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7/25/68

A NEW PROCESS FOR THE PRODUCTION OF LOW IMPURITY PHOSPHORIC ACID

Approved:

Chairman:

Date approved by Chairman: Nov. 21, 1972

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TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

A NEW PROCESS FOR THE PRODUCTION OF LOW IMPURITY PHOSPHORIC ACID

A THESIS

Presented to

The Faculty of the Graduate Division

by

Carl Bernard Drees

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy in the School of Chemical Engineering

Georgia Institute of Technology

November, 1972

LIST OF TABLES (Continued)

LIST OF TABLES (Continued)

LIST OF TABLES (Continued)

LIST OF FIGURES

SUMMARY

Neither of the two major commercial processes which are presently used for the manufacture of phosphoric acid produce an acid that is entirely technically and economically suitable for supplying the phosphorus constituent of clear liquid mixed fertilizers. Electric furnace grade phosphoric acid is chemically and physically well suited to be used as the source of phosphorus for clear liquid mixed fertilizers but is normally too expensive. Wet process phosphoric acid, on the other hand, is less expensive but when this acid is used, it is virtually impossible to manufacture a clear liquid mixed fertilizer that does not eventually precipitate solids or form a gel due to the impurities present in the acid. Among the main offending impurities are calcium, iron, aluminum and magnesium. Therefore, a potential market exists in the area of clear liquid mixed fertilizer production for a phosphoric acid which is more pure than commercial wet process acid but less expensive than commercial electric furnace acid.

The overall objective of this study was to investigate the technical feasibility of producing low impurity phosphoric acid and/or a dicalcium phosphate-containing fertilizer by using a chemical route which uses the conventional wet process method as a starting point. The proposed chemical process is based on the dissociation of monocalcium phosphate into phosphoric acid and dicalcium phosphate in the presence of an organic solvent. Either a low impurity phoshporic acid product or a dicalcium phosphate-containing fertilizer or both products may be

produced depending on the choice of recycle. In addition to determining the technical feasibility of the process, other specific objectives included the experimental study of the effect of certain process parameters on the yield and quality of the phosphoric acid product and the determination of near-optimum operating conditions for the entire process.

The approach taken to the experimental phase of the problem basically involved dissociating, at constant temperature in the presence of an organic solvent, small amounts of crude monocalcium phosphate which had been prepared from commercial ground phosphate rock in a manner simulating the preparation of monocalcium phosphate in the phosphate industry. Organic solvents studied included methanol, ethanol, normal propanol, normal butanol, isopentanol, normal hexanol, 2-methyl pentanol, normal octanol, 2-ethyl hexanol, normal decanol, normal dodecanol, acetone, methyl butyl ketone and tetrahydrofuran. The dissociation reaction was studied from 25°C to 70°C using reaction periods from 0.25 to 4.0 hours. The solid and liquid phases of the reacted slurry were separated and chemically analyzed for various chemical species. An inituitive approach was taken to determine near-optimum process operating conditions using the experimental data.

The major results of this work are:

(1) Monocalcium phosphate conversion to phosphoric acid and dicalcium phosphate increases as: a) the number of carbon atoms in the organic solvent decreases, b) dissociation temperature increases, c) solvent/monocalcium phosphate P_2O_5 ratio increases and d) the water content

of monocalcium phosphate increases.

(2) A process for the production of low impurity phosphoric acid and/or dicalcium phosphate using a route involving the dissociation of monocalcium phosphate in the presence of an organic solvent is technically feasible. When using methanol or acetone, recycle of dicalcium phosphate along with its impurities does not result in the build-up of impurities in the product acid.

(3) The dissociation of monocalcium phosphate containing 47 percent P_2O_5 at 55°C for 15 minutes in the presence of either 6.0 pounds of methanol or 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 is considered near-optimum for the production of a low impurity phosphoric acid product. The resultant product acid contains 54 percent P_2O_5 after fractionation of the solvent and approximately one percent of the major cation impurities, CaO, Fe_2O_3, Al_2O_3 and MgO. The acid contains 0.00 percent sulfate.

It is believed that the chemical process is economically sound and further development work on the process is recommended.

CHAPTER I

INTRODUCTION

General Background and Statement of Problem

At present, phosphoric* acid is commercially produced by two methods, the electric furnace method and the wet process method. The electric furnace process produces high purity phosphoric acid by means of the electrothermic reduction of phosphate rock with carbon (coke). Phosphate rock, which is composed chiefly of the mineral fluorapatite, $Ca_{10}(PO_4)_6F_2$, is added to the electric furnace along with silica and coke. The silica added to the furnace charge behaves as a strong acid at the high temperatures (about 1500°C) employed in furnace operations and combines with the calcium constituent of the fluorapatite to form a calcium silicate slag. The overall reaction, neglecting carbonates fluorides, and other non-phosphatic constituents, may be expressed as follows:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = P_4 + 6CaSiO_3 + 10CO \qquad (I\text{-}1)$$

In the manufacture of furnace phosphoric acid, the condensed elemental phosphorus is burned in air. The phosphorus oxide vapor (P_4O_{10}) formed is absorbed in water to produce phosphoric acid:

$$P_4 + 5O_2 = P_4O_{10} \qquad (I\text{-}2)$$

$$P_4O_{10} + 6H_2O = 4H_3PO_4 \qquad (I\text{-}3)$$

*The terms "phosphoric acid" and "orthophosphoric acid" are used interchangeably to mean an aqueous solution of H_3PO_4.

The resultant phosphoric acid product is a high purity material and contains only very small amounts of impurities. Electric furnace grade phosphoric acid is used to manufacture textiles, paper, food, drugs, detergents and, to a limited dgree, agricultural chemicals. Slack (81) has a very good general review of the manufacture of phosphoric acid by the electric furnace method.

Phosphoric acid is also produced commercially by the wet process method. The wet process method essentially involves the chemical attack of phosphate rock, composed chiefly of the mineral fluorapatite and a calcium carbonate impurity, by sulfuric acid. The overall reaction with sulfuric acid may be subdivided into three simplified steps.

First, the tricalcium phosphate constituent is converted to phosphoric acid and calcium sulfate:

$$Ca_3(PO_4)_2 + H_2SO_4 = 2H_3PO_4 + 3CaSO_4 \qquad (I\text{-}4)$$

Second, the calcium fluoride constituent of the fluorapatite reacts with sulfuric acid to produce hydrogen fluoride and calcium sulfate:

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4 \qquad (I\text{-}5)$$

Third, the calcium carbonate impurity is converted to carbon dioxide and calcium sulfate:

$$CaCO_3 + H_2SO_4 = CO_2 + CaSO_4 + H_2O \qquad (I\text{-}6)$$

The entire reaction between the major constituents and sulfuric acid, including the calcium carbonate impurity, is as follows:

$$Ca_{10}(PO_4)_6F_2 + CaCO_3 + 11H_2SO_4 = 6H_3PO_4 + 11CaSO_4 + 2HF + H_2O + CO_2 \quad (I\text{-}7)$$

The hydrogen fluoride produced may react with silica to form silicon tetrafluoride, which then hydrolizes to fluosilicic acid:

$$4HF + SiO_2 = SiF_4 + 2H_2O \quad (I\text{-}8)$$

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2 \quad (I\text{-}9)$$

The calcium sulfate formed in the reactions can be in three states of hydration: anhydrite, hemihydrate (sometimes called the semihydrate), or dihydrate (gypsum), depending on the reaction temperature and phosphoric acid concentration. When phosphate rock digestion conditions are maintained so as to form calcium sulfate dihydrate, the resulting magma of phosphoric acid and gypsum is filtered producing a phosphoric acid filtrate containing approximately 30 percent P_2O_5. This phosphoric acid filtrate is subsequently concentrated to a merchant grade acid containing 54 percent P_2O_5 (around 75 percent H_3PO_4) using vacuum evaporation.

The resulting merchant grade phosphoric acid produced by the wet process, when compared to electric furnace acid, is a relatively impure product and is a dark brown color except when calcined rock is used. Table 1 shows typical analyses of merchant grade orthophosphoric acid made from different types of phosphate rock by means of the wet process method (81, 88). It may be seen from Table 1 that the major impurities in wet process merchant acid are calcium, iron, aluminum, magnesium, and fluorine. Wet process phosphoric acid is used almost exclusively as a base material for the manufacture of agricultural chemicals. Noyes (67) and Slack (81) both give excellent general reviews of the wet process

Table 1. Composition of Typical Commercial Concentrated Wet Process Orthophosphoric Acids (81,88).

