist, and will be converted to mono-calcium phosphate anhydride.

From the above it appears that it should be possible to heat mono-calcium phosphate to a certain range of temperature, where the mono-calcium phosphate would decompose to di-calcium phosphate and phosphoric acid according to the following reaction.

$$CaH_4(PO_4)_2 \cdot H_2O \longrightarrow CaHPO_4 + H_3PO_4 + H_2O$$
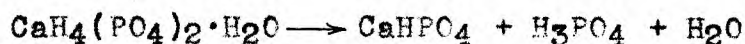
The liberated phosphoric acid could be reused to acidulate unde-

composed phosphate rock according to the following reaction:

$$Ca_3(PO_4)_2 + 4H_3PO_4 + 3H_2O \longrightarrow 3CaH_4(PO_4)_2 \cdot H_2O$$
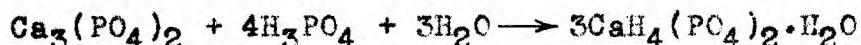
The final result of these two reactions is the complete conversion of a partially acidulated rock to di-calcium phosphate.
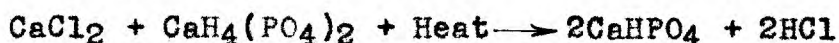
Analytical procedures of the Association of Official Agricultural Chemists were used for all analyses. The methods are described in detail in the Appendix.

LITERATURE REVIEW

Newberry and Barret (9) treated phosphate rock with a mixture of sulfuric acid and hydrochloric acid sufficient to form monocalcium phosphate. The calcium sulfate and insoluble residue from the acid solution was separated by filtration. The filtrate was evaporated to dryness and the dried product heated sufficiently high to drive off hydrochloric acid and convert the soluble salt into di-calcium phosphate. The hydrochloric acid was collected to be reused. The reactions in a simplified form are:

$$Ca_3(PO_4)_2 + H_2SO_4 + HCl \longrightarrow CaSO_4 + CaCl_2 + CaH_4PO_4$$

$$CaCl_2 + CaH_4(PO_4)_2 + Heat \longrightarrow 2CaHPO_4 + 2HCl$$

Theoretically, this process appears to have considerable merit, since only one-half as much sulfuric acid is required as that employed in manufacturing water soluble phosphate. In actual practice, however, the method has certain objectionable features. Unless the temperature at which hydrochloric acid is evolved is carefully controlled, highly insoluble calcium pyrophosphate is

formed, yet the dried mass must be sufficiently heated, otherwise
a certain amount of calcium chloride will remain in the residue,
rendering it hygroscopic and unfit for fertilizer use.

Pike (10) proposed to accidulate calcium phosphate rock sus-
pended in water with hydrochloric acid until the P_2O_5 is complete-
ly converted into phosphoric acid. The acid solution is then
treated with finely ground limestone to produce a solution of
mono-calcium phosphate and calcium chloride. An amount of milk
of lime is then added just sufficient to precipitate the P_2O_5 as
di-calcium phosphate which is separated from the solution by fil-
tration.

Fox and Clark (4) proposed a process somewhat similar to
Newberry and Barret consisting of, first, producing calcium mono-
chlorophosphate ($CaClH_2PO_4 \cdot H_2O$), then decomposing this compound
with steam at a temperature of 200 to 400° C. according to the
following equation:

$$CaClH_2PO_4 \cdot H_2O + Steam \longrightarrow CaHPO_4 + HCl + H_2O$$
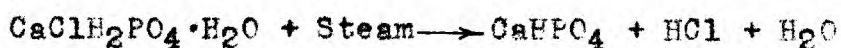
They claim that, under these conditions, no pyrophosphate is pro-
duced. The hydrochloric acid can be completely recovered and
used to decompose further quantities of phosphate rock.

Zbornik (12) proposed a process for converting the bulk of
the P_2O_5 of phosphate rock into di-calcium phosphate by treating
it with approximately one-half of the phosphoric acid normally re-
quired. The phosphoric acid and phosphate rock were mixed in an
autoclave under a pressure of more than 25 pounds per square
inch.

Seyfried (11) proposed to pass waste HCl gas through a column

of unground phosphate rock over which water is sprayed. Phosphoric acid, mono-calcium phosphate, and calcium chloride is continually withdrawn from the base of the tower as fresh rock is fed into the top. The acid solution then is partially neutralized with lime in a separate chamber to produce di-calcium phosphate.

Curtis (2) proposed to produce di-calcium phosphate from phosphoric acid. This process consists of adding coarsely ground lime to the acid until it is converted into a solution of mono-calcium phosphate, then mixing the solution with a slurry of very finely ground limestone to effect the conversion of mono-calcium phosphate into di-calcium phosphate.

Hughes and Cameron (5) proposed a process for producing di-calcium phosphate through the medium of sulfur dioxide and sulfurous acid at 25 to 100° C. at a pressure from 3 to 10 atmospheres.

Bogue (1) proposed a three-step process for the manufacture of di-calcium phosphate from bone and sulfur dioxide. In the first step, a saturated solution of sulfur dioxide is added to the crushed bone in a closed container, maintaining the acidity sufficiently high to keep the mineral matter in solution as mono-calcium phosphate and calcium acid sulfite. In the second step, the decanted solution is treated with steam. This results in the precipitation of a mixture of di-calcium phosphate and normal calcium sulfite with the regeneration of part of the sulfur dioxide. In the third step, the remaining sulfur dioxide is recovered by treating the mixed precipitate with sufficient hydrochloric acid to convert the calcium sulfite into calcium chloride.

Elmore and Farr (3) have studied the equilibrium in the system calcium oxide, phosphorous pentoxide and water. The solubilities of $CaHPO_4$, $Ca(H_2PO_4)_2 \cdot H_2O$ and $Ca(H_2PO_4)_2$ in 2-98 per cent H_3PO_4 at 40° C., 75° C. and 100° C., and 27.5-98 per cent H_3PO_4 at 25° C. were determined. The density of the saturated solution were determined. Di-calcium phosphate is the stable solid in equilibrium with 2-27 per cent acid at 25° C. and in 2-53 per cent acid at 100° C. $Ca(H_4PO_4)_2 \cdot H_2O$ is in equilibrium with 18-86 per cent H_3PO_4 at 25° C. and with 48-76.6 per cent H_3PO_4 at 100° C. $Ca(H_2PO_4)_2$ is the saturating solid in 86-98 per cent or 100 per cent acid at 100° C. The temperature coefficient of solubility is negative for di-calcium phosphate and positive for the other salts.

Memminger (8) states that, when phosphate rock is calcined at a high temperature, calcium carbonate is decomposed and the lime combines with free silica to form calcium silicate. In this way, the ratio of free lime to P_2O_5 may be decreased. Since the calcium silicate is not readily attacked by sulfuric acid, it will consume less sulfuric acid. The objection to the use of this material is that the partial sintering of the phosphate rock delays the action of the sulfuric acid during acidulation.

Iragne et al. (6) studied the effect of adding certain mineral salts on the precipitation of calcium phosphate. They claim that, in the production of phosphate fertilizers, the addition of mineral salts will permit the use of elevated pH (up to 9.5) without the formation of unavailable P_2O_5. Magnesium and aluminum salts were used.

MATERIALS

The phosphate rock used in this work was Florida land pebble containing 35.1 per cent phosphorus pentoxide (76.6 per cent bone phosphate of lime dry basis) and ground to 65.67 per cent through 100 mesh and 57.4 per cent through 200 mesh. The chemical and screen analyses of the rock used in this study are given in Table 3.

Table 3. Chemical and screen analysis of Florida land pebble phosphate rock.