Phosphate Rock Source	Acid Composition, Weight Percent									
	P_2O_5	CaO	Al_2O_3	Fe_2O_3	MgO	F	SO_4	K_2O	Na_2O	SiO_2
Florida	53.1	0.20	1.32	1.72	0.32	0.5	1.8	0.010	0.30	0.7
	54.8	0.05	0.90	1.10	0.66	0.3	0.7	0.003	0.03	-
	52.1	0.10	1.10	1.10	0.60	0.1	4.8	0.007	0.02	-
	53.1	0.06	1.70	1.23	0.58	0.8	2.6	0.010	0.12	0.7
	55.2	0.04	1.50	1.80	0.58	0.6	0.8	0.007	0.02	-
North Carolina	54.0	0.10	1.00	1.40	1.10	0.7	3.1	-	-	-
Western U.S.	52.7	0.13	1.80	0.40	0.77	0.7	1.9	0.035	0.03	-
	54.2	1.30	1.50	0.70	0.50	1.1	1.2	-	-	0.6
	54.0	0.00	1.89	0.78	0.43	0.2	6.2	0.020	0.21	0.9
	52.6	0.03	2.57	0.96	0.80	0.9	3.1	0.020	0.03	0.8
Tennessee	54.0	0.02	3.90	2.62	-	2.6	2.3	0.020	0.01	0.9

method.

One use of wet process phosphoric acid is to supply all or part of the phosphorus constituent of clear liquid mixed fertilizers. Clear liquid mixed fertilizers are solution fertilizers which contain at least two of the three major plant nutrients: nitrogen, phosphorus, and potassium. The market for clear liquid mixed fertilizers has experienced very rapid growth in the past few years and is expected to continue to grow in the future (1).

When using conventional wet process phosphoric acid it is virtually impossible to manufacture a clear liquid mixed fertilizer that does not eventually precipitate solids or form a gel due to the impurities present in the acid. Certain methods have been used to circumvent this problem of clear liquid mixed fertilizer degradation.

One method which has been successfully used to retard clear liquid mixed fertilizer degradation is the use of superphosphoric acid to supply either some or all of the phosphorus requirement. Superphosphoric acid is a commercial product which contains condensed phosphoric acids such as pyrophosphoric acid and tripolyphosphoric acid and has the ability of causing the sequestration of the impurities to occur thus preventing them from forming precipitated solids or gels.

Electric furnace grade orthophosphoric acid is sometimes used to supply phosphorus to clear liquid mixed fertilizers. However, this practice will probably become increasingly more unattractive from an economic standpoint if the cost of electric power rises sharply in the future due to the increased use of non-polluting fuels for turbine steam production.

Another method which has been successfully used to prevent clear liquid mixed fertilizer degradation is the usage of conventional wet process phosphoric acid which has been further processed to remove most of the offending impurities. A number of chemical processes have been developed which produce a low impurity phosphoric acid by preferentially extracting the acid with an organic solvent while rejecting the undesirable impurities in the raffinate (4, 5, 6, 30, 33, 57, 63, 64, 75, 89). Other papers have described the production of low impurity wet process phosphoric acid using other methods (27, 54, 73, 74). Slack (81) and Noyes (67) both have good reviews of methods which may be used to purify wet process orthophosphoric acid.

In the United States, dicalcium phosphate is produced commercially for use in foods and animal feed. Dicalcium phosphate is made by treating electric furnace phosphoric acid with lime. In the United States, fertilizer grade dicalcium phosphate is not presently produced although it is recognized to be an excellent fertilizer.

The overall objective of this study was to investigate the technical feasibility of producing low impurity phosphoric acid and/or dicalcium phosphate by using a certain chemical route which uses the conventional wet process method as a starting point. The proposed chemical process is based on the dissociation of monocalcium phosphate into phosphoric acid and dicalcium phosphate in the presence of an organic solvent according to the following reaction:

$$Ca(H_2PO_4)_2 = H_3PO_4 + CaHPO_4 \qquad \text{(I-10)}$$

A generalized schematic flow diagram showing the major steps involved in the proposed process is shown in Figure 1. The process consists of the following steps:

A. Reaction of phosphate rock, sulfuric acid and sometimes recycled dicalcium phosphate (DCP) in water to form crude phosphoric acid and gypsum. This step and the following step are essentially the same as in the production of orthophosphoric acid by the conventional wet process. The principal reaction in this step is:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O = 6H_3PO_4 + 10CaSO_4 \cdot 2H_2O + 2HF \quad (I\text{-}11)$$

If dicalcium phosphate is recycled the following reaction also occurs:

$$CaHPO_4 + H_2SO_4 + 2H_2O = H_3PO_4 + CaSO_4 \cdot 2H_2O \quad (I\text{-}12)$$

B. Filtration of the digestion products to remove insoluble gypsum and most of the impurities.

C. Reaction of the crude phosphoric acid with phosphate rock to produce monocalcium phosphate (MCP) according to the following reaction:

$$Ca_{10}(PO_4)_6F_2 + 12H_3PO_4 = 9Ca(H_2PO_4)_2 + CaF_2 \quad (I\text{-}13)$$

Since unconcentrated phosphoric acid containing around 30 percent P_2O_5 is used as a reactant, the resultant monocalcium phosphate reaction product will be a slurry.

D. Expulsion of water and some fluorine impurity by drying the monocalcium phosphate slurry. Most of the free water will probably, but not necessarily, be expelled from the monocalcium phosphate slurry during this step.

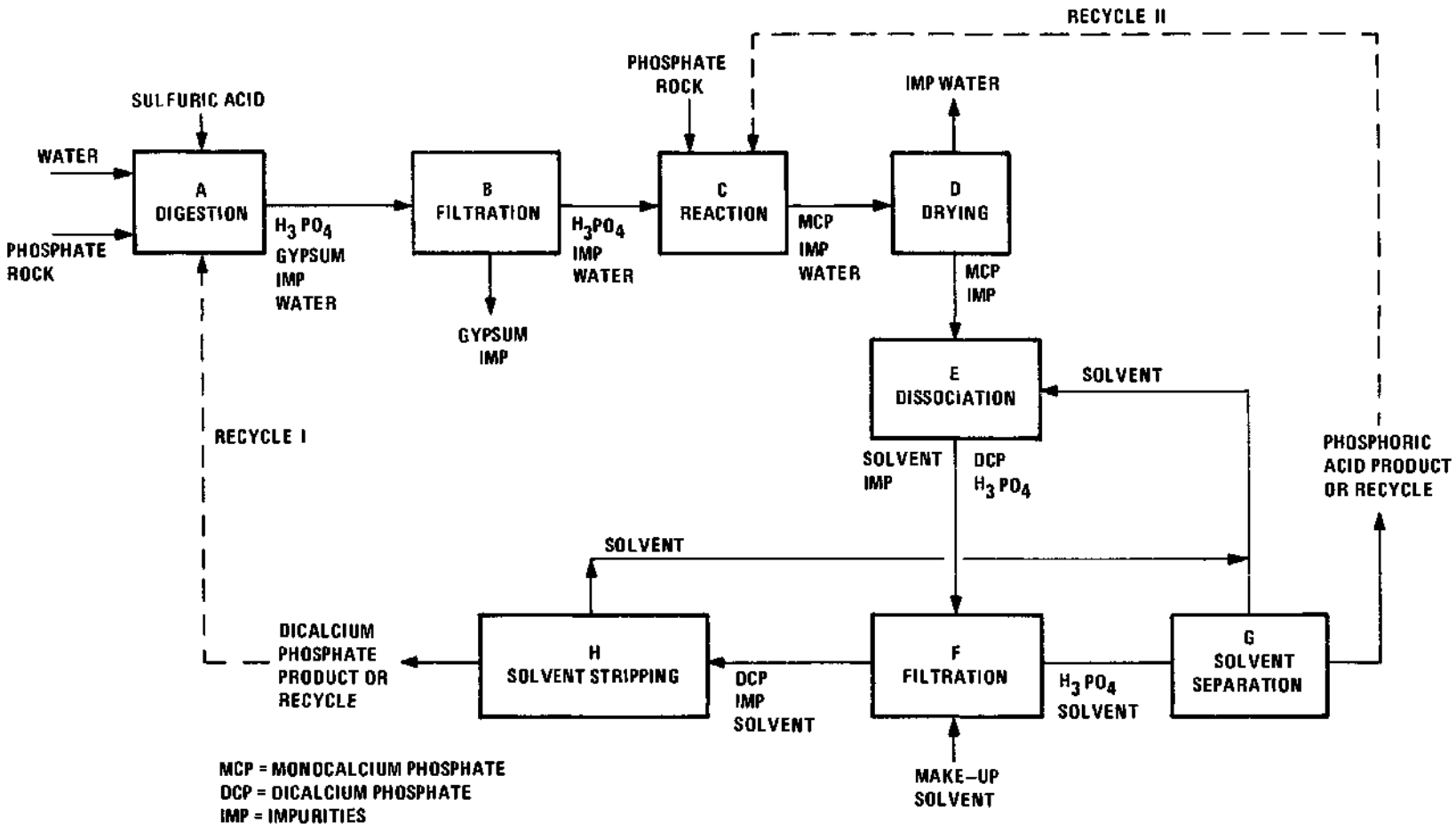

Figure 1. Schematic Diagram for Proposed Process

E. Dissociation of the monocalcium phosphate in the presence of an organic solvent (with perhaps some water present) which preferentially dissolves the phosphoric acid but not the dicalcium phosphate which forms or the impurities present. The chemical reaction occurring at this point is as follows:

$$Ca(H_2PO_4)_2 = H_3PO_4 + CaHPO_4 \qquad (I\text{-}10)$$

F. Filtration of the magma resulting from the dissociation reaction to separate a solution of purified phosphoric acid in the organic solvent from the solid dicalcium phosphate residue containing the impurities. Make-up organic solvent required to off-set losses will probably be best added here as a cake wash.

G. Separation and recovery of the low impurity phosphoric acid product from the solution of acid in organic solvent either by fractionation or extraction. The recovered organic solvent will then be recycled to step E.

H. Stripping of the occluded organic solvent from the dicalcium phosphate residue and subsequent recovery of the stripped solvent for recycle to step E.

The process up to this point will produce two products, namely, a low impurity phosphoric acid which will be suitable for clear mixed liquid fertilizer production and perhaps many other industrial applications, and an impure dicalcium phosphate which can be used as a fertilizer.

In addition, however, the proposed process could be used to produce only one product if desired, namely, either low impurity phosphoric acid or impure dicalcium phosphate. If only low impurity phosphoric acid product were desired, all of the dicalcium phosphate would be

recycled back to step A for attack with sulfuric acid as indicated by dotted line I on Figure 1. In this case the dicalcium phosphate would be converted back to crude phosphoric acid and gypsum and the impurities would be removed from the system in step B along with the gypsum. If only dicalcium phosphate product were desired, the low impurity phosphoric acid would all be recycled to step C as indicated by dotted line II where it would be converted to monocalcium phosphate during reaction with phosphate rock. It is therefore clear that by the choice of the recycle streams the product from the process could consist of only phosphoric acid, only dicalcium phosphate or any proportion of the two. It is believed that this process will offer the following advantages over other processes for producing a purified wet process acid: production of phosphoric acid of higher purity, higher overall recovery of low impurity phosphoric acid, and the production of a fertilizer grade dicalcium phosphate, if desired. In addition, this dicalcium phosphate product would theoretically require the usage of half the amount of sulfuric acid to produce a unit of available P_2O_5 as that required to produce a unit of available P_2O_5 in either normal or triple superphosphate.

The important factors in the proposed process that needed investigation were as follows:

Steps A and B. Reaction of phosphate rock, sulfuric acid, and recycled dicalcium phosphate and subsequent filtration of the digestion products. The effect of adding recycled dicalcium phosphate as a reactant in the conventional wet process chemistry needed to be established. The effect of recycled dicalcium phosphate on P_2O_5 recovery from the digestion magma also needed to be determined. In addition, the potential

increase of impurities in the crude acid filtrate due to the greater impurity load introduced by recycled dicalcium phosphate required investigation.

Step C. Production of monocalcium phosphate. The effect of the type of phosphate rock reactant on subsequent processing steps and chemical nature of the products needed study.

Steps D, E, and F. Drying of the monocalcium phosphate produced in step C followed by dissociation and filtration. The effect of the following variables on the rate and degree of completion of the reaction, purity of phosphoric acid, filtration rate, and degree of hydration of dicalcium phosphate needed to be determined. Variables which needed investigation were type of organic solvent, relative proportion of organic solvent and monocalcium phosphate P_2O_5, amount of free water allowed to remain in the monocalcium phosphate reactant, reaction time, and reaction temperature. Formation of dicalcium phosphate dihydrate is preferable from the agronomic standpoint and also because it would remove some of the water from the system, thus producing a more concentrated phosphoric acid product. Optimum conditions needed to be worked out for these three processing steps.

Step G. Separation and recovery of the low impurity acid product from the organic solvent. The product acid needed to be recovered from the organic solvent by either fractionation or extraction in a laboratory simulation of this step in order to determine the chemical properties of the product acid as well as to determine its visual appearance.

Step H. Solvent stripping from the dicalcium phosphate. The amount of solvent occluded in the wet dicalcium phosphate filter cake and

the chemical properties of the dried dicalcium phosphate product had to be determined.

Objectives

The objectives of this work are summarized below:

(1) To determine the technical feasibility of producing low impurity orthophosphoric acid and/or fertilizer grade dicalcium phosphate by a chemical process involving the dissociation of monocalcium phosphate in the presence of an organic solvent. The proposed chemical process would utilize the general processing steps outlined in the discussion above.

(2) To study the effect of certain process parameters on the yield of phosphoric acid and impurity rejection from the purified acid product. Product acid impurities to be studied include: CaO, Fe_2O_3, Al_2O_3, MgO and F. The process parameters to be investigated include the following: (a) type of phosphate rock reactant, (b) type of organic solvent, (c) proportion of organic solvent present, (d) amount of free water present in the crude monocalcium phosphate reactant, (e) reaction time, and (f) reaction temperature.

(3) To determine near optimum operating conditions for the entire process and to determine the flow rates and chemical compositions for the major processing steps involved in a continuous process using these optimum conditions.

(4) To verify the technical feasibility of producing a low impurity phosphoric acid and fertilizer grade dicalcium phosphate utilizing near optimum conditions using a batchwise beaker-scale simulation of the continuous process. The effluent from a batch simulation of each major

process step was used as a reactant for the subsequent processing step.

Review of the Literature

A number of studies have been made in the past concerned with the extraction of phosphoric acid by organic solvents and the solubility of phosphoric acid in various organic liquids. A variety of patents exist for chemical processes that produce a purified orthophosphoric acid based on the extraction of crude wet process phosphoric acid by organic solvents with the subsequent recovery of the purified acid product.

Seaton (79) discusses the solvent extraction of aqueous phosphoric acid by various organic solvents while Fox (27) discusses the use of alcohol in the manufacture of phosphoric acid and the phosphates in general. The dissociation constants of phosphoric acid in methanol, ethanol, propanol, and butanol were investigated by Kolchina et al. (43) while Luca and Enea (50) determined the dissociation constants of phosphoric acid in a fifty percent water-ethanol solution. While studying the reaction of phosphoric acid with various solvents, Morin and Martin (60) found that water, methanol, ethanol, and acetone all cause complexation, dissociation, and eventual ionization of phosphoric acid. Golynko et al. (29) have studied the extraction of aqueous phosphoric acid using the aliphatic alcohols containing from four to ten carbon atoms. They found that the largest quantities of phosphoric acid were extracted by the lower molecular weight alcohols. Extraction of phosphoric acid by the butanols and the pentanols were investigated by Moroto and Watanabe (61), Sabaev and Shokin (76), Soloveva et al. (83), and Zharovskii and Melnik (90). Ananthanarayanan and Rao (2) studied liquid-liquid equilibria in the water-phosphoric acid-isopentanol system at 35°C. Sabaev and Shokin (76)

investigated the extraction of phosphoric acid from aqueous solution with normal hexanol and normal heptanol. Liquid phase equilibria in the water-phosphoric acid-methyl ethyl ketone system are discussed by Krupatkin et al. (45), Krupatkin and Shcherbakova (46), and Moroto and Watanabe (61). Anathanarayanan and Rao (2) investigated liquid-liquid equilibria in the water-phosphoric acid-methyl isobutyl ketone system. Anathanarayanan and Rao (2) and Krupatkin and Stepanova (47) studied liquid phase equilibria in the water-phosphoric acid-cyclohexanol system while extraction of aqueous phosphoric acid by cyclohexanone was studied by Krupatkin et al. (45), Krupatkin and Shcherbakova (46), and Muldagaliev et al. (62). Extraction of phosphoric acid by diethyl ether has been investigated by Helferich and Baumann (33) and Zharovskii and Melnik (90) while extraction of aqueous phosphoric acid by furfural and benzaldehyde has been studied by Krupatkin et al. (45). Sabaev and Shokin (76) have studied the extraction of phosphoric acid by tributyl phosphate and Zharovskii and Melnik (90) have studied the extraction of phosphoric acid by the esters, butyl acetate and isoamyl acetate. Vapor pressure data at 20°C for diethyl ether, ethanol, and acetone dissolved in phosphoric acid have been made available by Berl and Will (13).

Slack (81) discusses some of the commercial processes which are presently being used to purify crude wet process phosphoric acid by extraction with organic solvents. Patents have been assigned to Baniel et al. (5), Montecatini Edison S.p.A. (57), Murakami et al. (63), and Nakaoka et al. (64) that involve the preparation of a purified wet process orthophosphoric acid by extraction with an alcohol of four or more carbon atoms. A patent has been assigned to Baniel and Blumberg (4)

which describes the purification of wet process phosphoric acid by extraction with cyclohexanone, dibutyl ether, and diethyl ether. Baniel et al. (6) hold a patent which involves the purification of wet process phosphoric acid by extraction with ketones, ethers, and esters containing from two to five carbon atoms. Tributyl phosphate is used as the extraction solvent to purify wet process phosphoric acid described in patents assigned to Baniel et al. (5), Goret and Winand (30) and Winand and Martin (89). Ross et al. (73) hold a patent which describes the production of low impurity phosphoric acid by a method involving the crystallization of phosphoric acid from concentrated wet process acid. The purification of wet process orthophosphoric acid by means of a crystallization method is further described by Ross et al. (74). Melamid and Grotzinger (54) have been assigned a patent which is concerned with the purification of diluted crude wet process phosphoric acid by means of heating in the presence of tar oils or tar derivatives followed by filtration. Rubin (75) has described a chemical process producing a low impurity phosphoric acid which uses either phosphate rock, normal superphosphate, or triple superphosphate as a raw material in conjunction with either sulfuric acid or ammonium sulfate. An unnamed solvent is employed for the purpose of extracting the phosphoric acid in one of the processing steps.