Composition	Per cent	Screen analysis U. S. standard mesh	Per cent
P_2O_5	35.10		
CaO	49.64		
Fe_2O_3	0.86	+70	7.77
Al_2O_3	1.22	-70 + 100	16.66
F	4.12	-100 + 140	7.92
CO_2	1.48	-140 + 200	10.35
H_2O	0.95	-200	57.40

The sulfuric acid used was analytical reagent grade obtained from the Mallinckrodt Chemical Works. The sulfuric acid was diluted with distilled water from 95 per cent (65° Be) to 71.17 per cent (56° Be) and allowed to cool to room temperature before use. The metal salts were all analytical reagent grade also.
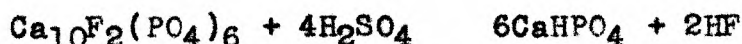
METHODS

Estimate of the Acid Required

The stoichimetric quantity of sulfuric acid needed to produce di-calcium phosphate from the Florida land-pebble phosphate rock described in Table 3 is computed below:

Basis: 100 grams phosphate rock weight per cent of P_2O_5 = grams P_2O_5

Weight of H_2SO_4 used for $CaHPO_4$:

$$Ca_{10}F_2(PO_4)_6 + 4H_2SO_4 \quad 6CaHPO_4 + 2HF$$

$$\frac{35.1 \times 4 \times 98}{142 \times 3} = 32.2 \text{ gm. of } H_2SO_4$$

Weight of CaO not in apatite:

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

Weight of H_2SO_4 used for excess CaO:

$$CaO + H_2SO_4 \quad CaSO_4 + H_2O$$

$$\frac{3.44}{56} \times 98 = 6.03 \text{ grams of } H_2SO_4$$

Weight of H_2SO_4 used for Fe_2O_3 and Al_2O_3

$$2FePO_4 + 3H_2SO_4 \quad Fe_2(SO_4)_3 + 2H_3PO_4$$

$$2AlPO_4 + 3H_2SO_4 \quad Al_2(SO_4)_3 + 2H_3PO_4$$
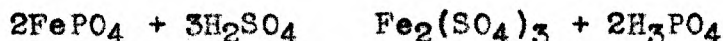
$$0.86 \times \frac{98 \times 3}{159.7} + 1.22 \times \frac{98 \times 3}{101.96} = 5.11 \text{ grams of } H_2SO_4$$

Total sulfuric acid required = 32.2 + 6.03 + 5.11

$$= 43.34 \text{ grams of } 100 \text{ per cent } H_2SO_4$$

Since there may be other materials present which would react with the sulfuric acid, this computation is only approximate. Therefore, a slight excess above the amount calculated was used. Forty-nine grams of acid were used for each 100 grams of rock.

Two approaches to the problem were made. In the first, the effect of the addition of metal salts before acidulation was investigated. The second was a process based on the work of Zbornik (12) in which phosphate rock was reacted with phosphoric acid in an autoclave at pressures greater than 25 pounds per square inch.

Addition of Mineral Salts

According to Iragne et al. (6), the addition of mineral salts permitted the use of elevated pH values up to 9.5 without the formation of unavailable P_2O_5 during the precipitation of calcium phosphates from phosphoric acid solutions. It seemed reasonable, therefore, that the addition of mineral salts might permit the formation of di-calcium phosphate during the acidulation of phosphate rock.

In this work, 85 ml of 71.2 per cent sulfuric acid (99 gms. of 100 per cent acid) and 4 grams of the mineral salt were placed in a 400 ml. beaker, then 200 grams of phosphate rock were added. The mass was stirred with a laboratory mixer for three minutes. The sample was then transferred to a pint fruit jar and cured at room temperature for one week. The sample was then ground, and analyzed for total P_2O_5, water soluble P_2O_5, citrate insoluble

P_2O_5, and moisture. The mineral salts used were K_2SO_4, $Al_2(SO_4)_3$, $Al_2(SO_4)_3 \cdot 18H_2O$, KCl, $MgSO_4$, KNO_3, $Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$. The results are shown in Table 4.

Autoclave Process

Description of Equipment. A small laboratory, agitated cast steel autoclave of two liters capacity was used. It was six inches in diameter and 12 inches in length, and was fitted with a cover which was held in place by ten one-inch bolts. Plate I shows the construction.

The diagram is a sectional one in which (a) represents a raised ring of steel on the underside of the cover. This fits into the groove in the top of the autoclave. The thermometer well (d) was screwed through the cover of the autoclave. The autoclave was heated by natural gas burned inside a cylindrical sheet metal case. The autoclave rested on a ring which supported the edge of the flange (g). The bottom of the autoclave was above the gas ring.

Plate I also shows the arrangement of the cover. The structure to bear the agitator shaft is shown by (b) passed through the center of the cover. The agitator blade was of the anchor type. The cover also was provided with a pressure gage and a gas escape valve. The agitator was driven at 30 rpm by a V-belt drive from a 1/2 hp. electric motor.

Table 4. Effect of mineral salts on the acidulation of phosphate rock.

Mineral salt	Blank	K_2SO_4	$Al_2(SO_4)_3$	$Al_2(SO_4)_3 \cdot 18H_2O$	KCl	$MgSO_4$	KNO_3	$Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$
Total P_2O_5, %	22.65	22.38	23.04	22.43	22.84	22.75	22.48	22.63
Water soluble P_2O_5, %	16.90	17.03	17.30	16.61	16.78	16.72	16.31	15.56
Citrate insoluble P_2O_5, %	4.85	4.47	4.68	4.56	4.88	4.92	5.09	3.88
Citrate soluble P_2O_5, %	0.90	0.88	1.06	1.26	1.18	1.11	1.08	3.19
Moisture %	6.52	7.10	4.95	7.55	7.08	6.93	6.32	7.28
Conversion[1] %	78.5	80.2	79.7	79.6	78.6	77.5	78.9	82.7

[1] Per cent of the total P_2O_5 present in available forms, i. e., as water soluble and citrate soluble P_2O_5.

EXPLANATION OF PLATE I

Drawing of autoclave

PLATE I

PULLEY

COVER OF
AUTOCLAVE

THERMOMETER WELL

$1\frac{1}{4}$

$6"$

$13\frac{1}{4}"$

AGITATOR
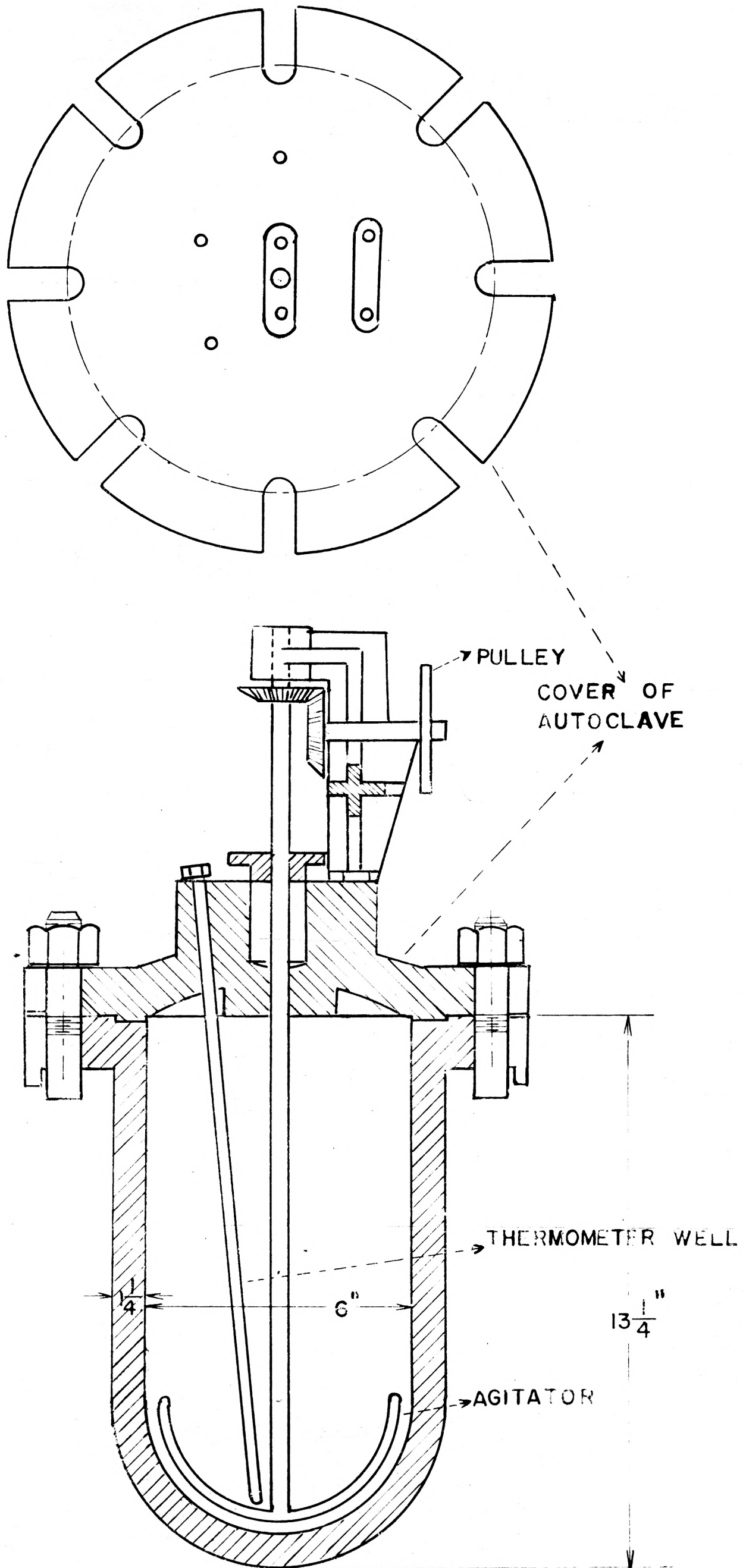
<u>Production of Partially Acidulated Rock</u>. Because of the difficulty of mixing the acid and the rock in the autoclave, the process was conducted in two steps. In the first step, the rock was reacted with the sulfuric acid in the autoclave, then removed, dried, and ground. In step two, this partially acidulated mass was further reacted in the autoclave under various conditions of temperature, pressure, particle size, and moisture content.