A number of references may be found in the literature which are concerned with the study of phenomena occurring in the water-phosphorus oxide-calcium oxide system. Many references deal with equilibrium solubility in this system at various temperatures (3, 7, 8, 11, 22, 23, 36, 44, 58, 69). Elmore and Farr (23) worked on a very thorough equilibrium

solubility study of this system. A few papers have studied equilibrium solubilities in the water-phosphorus oxide-calcium oxide system to which ammonium and nitrate ions have been added (24, 25, 26). Equilibrium solubility in the water-phosphorus oxide-calcium oxide-sulfur trioxide system has been investigated (17, 18) as has equilibrium solubility in the water-phosphorus oxide-calcium oxide-magnesium oxide system (9, 10). The formation of ion pairs in the water-phosphorus oxide-calcium oxide system has been studied at different temperatures (53, 59). The growth of dicalcium phosphate crystals from aqueous solution in the water-phosphorus oxide-calcium oxide system and the solubility of dicalcium phosphate dihydrate have been investigated (20, 48, 65). Peacock and Nickless (68) have studied the dissociation of pure phosphoric acid in water at various temperatures. The vapor pressure of monocalcium phosphate monohydrate as a function of temperature and its heat of dissociation were determined by Sorokin (84).

It is known that the dissociation of monocalcium phosphate to phosphoric acid and dicalcium phosphate occurs to a limited degree in water. Kharakoz (42) showed that the dissociation of monocalcium phosphate in water proceeds according to an ionic mechanism while Stollenwerk (85) showed that the dissociation proceeds at a unimolecular reaction rate. Guillaume (32) showed that the conversion of monocalcium phosphate in water to phosphoric acid and dicalcium phosphate increases with increasing temperature while Pozin et al. (70) showed that not only does conversion to phosphoric acid and dicalcium phosphate increase as the reaction temperature is increased from 20°C to 80°C but the reaction is essentially complete after ten minutes. Pozin et al. (70) worked with

a monocalcium phosphate/water weight ratio of 1.5. Belopolskii et al. (11) and Sanfourche and Focet (77, 78) showed that the conversion of monocalcium phosphate to phosphoric acid and dicalcium phosphate in water increases as the concentration of the monocalcium phosphate reactant is increased.

Methods for producing dicalcium phosphate and sometimes phosphoric acid have been developed which employ a process involving the leaching of normal superphosphate or triple superphosphate with water (17, 40, 55, 71). In these processes monocalcium phosphate, the chief chemical constituent of normal superphosphate and triple superphosphate, is dissolved in the water leach. The dissolved monocalcium phosphate subsequently dissociates to dicalcium phosphate and a weak solution containing phosphoric acid, unreacted monocalcium phosphate, and water soluble impurities contained in the original superphosphate prior to leaching. It is believed that dissociation of superphosphate (or monocalcium phosphate) in the presence of an organic solvent will be superior to the method described above because of higher resultant conversion to dicalcium phosphate and phosphoric acid and because a more concentrated phosphoric acid product results that contains lower amounts of solubilized impurities.

Methods have been described for producing a dicalcium phosphate product by neutralizing the water leach of either normal superphosphate or triple superphosphate with calcium hydroxide (49, 51, 56, 86). A patent has been assigned to Boylan and Feng (16) that describes the preparation of a dicalcium phosphate fertilizer by the direct sulfuric acid acidulation of phosphate rock. A patent assigned to the Iowa State College Research Foundation, Inc., (41) describes the production of a

fertilizer composed of monocalcium and dicalcium phosphates that is made by heating a mixture of phosphate rock and monocalcium phosphate to cause dissociation of the latter and reaction of the resulting phosphoric acid with the phosphate rock.

A few studies have been made concerned with the dissociation of monocalcium phosphate in the presence of organic solvents. Boulle and Dupin (15) have investigated the action of organic compounds upon solutions of monometallic orthophosphates. During their experiments reagent grade monocalcium phosphate was dissolved in water and treated with oxygenated organic compounds such as acetone, ethanol, dioxane, and tetrahydrofuran. The addition of the oxygenated organic compound caused the monocalcium phosphate to dissociate into a dicalcium phosphate precipitate and phosphoric acid which remained soluble. It was found that dioxane and acetone caused the anhydrous crystalline form of dicalcium phosphate to precipitate while ethanol caused the precipitation of dicalcium phosphate dihydrate. A patent has been assigned to The Societe Anon Potasse et Engrais Chimiques (82) that describes the production of dicalcium phosphate by leaching superphosphate with water followed by the subsequent dissociation of monocalcium phosphate dissolved in the leach into dicalcium phosphate and phosphoric acid after treatment with an organic solvent such as ethanol, dioxane, acetone or tetrahydrofuran. The phosphoric acid is then separated and recycled with sulfuric acid to treat natural phosphates. A patent assigned to Bennett (12) describes the preparation of dicalcium phosphate and phosphoric acid by heating moncalcium phosphate in the presence of an organic compound such as butanol or pentanol. A patent assigned to Goulding Fertilisers, Ltd., (31)

discusses a chemical process for the production of monopotassium phosphate by a route involving the methanolic dissociation of potassium phosphate. By-product phosphoric acid is recycled to the front end of the process where it is used to attack phosphate rock along with potassium bisulfate.

A good discussion of the wet process method for the manufacture of phosphoric acid may be found in Slack (81) and Noyes (67). Van Wazer (87) has a good review of the physical and chemical properties of orthophosphoric acid and its calcium salts and, in addition, describes their manufacture. Bjerrum (14) discusses the preparation and properties of several calcium orthophosphates. A patent assigned to Newton (66) describes the manufacture of monocalcium phosphate from phosphate rock and phosphoric acid whereas Marshall et al. (52) discuss the factors affecting the reaction of phosphate rock and phosphoric acid to form monocalcium phosphate. The solubility of apatite in the system water-phosphorus oxide-calcium oxide at several temperatures was investigated by Krasnov (44). Frey and Bye (28) have studied the kinetics and mechanism of the reaction of phosphoric acid and tricalcium phosphate. Hill et al. (37) have investigated the thermal decomposition of monocalcium phosphate to produce acid pyrophosphate and acid metaphosphate.

CHAPTER II

EXPERIMENTAL PROCEDURES AND MATERIALS

Equipment and Experimental Procedures

The equipment and procedures that were employed during the experimental portion of this work are described below.

Preparation of Wet Process Orthophosphoric Acid

Wet process orthophosphoric acid was prepared for subsequent use by the chemical attack of sulfuric acid on acidulation grade ground phosphate rock from either Florida or North Carolina. Wet process orthophosphoric acid was also prepared by chemical digestion with sulfuric acid of the dried dicalcium phosphate residues resulting from the previous dissociations of monocalcium phosphate in the presence of an organic solvent. In all preparations of wet process phosphoric acid, conditions were employed such that gypsum or the dihydrate form of calcium sulfate resulted in the reaction slurry.

Two-gallon batches of wet process phosphoric acid containing around 30 percent P_2O_5 were made in a 316 stainless steel reaction vessel with a volumetric capacity of around seven gallons. Predetermined amounts of the reactants sulfuric acid, acidulation grade ground phosphate rock, and water as required by the stoichiometry of the wet process phosphoric acid reaction were weighed to the nearest ounce. Assuming P_2O_5 losses of 3.5 percent due to undigested phosphate rock, the amount of technical grade sulfuric acid used was based on the amount

of H_2SO_4 required to produce a phosphoric acid containing a residual free two percent sulfate content after digesting 96.5 percent of the phosphate in the ground phosphate rock. Wet process acid containing around 25 percent P_2O_5 which had been prepared previously using the same reactants and reaction conditions was also weighed to the nearest ounce using an amount corresponding to 30 weight percent of the total reactor charge. This wet process phosphoric acid was used to dilute the reaction slurry and its use is analogous to the commercial procedure of recycling weak acid from the filter cake wash section of the filters along with some filtered strong acid as a reaction slurry diluent.

The reaction procedure was initiated by adding the water, ground phosphate rock and recycled phosphoric acid reactants to the seven gallon reactor while vigorously agitating its contents. Reactor agitation was accomplished by using a variable speed Model 8 stirrer equipped with a two-bladed, five inch diameter propeller manufactured by the Eastern Industrial Division of LFE. After 15 minutes agitation, the technical grade sulfuric acid was added slowly over a period of one hour while vigorously agitating the reaction vessel contents. In order to prevent the formation of calcium sulfate hemihydrate, the temperature of the reaction slurry was never allowed to rise above 80°C during sulfuric acid addition. After the addition of sulfuric acid reactant had been completed, the temperature of the vigorously agitated reaction slurry was maintained between 75°C and 80°C by heating with a large hot plate. In order to insure a high phosphate rock digestion efficiency and the growth of easily filterable gypsum crystals, a total digestion period of six hours was allowed from the initial mixing of the rock, water, and re-

cycled acid until filtration was started.

The reaction magma was filtered in a 24 centimeter diameter polypropylene filter funnel through Whatman Number 1 filter paper into a four liter pyrex filter flask using water aspiration to provide a vacuum in the filtrate receiver. A volume of reaction magma was filtered such that a gypsum cake thickness of between two and three inches resulted. After filtration of the reaction slurry, the filter funnel and cake were transferred to another four liter pyrex filter flask and the filter cake was washed by adding enough wash water to cover the cake to a depth of about two inches. The resulting filtrate was retained for use as a reaction slurry diluent in subsequent wet process phosphoric acid preparations.

Some wet process orthophosphoric acid containing around 30 percent P_2O_5 prepared from ground phosphate rock in the manner described above was concentrated to merchant grade strength (54 percent P_2O_5) by means of vacuum evaporation for use in subsequent experimentation. Approximately two liters of wet process acid containing around 30 percent P_2O_5 were placed in a three-necked, four liter pyrex boiling flask which was heated with an electric mantle and which was agitated by a two-bladed propeller driven by an electric motor. A water-cooled glass condenser was connected to the water vapor outlet which eventually discharged the water condensate into a two-necked flask. A vacuum was drawn on the condensate receiver by attaching a connection to a water aspirator. The agitated contents of the boiling flask were heated to the boiling point after drawing a vacuum on the system. Water evaporation was continued until the volume of water condensate had reached a predetermined level commensurate with the desired final concentration of the phosphoric acid.

The concentrated phosphoric acid was subsequently analyzed for various chemical species.

Wet process orthophosphoric acid was also prepared by the sulfuric acid digestion of the dried dicalcium phosphate residues resulting from monocalcium phosphate dissociation reactions in the presence of an organic solvent. Predetermined amounts of technical grade sulfuric acid, ground dicalcium phosphate, and water as required by the stoichiometry of the reaction were weighed to the nearest one-tenth of a gram. Assuming P_2O_5 losses of 3.5 percent due to undigested dicalcium phosphate, the amount of technical grade sulfuric acid used was based on the weight of H_2SO_4 required to produce a phosphoric acid containing a residual free two percent sulfate content after converting 96.5 percent of the phosphate in the ground dicalcium phosphate. Wet process acid containing 25 percent P_2O_5 which had been prepared previously using the same reactants and reaction conditions was also weighed to the nearest one-tenth gram using an amount corresponding to 25 weight percent of the total reactor charge. This wet process phosphoric acid was used to dilute the reaction slurry so that its solids content was about that of the reaction slurry encountered in commercial wet process acid manufacture.

The reaction procedure was initiated by adding the water, ground dicalcium phosphate, and recycled phosphoric acid reactants to a 600 milliliter pyrex beaker while vigorously agitating its contents with a magnetic stirring bar. After 15 minutes agitation, the technical grade sulfuric acid was added slowly over a period of an additional 15 minutes while vigorously agitating the contents of the beaker. The temperature of the reaction slurry was never allowed to rise above 80°C in order to

prevent the formation of calcium sulfate hemihydrate. After completion of the sulfuric acid addition, the temperature of the vigorously agitated reaction slurry was maintained between 75°C and 80°C using a combination hot plate-magnetic stirrer. In order to insure a high P_2O_5 digestion efficiency and the growth of easily filterable gypsum crystals, a total digestion period of six hours was allowed from the initial mixing of the dicalcium phosphate, water, and recycled acid until slurry filtration was initiated.

The reaction slurry was filtered in a 7 centimeter diameter Buchner filter funnel through Whatman Number 1 filter paper into a 500 milliliter pyrex filter flask using water aspiration to provide a vacuum in the filtrate receiver. The thickness of the resulting filter cake was between one and two inches. The time required for filtration was recorded to be used for the determination of the filtration rate. After filtration of the reaction slurry, the filter funnel containing the cake was then transferred to another filter flask and the filter cake was washed with enough distilled water to leach the remaining water soluble P_2O_5. The washed gypsum filter cake was oven dried, weighed, and chemically analyzed for P_2O_5 in order to determine the amount of undigested phosphate. The phosphoric acid filtrate was also weighed and then chemically analyzed for various species.

Preparation of Monocalcium Phosphate and Monocalcium Phosphate/Gypsum Slurries

Batches of monocalcium phosphate slurry containing approximately 32 percent P_2O_5 were prepared by reacting acidulation grade ground phosphate rock from either Florida or North Carolina with wet process acid containing about 30 percent P_2O_5 which had been previously prepared from ground

phosphate rock from either Florida or North Carolina, respectively. The wet process acid was weighed to the nearest one-tenth gram in a tared 316 stainless steel reaction beaker large enough to contain the monocalcium phosphate slurry product. The phosphoric acid was heated with a hot plate to 80°C while agitating with either a magnetic stirrer or propeller type mixer. A weighed amount of ground phosphate rock corresponding to that required for the theoretical CaO/P_2O_5 ratio of monocalcium phosphate was then added slowly to the hot agitated acid over a period of 15 minutes in order to minimize foaming and local concentration gradients. The resultant slurry was agitated for two hours total time while maintaining the temperature at 80°C. The resulting monocalcium phosphate slurry was subsequently analyzed for various chemical species.

A slurry containing a mixture of monocalcium phosphate and gypsum was prepared by reacting ground phosphate rock, technical grade sulfuric acid, water, and previously prepared wet process orthophosphoric acid containing about 30 percent P_2O_5. The resulting slurry was then subsequently used in an experiment to investigate the dissociation phenomenon in normal superphosphate. Predetermined amounts of each of the reactants were weighed to the nearest one-tenth gram. The wet process phosphoric acid, water, and ground phosphate rock were added to a 400 milliliter pyrex beaker and these three reactants were vigorously agitated with a magnetic stirrer for five minutes. The technical grade sulfuric acid was then slowly added over a 15 minute period and the entire mixture was then heated to 80°C with a hot plate while vigorous agitation continued for the remainder of the reaction period. The slurry was then submitted to subsequent experimentation two hours after the initial mixing of the

phosphoric acid, water, and ground phosphate reactants.

Drying of Wet Slurries and Filter Cakes

Portions of the batches of monocalcium phosphate slurries containing approximately 32 percent total P_2O_5 were dried and used for subsequent experimentation. An amount of the monocalcium phosphate slurry was weighed in a tared beaker and placed in a Thelco Model 17 oven manufactured by the Precision Scientific Company. The temperature of the oven could be controlled within ± 2°C of the desired temperature. The total weight of the beaker and drying slurry was checked periodically until the weight of the slurry had dropped to a point corresponding to the desired P_2O_5 concentration. Monocalcium phosphate slurry was concentrated up to a total P_2O_5 content of 47 percent at a temperature of 105°C. However, in order to dry the slurry to a total P_2O_5 content in excess of 47 percent, it was necessary in some cases to increase the drying temperature to as high as 200°C. The period required for drying the slurry to a desired P_2O_5 concentration ranged from four hours to 22 days.

The gypsum filter cakes resulting from the preparation of wet process phosphoric acid and the dicalcium phosphate filter cakes resulting from the dissociation of monocalcium phosphate in the presence of an organic solvent were dried overnite at 105°C in a Thelco Model 17 oven.

Particle Size Reduction of Materials

During the course of this work, it was occasionally necessary to reduce the particle size of some of the solid materials. Substances such as North Carolina phosphate rock, dried monocalcium phosphate slurry, and the dried dicalcium phosphate residues resulting from monocalcium phosphate

dissociation reactions had to be subjected to a particle size reduction procedure.

Small amounts of easily ground material such as dried monocalcium phosphate and dried dicalcium phosphate residue were pulverized by hand with a mortar and pestle until the largest particle passed through a U. S. Standard 18 mesh screen (1.00 millimeter diameter).

A Mikro Sample Mill manufactured by the Pulverizing Machinery Company was used to grind the North Carolina flotation concentrate and larger amounts of monocalcium phosphate slurry which had been dried so that its P_2O_5 content was 47 weight percent. The flotation concentrate was passed repeatedly through the mill until 70 weight percent of the ground phosphate rock passed through a 200 mesh U. S. Standard screen (0.074 millimeter diameter). The dried monocalcium phosphate was ground with the mill until the largest particle passed through a U. S. Standard 18 mesh screen (1.00 millimeter diameter).