The procedure used in step one to produce the partially acidulated mass is as follows:

Four hundred grams of the Florida phosphate rock described in Table 3 and 170 cc of 71.2 per cent sulfuric acid were placed in the autoclave. The pressure was maintained at atmospheric, while the temperature rose to 90° C. As a result of the poor mixing attained in the autoclave, the reaction did not go to completion so that the product contained much free acid and was sticky and difficult to handle. The product was, therefore, dried at 80° C. for 24 hours before use. Each batch was then ground to pass a 40-mesh screen. Four batches of partially acidulated rock were made by this process. These four batches were combined and used for the experimental work in step two. The analysis of the combined batches is given in Table 5.

In addition, one more batch of partially acidulated rock was produced and used for the investigation of the effect of particle size and of mixing time. This was not analyzed, but was assumed to be similar to the first lot in composition.

Table 5. Chemical analysis of partially acidulated rock.

Moisture, %	1.65
Total P_2O_5, %	23.12
Citrate insoluble P_2O_5, %	5.26
Water soluble P_2O_5, %	13.82
Citrate soluble P_2O_5, %	4.04
Conversion[1], %	77.1

[1] The per cent of the total P_2O_5 present in available forms, i. e., as water soluble or citrate soluble P_2O_5.

Effect of Temperature. According to Elmore and Farr (3), heating mono-calcium phosphate mono-hydrate will increase the conversion of mono-calcium phosphate mono-hydrate to di-calcium phosphate. It appeared reasonable, therefore, to heat the partially acidulated rock to various temperatures and to ascertain the amount of di-calcium phosphate and mono-calcium phosphate present at each temperature. Since the reaction forms phosphoric acid, the eventual conversion of all of the partially acidulated rock to di-calcium phosphate should result.

The autoclave was preheated to the desired temperature range. Four hundred grams of the partially acidulated rock described in Table 5 were charged to the autoclave. The autoclave cover was put in place with the gas escape valve open. The motor operating the stirrer was started. The desired temperature was reached in about ten minutes, and this temperature was maintained for 30 minutes by adjusting the gas flow. The autoclave was then opened

and allowed to cool to room temperature. The product was sampled for analysis.

The analytical data are shown in Table 6 and Fig. 5. It is assumed here that water soluble P_2O_5 is mono-calcium phosphate, citrate soluble P_2O_5 is di-calcium phosphate, and citrate insoluble P_2O_5 is tri-calcium phosphate.

Effect of Moisture and Pressure on the Conversion of the Partially Acidulated Rock to Di-calcium Phosphate. For this series of experiments, four portions of the partially acidulated rock of 1200 grams each were used. A different quantity of water was added to each portion and mixed thoroughly. The moisture contents of the resulting samples were about 3 per cent, 7 per cent, 11 per cent, and 15 per cent. After preheating the autoclave, 300 grams of this partially acidulated rock were charged. The autoclave cover was bolted down, the agitator started, and heat applied. When the desired pressure was reached, the gas was adjusted to maintain the pressure and its corresponding temperature for 30 minutes.

As the decomposition occurred, the partially acidulated rock became difficult to stir. At the same time, the pressure and temperature increased. The reason is that the decomposition of mono-calcium phosphate to di-calcium phosphate and phosphoric acid, and the reaction of the undecomposed phosphate rock with the liberated phosphoric acid, are exothermic reactions. When the pressure ceased to increase, the reaction was assumed to be complete. The autoclave was then cooled down to room temperature, and the

Table 6. Effect of temperature on the conversion of phosphate rock to available forms of phosphate.

Temperature range, $^\circ$ C.	60-70	100-110	150-160	180-190	210-220	230-240
Total P_2O_5, %	23.34	23.28	23.85	23.91	24.37	24.82
Citrate insoluble P_2O_5, %	5.06	5.12	4.37	4.69	12.38	14.04
Water soluble P_2O_5, %	14.32	14.18	14.96	15.18	8.25	8.66
Citrate soluble P_2O_5, %	3.96	3.98	4.52	4.14	3.74	2.12
Conversion[1], %	78.4	78.0	81.6	80.5	49.4	43.5
Moisture, %	1.55	1.61	1.06	0.68	0.43	0.38

[1] The per cent of the total P_2O_5 present in available forms, i. e., as water soluble or citrate soluble P_2O_5.

pressure was released by opening the gas escape valve. The sample was removed immediately and stored for analysis. The chemical analyses of these runs is shown in Table 7.

Effect of Mixing Time. Since the conversion of partially acidulated rock to di-calcium phosphate is similar to the reaction of mono-calcium phosphate with phosphate rock, thorough mixing in the autoclave is necessary to obtain complete reaction and maximum yield of available P_2O_5.

To investigate the effect of the time of mixing a series of runs were made at various reaction times. Three hundred grams of the partially acidulated rock, which was described in Table 5, were charged to the autoclave for each batch. The pressure was held at 30 psig for 10, 20, 30, and 40 minutes of mixing time. The other procedures were the same as before. The chemical analyses of the products are shown in Table 8.

Effect of Particle Size. The effect of the particle size of the partially acidulated rock on the conversion to di-calcium phosphate was determined by separating the partially acidulated rock into four portions with 20, 40, 70, and 100 mesh screens. Four 200 gram samples of partially acidulated rock were prepared in each size. Each was placed separately in the autoclave under 25-30 psig for 30 minutes. The other procedures and conditions were the same as before. After reacting for 30 minutes, the sample was analyzed. The results are shown in Table 9.

Table 7. Effect of moisture and pressure on the conversion of phosphate rock to available forms of phosphate.

	Pressure, lbs./sq. in. 5 - 10 Temperature, °C. 108 - 116				15 - 20 121 - 127				25 - 30 130 - 135				35 - 40 148 - 152			
Moisture content of charge, %	3.83	7.16	12.31	15.38	4.52	7.95	11.92	14.86	3.15	6.95	11.52	15.08	1.34	5.37	8.92	11.65
Total P_2O_5, %	22.51	21.80	20.70	19.80	22.09	21.64	20.87	19.94	22.67	21.95	20.90	19.88	22.80	21.93	21.06	21.05
Citrate insoluble P_2O_5, %	5.01	4.83	4.60	4.81	4.94	4.68	4.73	4.65	1.86	2.28	3.73	4.26	1.92	2.31	3.62	4.15
Water soluble P_2O_5, %	14.15	13.67	12.81	12.40	13.98	13.50	12.62	12.31	2.35	8.05	10.52	12.57	3.08	7.65	11.83	13.88
Citrate soluble P_2O_5, %	3.35	3.30	3.29	2.59	3.17	3.46	3.52	2.98	18.46	11.62	7.01	3.05	17.80	11.94	5.61	2.47
Conversion[1], %	77.8	77.7	78.0	75.8	77.7	78.2	77.4	76.8	92.0	89.8	83.8	78.6	91.8	89.4	82.8	79.8
Moisture content of product, %	2.54	3.88	8.66	9.82	3.62	5.73	8.75	10.21	1.06	4.53	7.38	10.01	1.31	3.82	6.72	9.08

[1] The per cent of the total P_2O_5 present in available forms, i. e., as water soluble or citrate soluble P_2O_5.

Table 8. Effect of mixing time on the conversion of phosphate rock to available forms of phosphate.

Mixing time, minutes	10	20	30	40
Total P2O5, %	22.36	22.87	22.91	23.01
Water soluble P2O5, %	8.32	3.02	2.45	2.12
Citrate insoluble P2O5, %	4.06	2.04	1.99	2.02
Citrate soluble P2O5, %	9.98	17.78	18.47	18.87
Moisture, %	1.26	1.07	0.98	0.96
Conversion[1], %	82.0	89.1	91.2	91.4

[1] The per cent of the total P_2O_5 present in available forms, i. e., as water soluble or citrate soluble P_2O_5.

Table 9. Effect of particle size on the conversion of phosphate rock to available forms of phosphate.

Particle size (charge)	-10 + 20	-20 + 40	-40 + 70	-70 + 100
Total P_2O_5, %	22.8	22.35	22.72	22.81
Water soluble P_2O_5, %	6.01	3.07	3.22	2.08
Citrate insoluble P_2O_5, %	4.08	2.86	2.31	1.73
Citrate soluble P_2O_5, %	13.71	16.42	17.19	19.00
Moisture, %	2.86	2.31	1.23	0.86
Conversion[1], %	81.3	87.4	89.8	92.5
Weight % of product retained on screen of given mesh				
8	0	2.3	8.2	5.3
10	5.3	6.9	6.9	14.1
20	94.49	8.1	12.8	11.3
40	0.21	82.7	31.6	19.5
70			41.5	34.8
100				15.0

[1] The per cent of the total P_2O_5 present in available forms, i. e., as water soluble or citrate soluble P_2O_5.

<u>Chemical Reaction of Mono-calcium Phosphate Mono-hydrate</u>
<u>and Tri-calcium Phosphate</u>. From the preceding experiments, it appeared that mono-calcium phosphate mono-hydrate would react with tri-calcium phosphate under certain conditions of temperature and pressure to produce di-calcium phosphate. To further investigate this reaction, analytical reagent grade mono-calcium phosphate mono-hydrate and tri-calcium phosphate were reacted in the autoclave as follows. One hundred sixty-eight grams tri-calcium phosphate and 132 grams mono-calcium phosphate mono-hydrate were charged to the autoclave. The autoclave was heated until a pressure of 30-35 psig was reached. The chemical composition of the product was total P_2O_5, 49.82 per cent; water soluble P_2O_5, 12.25 per cent; citrate insoluble P_2O_5, 4.84 per cent; citrate soluble P_2O_5, 32.80 per cent; H_2O, 1.56 per cent; and conversion 90.40 per cent.

DISCUSSION OF RESULTS

Effect of Addition of Mineral Salts

As can be seen from Table 4, all of the mineral salts which were used had no effect except $Al_2(SO_4)_3 \cdot (NH_4)SO_4 \cdot 24H_2O$, which had a very slight effect. It may be that this compound was decomposed to liberate ammonia, thus increasing the pH value. Under this condition, mono-calcium phosphate would change into di-calcium phosphate and ammonium phosphate. The effect is the same as ammoniation of superphosphate. The final reaction involved is not

entirely clear because of the complex nature of the system.

Effect of Autoclaving after Partial Acidulation

Since, for a given quantity of partially acidulated rock, the amounts of P_2O_5 and CaO are fixed, the only remaining variables are the temperature, the quantity of water present, the pressure, the mixing time, and the particle size. Each of these was investigated individually.

The process developed converted 80 per cent of the phosphate rock to di-calcium phosphate. The total conversion to available forms was 92 per cent. The acid required to produce di-calcium phosphate by this process was only about 70 per cent of that required for the production of superphosphate.

At pressures below 25 psig, no reaction occurred. The probable reason for this is that the corresponding temperatures were not sufficiently high to decompose mono-calcium phosphate mono-hydrate into di-calcium phosphate. Mono-calcium phosphate mono-hydrate will decompose in the presence of water into di-calcium phosphate and phosphoric acid at temperatures higher than its dehydrating temperature.

At pressures above 25 psig, with an equilibrium temperature of 130° C. or higher, the conversion of mono-calcium phosphate mono-hydrate to di-calcium phosphate and phosphoric acid was accomplished. This is shown in Fig. 1 and Fig. 2 by the increase in the quantity of citrate soluble P_2O_5, the decrease in citrate insoluble P_2O_5, and the decrease in water soluble P_2O_5, with a
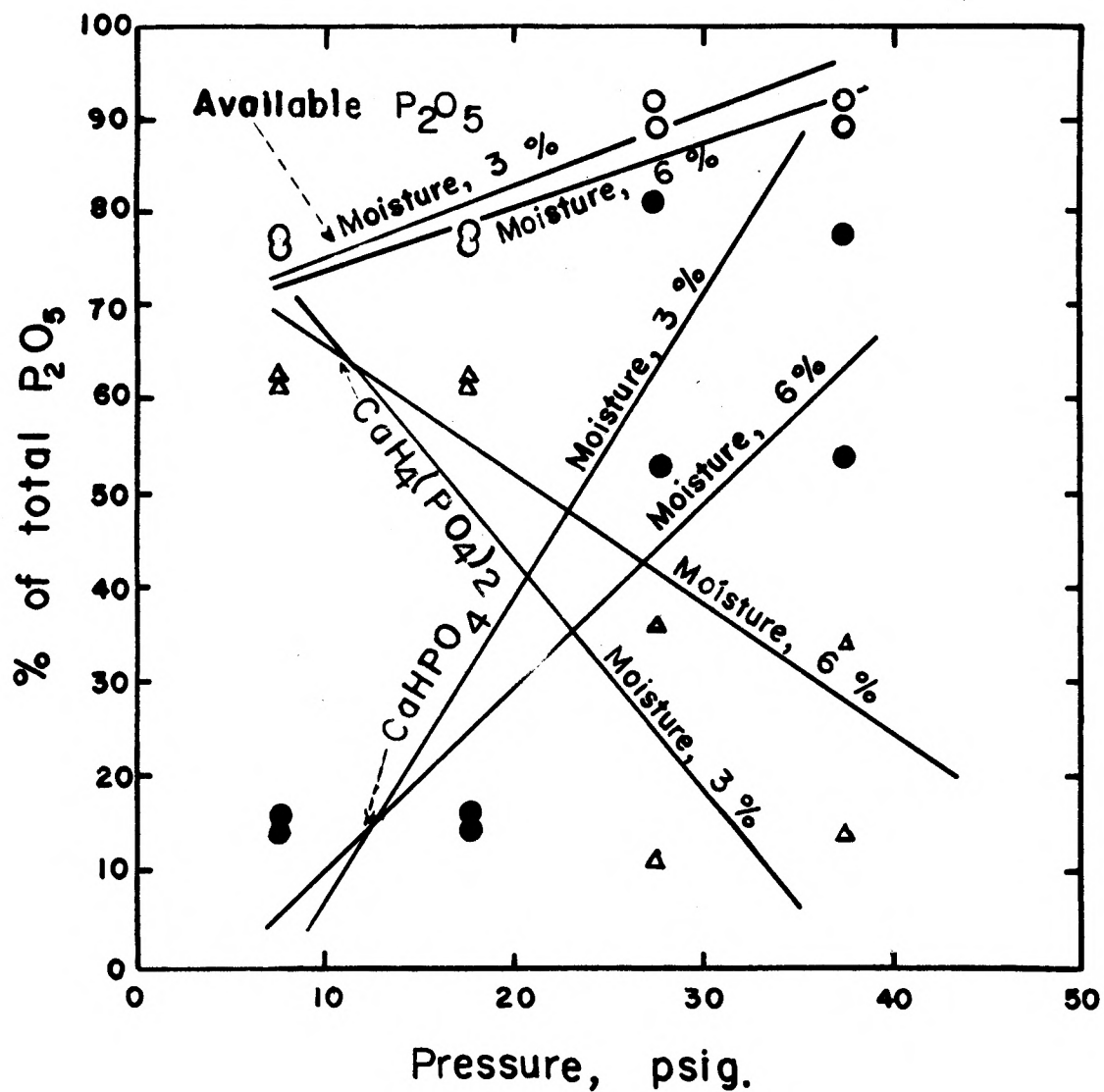
Fig. I. Effect of pressure on the conversion of phosphate rock to mono- and di-calcium phosphates.
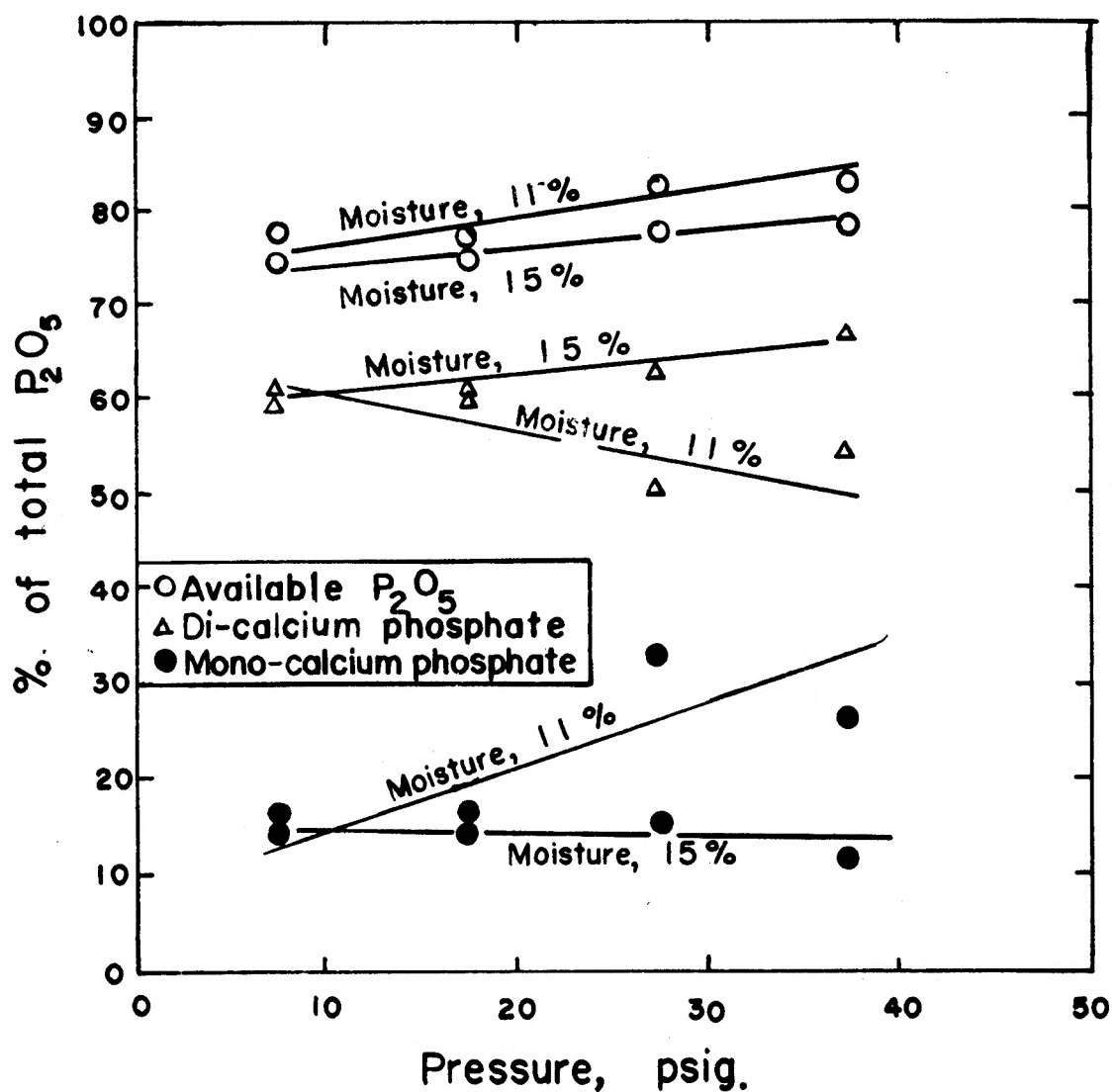
Fig. 2. Effect of pressure on the conversion of phosphate rock to mono- and di-calcium phosphates.