Monocalcium Phosphate Dissociation Experiments

The dissociation of monocalcium phosphate in the presence of an organic solvent was studied using various reaction time periods, reaction temperatures, and organic solvents. A three-necked pyrex flask with a capacity of 500 milliliters was used for the dissociation studies. A two-bladed propeller and shaft made of 316 stainless steel and driven by an electric motor was inserted in the center neck while the two off-center necks were used for a reflux condenser and sample port. Approximately 100 grams of the monocalcium phosphate reactant were weighed into the flask and the flask was then placed in a water bath which had been pre-set at the desired reaction temperature. A Blue M Electric Company

Model MR-3262A water bath was used with the capability of maintaining the bath temperature within ± 0.1°C of a temperature between 0°C and 90°C. A quantity of organic solvent corresponding to the desired solvent/monocalcium phosphate P_2O_5 ratio was weighed into a flask and the solvent was then heated on a steam bath to the desired reaction temperature. The heated solvent was transferred to the reaction flask and vigorous agitation was started immediately. The agitator was rotated at 425 revolutions per minute as measured by a stroboscopic method. The temperature of the agitated slurry was checked periodically. Samples of the agitated slurry were withdrawn from the flask at various time intervals using a 25 milliliter pipette whose tip had been removed so that any large solid particles in the slurry would not be prevented from being sampled. The sample was immediately filtered through a porous porcelain Selas crucible which retained particles larger than nine microns using a water aspirator to pull a vacuum on the filtrate receiver. A filter cake thickness of approximately one inch resulted. After recording the time required for filtration of the slurry to be used for calculation of the filtration rate, the resulting filter cake was washed with a very small amount of ambient temperature solvent used in the reaction. The filter cake was dried at 105°C and the filtrate was quantitatively transferred to a beaker from which the solvent was evaporated by the use of an infrared lamp. Both filter cake and filtrate were subsequently analyzed for various chemical species.

In some cases, it was desirable to filter the entire content of the reaction flask instead of a small sample of reaction slurry. During these experiments, the reaction was performed in a manner exactly as

described above until the desired reaction time period had been achieved. At this time, the reaction flask was quickly removed from the water bath and the slurry was filtered in a nine centimeter diameter Buchner funnel through Whatman Number 42 filter paper while using a water aspirator to provide the vacuum in the filtration flask. The filter cake was washed with a very small amount of ambient temperature solvent used in the reaction. The time required to filter the slurry was measured to be subsequently used to calculate the filtration rate. Since it was desirable to recover all the solvent in the filtrate, the filter flask was immersed in an ice water bath to minimize solvent evaporation due to the boiling of the hot filtrate under reduced pressure. As a further measure to maximize filtrate solvent recovery, any solvent vapors escaping the filtrate receiver were condensed in another flask immersed in ice water downstream of the filtrate receiver before the water aspirator.

Some experimental runs were performed during which wet process phosphoric acid, ground phosphate rock, and various organic solvents were agitated together in an attempt to produce a low impurity phosphoric acid product. Essentially the same procedure outlined above was used for these experiments. An amount of ground phosphate rock was weighed into the boiling flask and a quantity of wet process phosphoric acid corresponding to the amount required to form monocalcium phosphate was weighed separately. A quantity of the organic solvent corresponding to the desired solvent/total P_2O_5 ratio and the phosphoric acid were mixed and heated to the desired reaction temperature. The heated solvent and phosphoric acid solution were then transferred to the reaction flask and vigorous agitation was started immediately. The subsequent details of these experiments parallel

the procedure outlined above exactly.

A few experimental runs were made during which dissociation was attempted of monocalcium phosphate that had been dried at a temperature high enough to expel water of constitution. The dried and ground monocalcium phosphate was weighed into a three-necked flask and an amount of organic solvent corresponding to the desired ratio of solvent/total P_2O_5 was heated to the desired reaction temperature after addition to the solvent of a predetermined amount of distilled water to aid the dissociation reaction. The heated solvent and water solution were then transferred to the reaction flask and vigorous agitation was immediately started. The subsequent details of these experimental runs parallel the procedure described above exactly.

Fractionation of the Monocalcium Phosphate Dissociation Filtrate

In some experiments, it was desired to separate the organic solvent from the low impurity phosphoric acid product in the filtrate resulting from the dissociation of monocalcium phosphate. The filtrate was batch distilled at atmospheric pressure using a vertically arranged glass Vigreaux column 475 millimeters in length to produce a sharp separation of phosphoric acid and recovered solvent. The column overhead temperature was constantly monitored with a high precision mercury thermometer and not allowed to rise more than 0.2°C above the boiling point of the pure solvent at the prevailing atmospheric pressure. The prevailing atmospheric pressure was determined with a mercurial barometer. The distilled solvent was condensed in a water cooled condenser and recovered in a flask. Heat was applied to the glass boiling pot with a heating mantle at a rate such that the rate of reflux returning to the pot was

about twice the rate of distillate production. The distillation was terminated when the overhead vapor temperature started to rise more than the allowed 0.2°C above the pure solvent boiling point. A sample of the low impurity product orthophosphoric acid after solvent distillation was chemically analyzed for various constituents.

Materials

A number of different materials were used in this study.

Organic Solvents Used for Monocalcium Phosphate Dissociation

The organic solvents used in the monocalcium phosphate dissociation experiments were obtained from various sources. Some solvents were reagent grade materials while others were commercial grade industrial chemicals. A summary of the cost of the different solvents in commercial quantities is shown in Table 2.

Methanol. Certified ACS reagent grade absolute methanol from the Fisher Scientific Company was used in this study.

Ethanol. The ethanol used in this work was a denatured, anhydrous solvent obtained from Will Scientific, Inc. Each 100 volumetric parts of absolute ethanol were denatured with five volumetric parts of ethyl acetate and one volumetric part of gasoline.

Normal Propanol. The normal propanol used in this work was an anhydrous reagent grade chemical obtained from the J. T. Baker Chemical Company.

Normal Butanol. The normal butanol used for this study was a technical grade chemical obtained from the Fisher Scientific Company.

Iso-pentanol. The iso-pentanol used in this work was a technical grade amyl alcohol containing 85 percent iso-pentanol supplied by the

Table 2. Bulk Price of Commercial Organic Solvents Purchased by Tankcar (19).

Organic Solvent	Price, Dollars per Pound	Pricing Basis
Methanol	0.02	Freight on Board, Gulf Coast Producer
Ethanol, Denatured SD1	0.10	Delivered, Eastern USA
Normal Propanol	0.13	Delivered
Normal Butanol	0.12	Freight Allowed
Primary Pentanol, Mixed Isomers	0.18	Freight Allowed
Normal Hexanol	0.13	Freight Allowed
2-Methyl Pentanol	0.16	Delivered
Normal Octanol	0.25	Freight Allowed, Eastern USA
2-Ethyl Hexanol	0.11	Delivered
Normal Decanol	0.24	Freight Allowed, Eastern USA
Normal Dodecanol	0.26	Freight Allowed
Acetone	0.06	Delivered, Eastern USA
Methyl Butyl Ketone	0.14	Delivered
Tetrahydrofuran	0.37	Delivered, Eastern USA

Fisher Scientific Company.

Normal Hexanol. The normal hexanol used in this work was a commercial chemical with a trade name of Alfol 6 obtained from the Continental Oil Company. By chemical analysis, this material contained the following chemical species: 0.04 weight percent butanols, 99.3 weight percent normal hexanol, 0.3 weight percent octanols, and 0.09 weight percent water.

2-Methyl Pentanol. The 2-methyl pentanol used in this study was an industrial grade material supplied by Eastman Chemical Products, Inc. Some properties of this material specified by the manufacturer are listed here. Water content is 0.30 weight percent maximum. The distillation range at one atmosphere is between 142.0°C and 150.0°C. The specific gravity at 20°C relative to water at 20°C is between 0.820 and 0.825.

Normal Octanol. The normal octanol used in this work was a commercial chemical with a trade name of Alfol 8 obtained from the Continental Oil Company. By chemical analysis, this material contained the following chemical species: 0.02 weight percent hexanols, 99.5 weight percent normal octanol, 0.03 weight percent decanols, and 0.03 weight percent water.

2-Ethyl Hexanol. The 2-ethyl hexanol used in this study was an industrial grade material supplied by Eastman Chemical Products, Inc. Some properties of this material specified by the manufacturer are listed here. The specific gravity at 20°C relative to water at 20°C is between 0.8325 and 0.8345.

CO-898. The CO-898 used in this study is an industrial chemical obtained from the Procter and Gamble Company. Chemical analyses specified

by the manufacturer are listed here. The material contains a minimum of 98.0 weight percent octanols and maximum concentrations of hexanols, decanols, and dodecanols of 2.0 weight percent, 2.0 weight percent and 0.5 weight percent, respectively. The maximum concentration of water in the material is 0.1 weight percent.

Umbrex N. Umbrex N, a substance used in this work, is a commercial material obtained from the Procter and Gamble Company. Chemical analyses specified by the manufacturer are listed here. The material contains a maximum concentration of hexanols, dodecanols, and water of 6.0 weight percent, 1.0 weight percent and 0.1 weight percent, respectively. The octanol content ranges from 51 to 58 weight percent while the decanol content ranges from 34 to 42 weight percent. A typical chemical analysis is as follows: 4.0 weight percent hexanols, 56.0 weight percent octanols, 39.0 weight percent decanols, and 0.04 weight percent moisture.

Normal Decanol. The normal decanol used in this work was a commercial chemical with a trade name of Alfol 10 obtained from the Continental Oil Company. By chemical analysis, this material contained the following chemical species: 99.4 weight percent normal decanol, 0.6 weight percent dodecanols, and 0.03 weight percent water.

Normal Dodecanol. The normal dodecanol used in this work was a commercial chemical with a trade name of Alfol 12 supplied by the Continental Oil Company. By chemical analysis, this material contained the following chemical species: trace amounts of hexanols, octanols, and decanols, 98.4 weight percent normal dodecanol, 0.2 weight percent tetradecanols, and 0.03 weight percent water.

Acetone. The acetone used in this work was a reagent grade

chemical obtained from Merck and Company, Inc., which conformed to ACS specifications.

Methyl Butyl Ketone. The methyl butyl ketone used in this study was an industrial grade material supplied by Eastman Chemical Products, Inc.

Tetrahydrofuran. Certified tetrahydrofuran from the Fisher Scientific Company was used in this study. This material had a boiling range of 65.9°C to 66.1°C and a moisture content of 0.02 weight percent.

Phosphate Rock Materials

Two types of phosphate rock were used in this work. The phosphate rock from Florida was obtained in a form already ground to an acidulation grade. The North Carolina phosphate rock obtained from the Texas Gulf Sulfur Company was a flotation concentrate which was subsequently pulverized to an acidulation grind before usage in this work. Both types of rock were dried at 105°C before using. Tables 3 and 4 show the chemical composition and particle size distribution, respectively, of these ground phosphate rock materials.

Wet Process Orthophosphoric Acids

The wet process orthophosphoric acids used in this work were prepared by the acidulation with sulfuric acid of ground phosphate rock from either Florida or North Carolina. A portion of the wet process phosphoric acid prepared from Florida phosphate rock was concentrated to merchant grade strength for usage in subsequent experimentation. The chemical composition of these phosphoric acids is shown in Table 3.

Monocalcium Phosphate Materials

Impure monocalcium phosphate containing various amounts of free

Table 3. Chemical Composition of Experimental Phosphatic Materials.

Material Description	Composition, Weight Percent									
	Water Soluble P_2O_5	Citrate Insoluble P_2O_5	Total P_2O_5	CaO	Al_2O_3	Fe_2O_3	MgO	F	Free Water	Water of Crystallization Plus Free Water
Ground Florida phosphate rock	-	-	34.28	49.50	1.28	1.33	0.25	3.84	0.00	-
Ground North Carolina phosphate rock	-	-	32.93	54.01	0.80	0.87	0.27	3.99	0.00	-
Wet process acid from Florida rock (I)	-	-	30.99	0.13	0.66	1.18	0.30	1.91	-	-
Wet process acid from Florida rock (II)	-	-	28.30	0.04	0.43	1.16	0.28	1.81	-	-
Concentrated wet process acid from Florida rock	-	-	52.11	0.23	1.19	2.03	0.58	0.81	-	-
Wet process acid from North Carolina rock	-	-	26.93	0.10	1.47	2.09	0.52	1.30	-	-
Undried MCP from Florida rock (I)	30.36	0.52	31.86	13.13	0.98	1.20	0.21	2.46	32.69	36.11
Undried MCP from Floride rock (II)	30.53	0.49	32.58	13.48	0.77	1.24	0.30	2.53	32.21	36.93
Dried MCP from Florida rock	-	-	34.97	14.46	0.83	1.33	0.32	-	-	32.31
Dried MCP from Florida rock	-	-	38.04	15.74	0.90	1.45	0.35	-	-	26.36
Dried MCP from Florida rock	-	-	41.17	17.03	0.98	1.56	0.38	-	-	20.30

Table 3. (Continued)

Material Description	Composition, Weight Percent									
	Water Soluble P_2O_5	Citrate Insoluble P_2O_5	Total P_2O_5	CaO	Al_2O_3	Fe_2O_3	MgO	F	Free Water	Water of Crystallization Plus Free Water
Dried MCP from Florida rock	-	-	43.97	18.19	1.04	1.67	0.41	-	-	14.89
Dried MCP from Florida rock (I)	46.57	0.12	47.00	19.40	1.67	2.09	0.49	2.68	0.74	6.83
Dried MCP from Florida rock (II)	45.19	0.48	47.17	19.98	1.60	2.13	0.45	1.89	0.20	7.34
Dried MCP from Florida rock	-	-	49.97	20.70	1.77	2.22	0.52	-	0.00	0.95
Dried MCP from Florida rock	-	-	52.55	21.74	1.25	2.00	0.49	-	0.00	0.00
Dried MCP from Florida rock	-	-	53.74	22.23	1.28	2.04	0.50	-	0.00	0.00
Dried MCP from Florida rock	-	-	56.08	23.11	1.72	2.11	0.37	-	0.00	0.00
Dried MCP from Florida rock	-	-	57.41	23.75	1.36	2.18	0.53	-	0.00	0.00
Dried MCP from North Carolina rock	43.84	1.24	46.60	19.36	1.83	2.54	0.80	1.32	1.56	6.50

Table 4. Particle Size Distribution of Experimental Phosphatic Materials.

Material Description	Cumulative Weight Percentage of Material Retained by U.S. Standard Screen						
	18	20	35	50	60	100	200
Ground Florida phosphate rock	-	0.03	0.05	0.23	0.48	2.57	27.60
Ground North Carolina phosphate rock	-	0.00	0.05	0.10	0.10	0.15	30.90
Dried MCP from Florida rock containing 47% P_2O_5 (I)	0.00	-	24.30	43.90	47.50	63.90	-
Dried MCP from Florida rock containing 47% P_2O_5 (II)	0.00	-	23.50	40.40	46.70	60.00	-
Dried MCP from North Carolina rock containing 47% P_2O_5	0.00	-	26.70	45.90	48.10	62.50	-

water were used during the course of this study. All monocalcium phosphate material were initially prepared by reacting ground phosphate rock from either Florida or North Carolina with wet process phosphoric acid containing approximately 30 weight percent P_2O_5 which had been produced using ground phosphate rock from the same region. Portions of this impure monocalcium phosphate slurry, which contained approximately 32 weight percent P_2O_5, were dried so that the resultant monocalcium phosphate material contained from 35 to 57 weight percent P_2O_5. Those dried monocalcium phosphate materials that were dry enough were ground so that the largest particle passed through a U. S. Standard 18 mesh screen. The chemical composition and particle size distribution of these monocalcium phosphate materials are shown in Table 3 and Table 4, respectively.

Two batches of impure monocalcium phosphate containing approximately 32 weight percent P_2O_5 were prepared from Florida ground phosphate rock and acid. Batch I undried monocalcium phosphate slurry containing 31.86 weight percent total P_2O_5 was used as the reactant for the dissociation experiments involving the following organic solvents: methanol, ethanol, normal propanol, normal butanol, iso-pentanol, normal hexanol, normal octanol, normal decanol, normal dodecanol, acetone, and tetrahydrofuran. Batch II undried monocalcium phosphate slurry which contained 32.58 weight percent total P_2O_5 was used as the reactant for the dissociation experiments involving 2-methyl pentanol, 2-ethyl hexanol, CO-898, Umbrex N, and methyl butyl ketone solvents. In addition, Batch II undried slurry was dried to product monocalcium phosphate containing from 35 to 57 weight percent total P_2O_5 including the first batch of monocalcium phosphate containing 47.00 weight percent total P_2O_5.

Two batches of impure monocalcium phosphate containing approximately 47 weight percent total P_2O_5 were prepared from Florida ground phosphate rock and acid. Batch I dried monocalcium phosphate containing 47.00 weight percent total P_2O_5 was used as a reactant for the initial exploratory dissociation experiments involving methanol, normal hexanol and normal octanol solvents. Batch II dried monocalcium phosphate containing 47.17 weight percent total P_2O_5 was used as a reactant in the initial exploratory dissociation experiment involving acetone and was also used as a reactant in the continuous process simulation experiments involving methanol and acetone solvents.

Miscellaneous Chemicals and Materials

A number of miscellaneous chemicals and materials that fail to be grouped within any of the classifications listed above were used for the study.

The sulfuric acid that was used for digesting ground phosphate rock during the preparation of wet process orthophosphoric acid was a 66° Baume technical grade acid containing 93.1 weight percent H_2SO_4. This material was obtained from the Fisher Scientific Company.

The acids used in digesting experimental samples in preparation for chemical analysis and the numerous chemicals used in analyzing these samples for the various chemical species were all reagent grade chemicals obtained from the Fisher Scientific Company, Will Scientific, Inc., or J. T. Baker Chemical Company. These chemicals include buffering reagents, precipitation reagents, indicators, and titration reagents.

General Description of the Chemical Analytical Methods

A brief general description of the analytical methods employed for the purpose of analyzing for various chemical species is given here. Whenever possible, analytical methods were used which have been approved and adopted by the Association of Official Agricultural Chemists (39).