corresponding increase in the conversion of P_2O_5 to available forms.

As the moisture content of the partially acidulated rock charged to the autoclave was increased, the quantity of di-calcium phosphate produced decreased, as is shown in Fig. 3 and Fig. 4. This is in accordance with the data of Elmore and Farr (3) for equilibria in the system $CaO \cdot P_2O_5 \cdot H_2O$, which shows that, at elevated temperatures, the production of mono-calcium phosphate is favored by increasing the moisture content.

Temperature alone had little effect on the partially acidulated rock up to 190° C. Above here the water soluble P_2O_5, mono-calcium phosphate, decreased while the citrate insoluble P_2O_5 increased. It may be that, at the higher temperatures, mono-calcium phosphate lost some of its water of constitution and formed acid calcium pyrophosphate. The reaction is represented as follows:

$$CaH_4(PO_4)_2 + heat \longrightarrow CaH_2P_2O_7 + H_2O$$
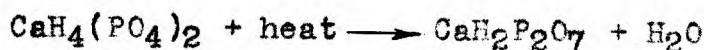
Finally, on heating to still higher temperatures calcium pyrophosphate may have decomposed further, giving up a further quantity of water and going to calcium meta-phosphate. The reaction may be represented thus:

$$CaH_2P_2O_7 + heat \longrightarrow Ca(PO_3)_2 + H_2O$$

According to Elmore and Farr (3), elevated temperatures favor the conversion of mono-calcium phosphate mono-hydrate to di-calcium phosphate. The data shown in Fig. 5, however, indicates that temperature did not produce such a reaction. The reason may
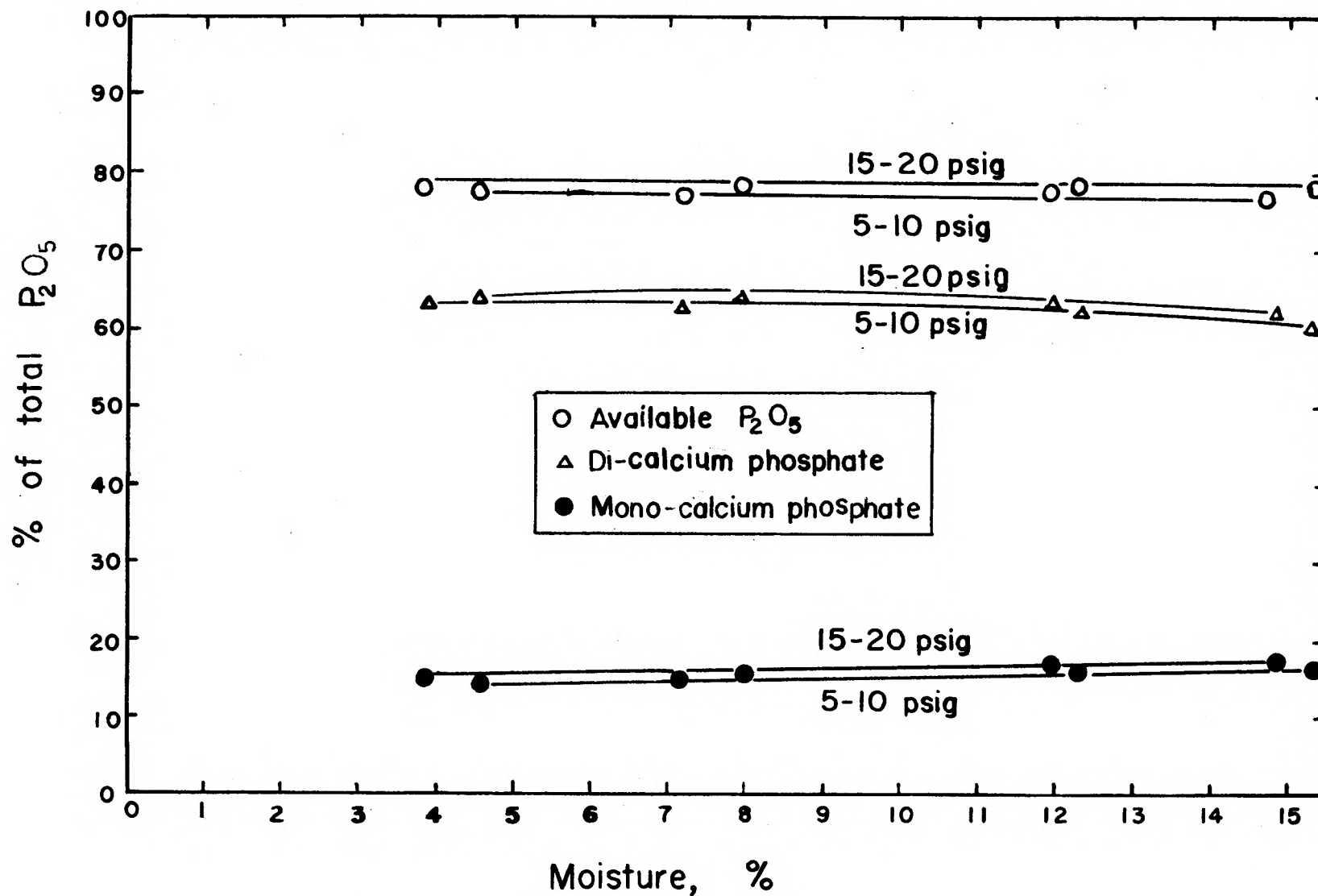
Fig. 3. Effect of moisture on the conversion of phosphate rock to mono- and di-calcium phosphates.
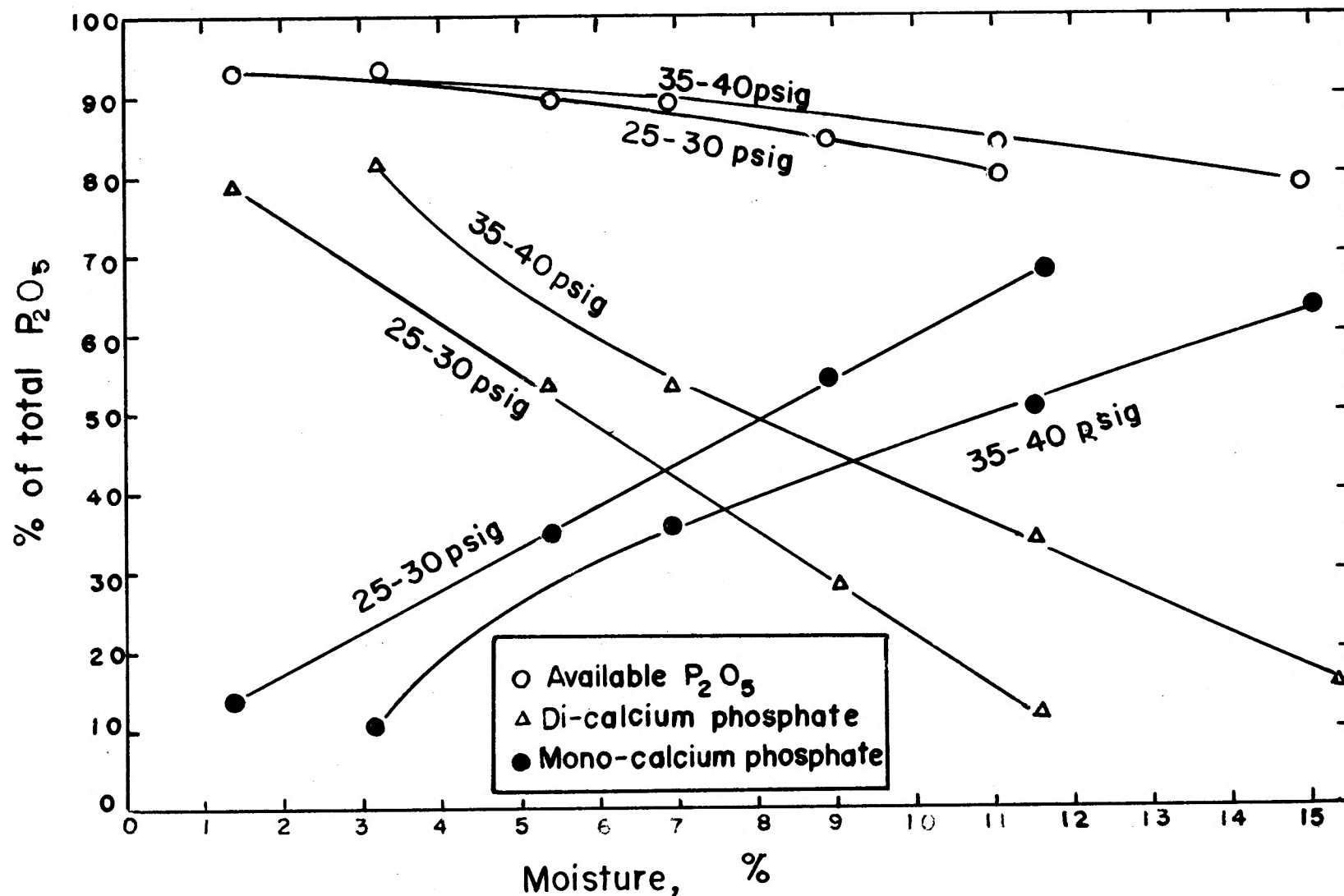
Fig. 4   Effect of moisture on the conversion of phosphate rock to mono- and di-calcium phosphates
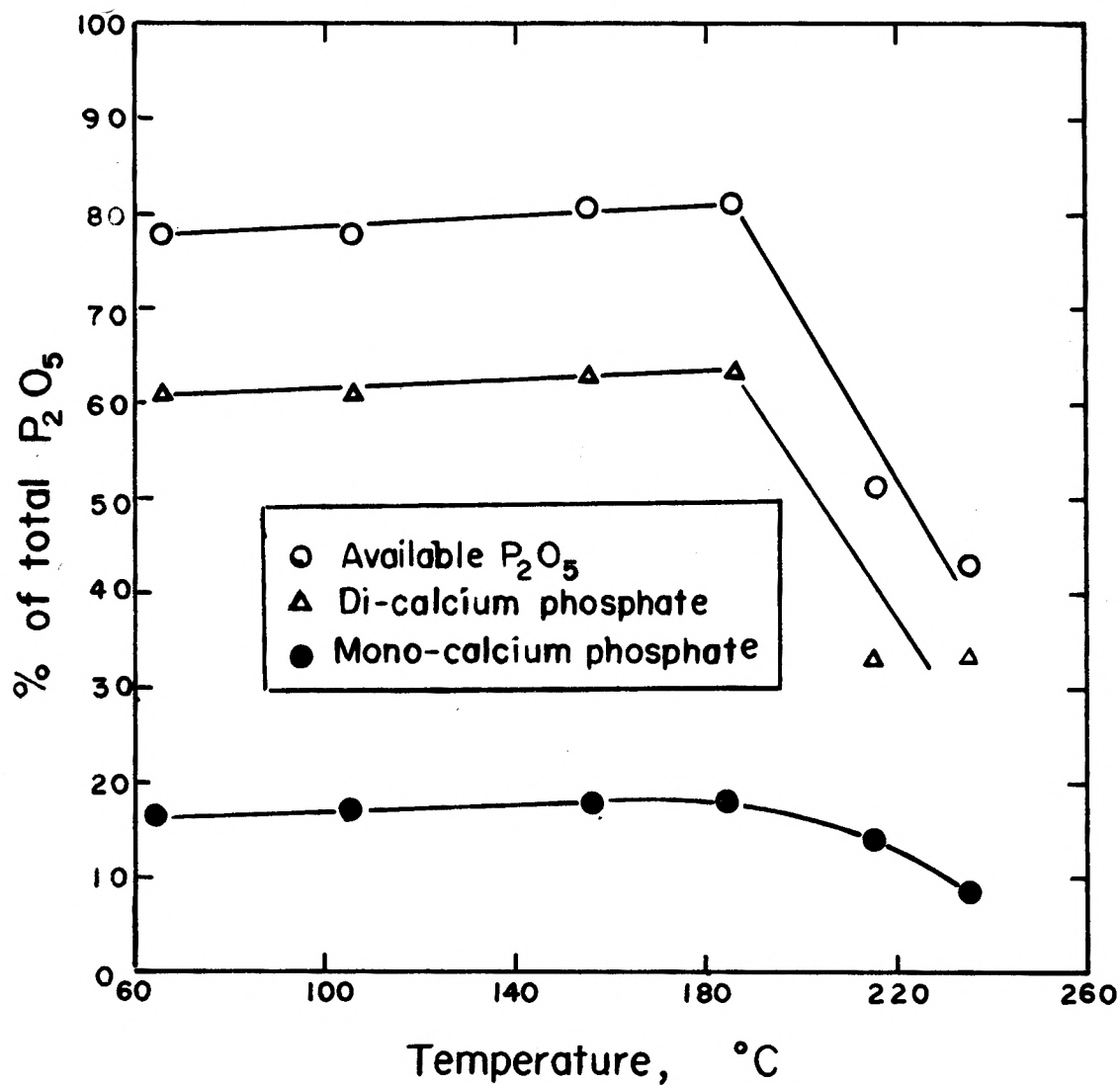
Fig. 5. Effect of temperature on the conversion of phosphate rock to mono- and di-calcium phosphates.

be that mono-calcium phosphate mono-hydrate was decomposed to
mono-calcium phosphate.

Mixing times of less than 10 minutes were not effective,
while the reaction appeared to be complete after 30 minutes.
This is shown in Fig. 6.

Particle size of the partially acidulated rock appeared to
be an important variable. Sizes larger than 20 mesh gave low con-
version, and sizes finer than 70 mesh were required to obtain
high conversions. These results were expected, because intimate
contact between particles and high surface areas are required for
solid-solid or solid-liquid reactions. The results are shown in
Fig. 7.

SUMMARY

A process is described in which a partially acidulated phos-
phate rock is treated in an autoclave under a gauge pressure
greater than 25 pounds per square inch at 130^0 - 200^0 C. As the
moisture content of the acidulated rock charged to the autoclave
is increased, the decomposition of mono-calcium phosphate to di-
calcium phosphate and phosphoric acid becomes less pronounced.
In this work when the moisture content of the mass charged was
above six per cent, no useful result was obtained.

The amount of acid required to produce the di-calcium phos-
phate is only about 70 per cent of that required for producing
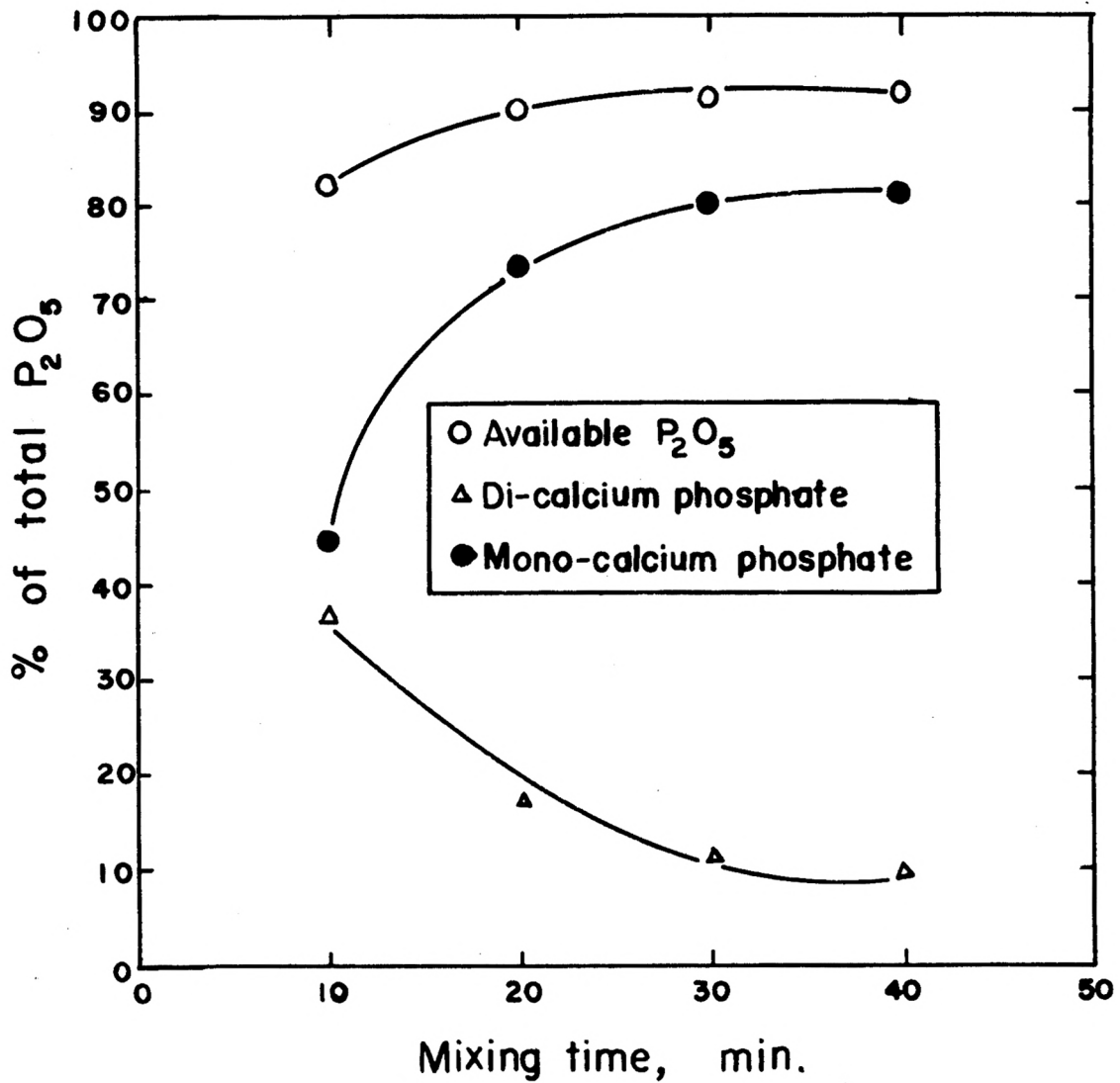superphosphate based on the available P_2O_5 content of the product.

Fig. 6. Effect of mixing time on the conversion of phosphate rock to mono- and di-calcium phosphates.
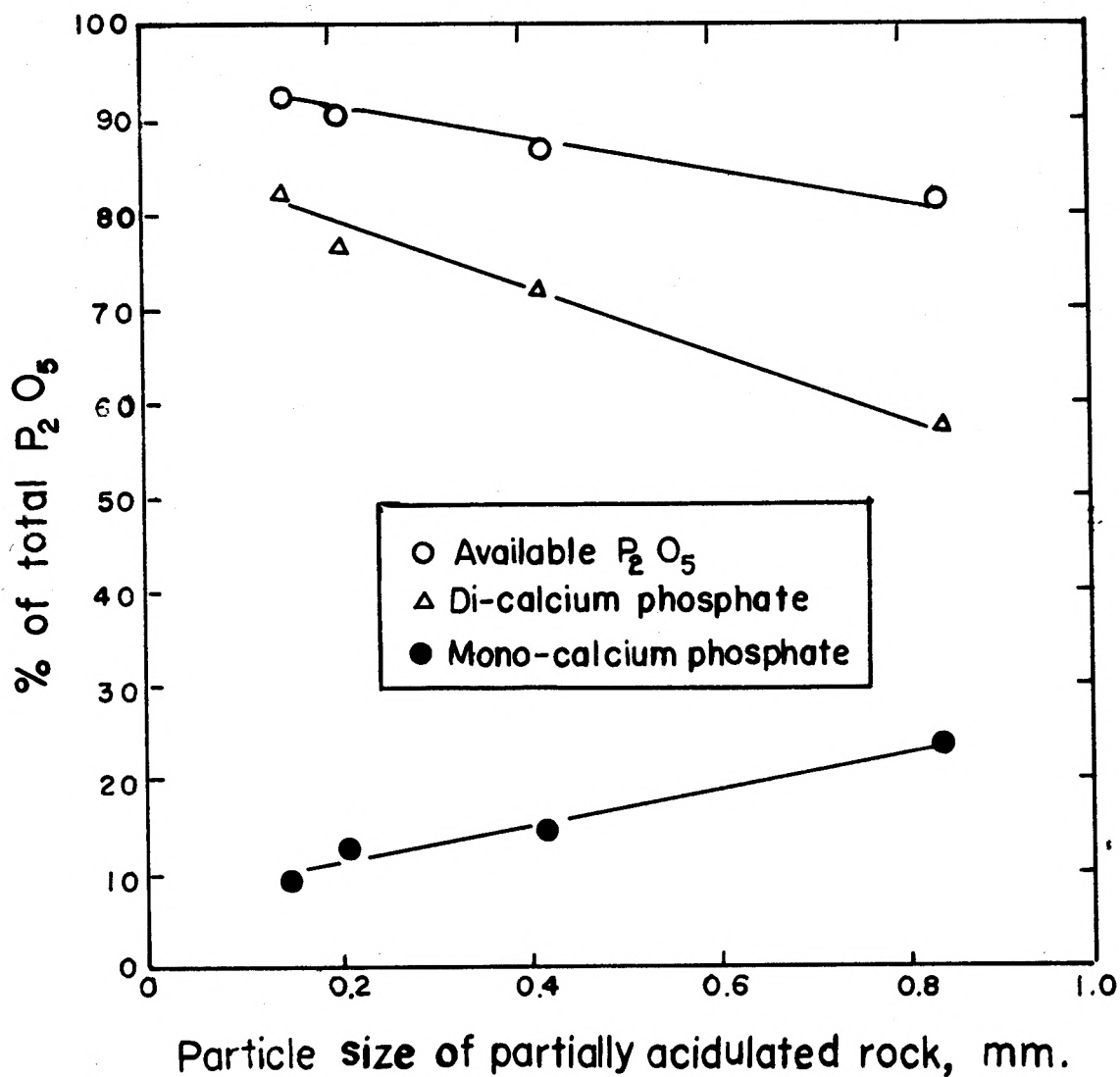
Fig. 7. Effect of particle size on the conversion of phosphate rock to mono- and di-calcium phosphates.

The conversion of P_2O_5 in the rock to available forms was 92 per cent.

ACKNOWLEDGMENTS

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APPENDIX

Analytical Procedures

Sampling:

All samples were cured at room temperature for one week. The samples were then ground to pass through a 70 mesh screen. The grinding was done as rapidly as possible to avoid loss or gain of moisture during the operation. The ground sample was mixed thoroughly and stored in tightly stoppered bottles.

Analytical Methods:

a. Moisture Determination.

Two grams of the sample were placed on a 9 cm. watch glass and dried at 25 to 30° C. in a vacuum dryer over anhydrous calcium chloride under 22 inches of vacuum for 18 hours. The sample was weighed again and the loss in weight divided by the weight of the original sample taken as the per cent of free water.

b. Total Phosphoric Acid.

Two grams of sample were placed in a 200 ml volumetric flask. Thirty ml of nitric acid and 5 ml of hydrochloric acid were added and boiled on the hot plate until the brown fumes disappeared. The mixture was then cooled to room temperature and diluted to the mark.

Ten ml of the clear, supernatant solution were pipetted into a 300 ml Erlenmeyer flask. Ten ml of nitric acid were added, and ammonium hydroxide was added until the precipitate that formed dissolved only slowly on vigorous stirring. The solution was diluted to 100 ml and cooled down to 25 to 30° C. If the sample

would not give a precipitate with NH_4OH, it was made slightly alkaline by adding a drop of methyl orange with NH_4OH $(1 + 7)$ and then slightly acid with HNO_3 $(1 + 3)$.

A molybdate solution was prepared by dissolving 100 g of MoO_3 in a solution of 144 ml of NH_4OH, and 271 ml of H_2O, cooling and pouring into a cool solution of 489 ml of HNO_3 in 1148 ml of H_2O. To 100 ml of this stock solution 5 ml of HNO_3 were added and the solution filtered just before using.

The molybdate solution was added according to the following schedule:

Range of % P_2O_5	Ml molybdate solution
0 - 5	20 - 25
5 - 20	30 - 35
20 - 35	40 - 45

The sample was placed in a shaking apparatus and shaken for 30 minutes at room temperature. The solution was decanted at once through a cone vacuum filter and the precipitate was washed by decantation. The precipitate was transferred to the filter and washed under suction with carbon dioxide free distilled water until the filtrate was acid-free. The filtrate was tested by adding one drop of phenolphthalein to a 10 cc test tube which was placed so as to catch the filtrate. The pink color had to be retained.

The precipitate and paper were transferred to the 300 ml Erlenmeyer in which the precipitation was done. Standard NaOH (0.324 N) was added to dissolve the precipitate, but not over 3 ml excess was used. The solution was back titrated with 0.324 N standard HCl using phenolphthalein as the indicator.

c. Water Soluble P_2O_5.

One gram of sample was weighed and placed on an 11 cm filter paper on a 9 cm Buchner funnel and washed with successive small portions of H_2O under suction until the filtrate measured about 200 ml. The filtrate was transferred to a 250 ml volumetric flask, diluted to the mark, and mixed well. The determination of per cent of P_2O_5 is exactly as for total P_2O_5.

d. Citrate Insoluble P_2O_5.

After the water soluble P_2O_5 was removed as before, the filter and residue were transferred to a 200 ml volumetric flask containing 100 ml ammonium citrate solution which was heated previously to 65° C. The flask was closed tightly with a smooth rubber stopper and shaken vigorously until the filter paper was reduced to a pulp. It was then placed in a water bath regulated to maintain the temperature at exactly 65° C. The level of water in the bath was kept above that of the citrate solution in the volumetric flask which was shaken every five minutes. At the expiration of exactly one hour from the time the filter and residue were introduced, the flask was removed from the bath and the contents were filtered immediately by suction as rapidly as possible through 9 cm Whatman No. 5 filter paper. The precipitate was washed with water at 65° C. until the volume was about 350 ml. Time was allowed for thorough draining before a new portion of water was added. The wet filter with its contents was transferred to the 200 ml volumetric flask and the per cent P_2O_5 determined exactly as for total P_2O_5.

THE PRODUCTION OF DI-CALCIUM PHOSPHATE BY THE DIRECT
ACIDULATION OF PHOSPHATE ROCK

by

KUO-KANG FENG

B. S., National Taiwan University,
Taipeh, Taiwan, China, 1950

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AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the
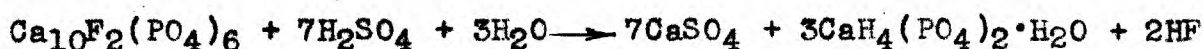
requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1956

The purpose of acidulating phosphate rock is to convert the phosphate in the mineral, apatite, into forms which are available to plants. Mono-calcium phosphate, which is water soluble, and di-calcium phosphate, which is soluble in neutral ammonium citrate solutions, are considered to be available. The main reaction forming mono-calcium phosphate may be represented as follows:

$$Ca_{10}F_2(PO_4)_6 + 7H_2SO_4 + 3H_2O \longrightarrow 7CaSO_4 + 3CaH_4(PO_4)_2 \cdot H_2O + 2HF$$

The main reaction forming di-calcium phosphate may be represented thus:

$$Ca_{10}F_2(PO_4)_6 + 4H_2SO_4 + 12H_2O \longrightarrow 4CaSO_4 + 6CaHPO_4 \cdot 2H_2O + 2HF$$
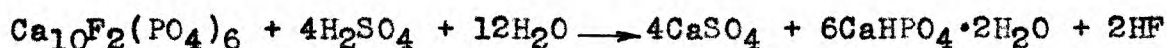
If the reaction forming di-calcium phosphate was attained, the amount of sulfuric acid required would only be about one-half as great as that necessary for the reaction forming mono-calcium phosphate. The reaction forming di-calcium phosphate is very difficult to attain, and the final product nearly always consists of a mixture of mono-calcium phosphate and undecomposed phosphate rock.

Thermodynamic feasibility of the di-calcium phosphate reaction was studied. From free energy calculations, the reaction appeared possible.

The main object of the present investigation was to find a way of producing di-calcium phosphate from phosphate rock and sulfuric acid. Two approaches were used. In the first, the effect of various mineral salts of potassium, magnesium, and aluminum on the acidulation of phosphate rock was studied. In the second, an autoclave process involving the use of moderate pres-

sures was investigated.

None of the mineral salts used in this study had an appreciable effect on the reactions during the acidulation of phosphate rock except $Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$, which had a slight effect.

In the second part of this work, phosphate rock was acidulated with a quantity of sulfuric acid slightly in excess of that required to form di-calcium phosphate but much less than that required to form mono-calcium phosphate. This partially acidulated rock was then autoclaved under various conditions of temperature, pressure, moisture content, particle size, and for various lengths of time. The optimum conditions were found to include pressures above 25 psig; low moisture contents of three per cent or less; temperatures corresponding to this moisture content and pressure, 130° to 140° C.; particle size less than 70 mesh, and reaction time of 30 minutes. Under these conditions, the conversion of phosphate to available forms increased from 77 per cent in the partially acidulated rock before autoclaving to 92 per cent after autoclaving. Of the total phosphate in the autoclaved material, 10 per cent was present as water soluble P_2O_5 (mono-calcium phosphate), 82 per cent as citrate soluble (di-calcium phosphate), and 8 per cent as citrate insoluble P_2O_5.