Analysis for Phosphorus

There were three types of analyses which were used in this work to determine phosphorus content.

Total Phosphorus. The Association of Official Agricultural Chemists (AOAC) official method 9 was employed for this analysis (39). This volumetric ammonium molybdate method basically involves digesting the sample in aqua regia followed by the precipitation of the phosphorus in a suitable aliquot using ammonium molybdate as the precipitation reagent. The precipitate is then washed and titrated with standard sodium hydroxide solution to a phenolphthalein end point.

Water Soluble Phosphorus. The AOAC official method was employed for this analysis (39). The method basically involves leaching the water soluble phosphorus from a weighed sample of the solid material with distilled water. The water leach is analyzed for phosphorus using the volumetric ammonium molybdate method described above for total phosphorus.

Citrate Insoluble Phosphorus. The AOAC official method 10 was employed for this analysis (39). The method basically involves dissolving phosphorus from a weighed sample of the solid in hot neutral ammonium citrate solution after removing the water soluble phosphorus. The

remaining citrate insoluble phosphorus in the sample is then digested in aqua regia and analyzed for phosphorus using the volumetric ammonium molybdate method described above for total phosphorus.

Analysis for Calcium

The AOAC official method 33 was employed for this analysis (39). This analysis for water soluble calcium basically involves digesting the sample in aqua regia followed by the precipitation of the calcium in a suitable aliquot using ammonium oxalate as the precipitating reagent. The calcium oxalate precipitate is then washed and titrated with standard potassium permanganate solution.

Analysis for Iron and Aluminum

A spectrophotometric method using ferron was employed for these analyses. This method of analysis for iron and aluminum basically involves digesting the sample in aqua regia followed by the neutralization to a pH of 5.5 of an appropriate sample aliquot. Ferron (8-hydroxy-7-iodo-5-quinoline sulfonic acid) is used to develop a color with iron and aluminum ions in a buffered solution. Light absorption at appropriate wave lengths was measured with a Bausch and Lomb Spectronic 20 spectrophotometer and compared with standard curves.

Analysis for Magnesium

The AOAC official method 36 was employed to analyze for acid soluble magnesium (39). This gravimetric method essentially involves digesting the sample in aqua regia followed by the removal of calcium by precipitation as calcium oxalate. Diammonium phosphate is then added to the solution to precipitate the magnesium present as acidic magnesium phosphate. After washing the precipitate, water of constitution is expelled by cremation

in a muffle furnace. The remaining precipitate is weighed as magnesium pyrophosphate.

Analysis for Fluorine

The AOAC official method 9 for fluorine in pesticides was employed for this analysis (39). This distillation method essentially involves digesting a weighed sample with perchloric acid in a Claisen distilling flask while stripping the evolved hydrogen fluoride with steam. The hydrogen fluoride is absorbed in sodium hydroxide and then titrated with standard thorium nitrate solution.

Analysis for Free Water

The AOAC official method 5 was used for this analysis (39). This vacuum desiccation method essentially involves drying a weighed sample of the solid over anhydrous magnesium perchlorate at ambient temperature under an absolute pressure of nine inches of mercury.

Analysis for Free Water Plus Water of Crystallization

A method developed by Hill and Jacob (38) was used for this analysis. The method basically involves drying a weighed sample for 24 hours at 105°C.

Analysis for Particle Size Distribution

Particle size distributions were determined by using a screening method. The method basically involves screening a weighed sample through a set of standard screens using a successively decreasing grid size. A mechanical device called a Ro-Tap is used to facilitate the passage of sample particles through the screen openings.

CHAPTER III

EXPERIMENTAL RESULTS AND DISCUSSION

Exploratory Experimentation

A number of exploratory experimental runs were made to investigate the dissociation of crude commercial monocalcium phosphate in the presence of various organic solvents. The data resulting from these experiments were used to evaluate the relative merits of each organic solvent when used in the dissociation of crude commercial monocalcium phosphate.

Condensed data which resulted from these exploratory experimental runs are presented in Tables 5 and 6. The detailed results are given in Appendix A. Table 5 shows, at various reaction conditions, the average P_2O_5 yield in the product phosphoric acid and the average concentration of the major cation impurities in product phosphoric acid containing 54 percent P_2O_5 along with the average filtration rate of the dissociation slurry which resulted from the dissociation with various organic solvents of crude monocalcium phosphate prepared from Florida phosphate rock. Table 6 presents analogous data for phosphoric acid produced by the dissociation with methanol and acetone of crude monocalcium phosphate prepared from North Carolina phosphate rock. These tables also show the solvent P_2O_5 ratios and the reaction and filtration temperatures used in these explatory dissociation experiments. A nearly constant ratio of approximately 6.2 pounds of solvent per pound of total P_2O_5 in the unreacted monocalcium phosphate was used for those experiments involving

Table 5. Average P_2O_5 Yield, Average Impurity Concentration and Average Filtration Rate for Phosphoric Acid from the Dissociation of Crude Monocalcium Phosphate with Various Organic Solvents. (The Crude Monocalcium Phosphate was Prepared from Florida Phosphate Rock).

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent per Pound of Total P_2O_5 in Unreacted MCP	Reaction and Filtration Temperature, °C	Average P_2O_5 Yield in Product Acid**, Percent	Average Percent Impurity in Product Acid Containing 54% P_2O_5**					Average Filtration Rate,** lbs. of Filtrate P_2O_5/Hr/Sqft Filtration Area
					CaO	Fe_2O_3	Al_2O_3	MgO	Total Major Cations	
Methanol	31.86	6.35	25	31.8	0.99	0.08	0.28	0.80	2.15	15
Methanol	31.86	6.30	55	34.9	0.73	0.08	0.18	0.70	1.69	29
Ethanol	31.86	6.15	55	27.7	<0.23	0.06	0.29	0.23	<0.81	29
Ethanol	31.86	6.27	70	30.7	<0.19	0.10	0.34	0.23	<0.86	48
Normal Propanol	31.86	6.29	25	30.7	<0.10	0.09	0.17	0.26	<0.62	50
Normal Propanol	31.86	6.31	70	29.2	0.11	0.07	0.30	0.15	0.63	121
Normal Butanol	31.86	6.28	25	24.4	<0.11	0.07	0.22	0.02	<0.42	52
Normal Butanol	31.86	6.29	70	25.8	<0.12	0.08	0.27	0.05	<0.52	96
Isoamyl Alcohol (85%)	31.86	6.29	40	15.2	<0.18	0.05	0.36	0.05	<0.64	81

Table 5. (Continued)

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent per Pound of Total P_2O_5 in Unreacted MCP	Reaction and Filtration Temperature, °C	Average P_2O_5 Yield in Product Acid**, Percent	Average Percent Impurity in Product Acid Containing 54% P_2O_5**					Average Filtration Rate** lbs. of Filtrate P_2O_5/Hr/Sqft Filtration Area
					CaO	Fe_2O_3	Al_2O_3	MgO	Total Major Cations	
Normal Hexanol	31.86	6.31	70	13.5	<0.24	0.08	0.65	0.03	<1.00	55
Normal Hexanol	47.00	6.17	70	12.3	0.14	0.51	0.70	0.28	1.63	7
2-Methyl Pentanol	32.58	6.16	70	1.7	5.76	3.04	3.54	-	>12.34	-
Normal Octanol	31.86	6.31	70	10.5	3.54	0.84	0.55	0.55	5.48	-
Normal Octanol	47.00	6.19	70	15.8	1.15	0.52	0.45	0.20	2.32	13
2-Ethyl Hexanol	32.58	6.19 (First treatment)	70	2.6	<0.41	0.19	1.42	-	>1.61	-
		6.23 (Second treatment)	70	2.5	<0.43	0.03	0.87	-	>0.90	-
		6.20 (Third treatment)	70	4.4	<0.24	0.03	0.50	-	>0.53	-

Table 5. (Concluded)

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent per Pounds of Total P_2O_5 in Unreacted MCP	Reaction and Filtration Temperature, °C	Average P_2O_5 Yield in Product Acid **, Percent	Average Percent Impurity in Product Acid Containing 54% P_2O_5**					Average Filtration Rate,**lbs. of Filtrate P_2O_5/Hr/Sqft Filtration Area
					CaO	Fe_2O_3	Al_2O_3	MgO	Total Major Cations	
CO-898	32.58	6.28	70	15.1	1.45	0.45	0.63	0.23	2.76	-
Umbrex N	32.58	6.32	70	7.2	3.17	0.44	1.70	-	>5.31	-
Normal Decanol	31.86	6.25	70	28.0	9.13	0.04	0.84	0.35	10.36	-
Normal Dodecanol	31.86	6.12	70	6.4	15.73	1.15	1.72	-	>18.60	-
Acetone	31.86	6.30	25	26.2	<0.10	0.09	0.31	-	>0.40	291
Acetone	31.86	6.42	50	28.5	<0.10	0.10	0.26	0.17	<0.63	291
Methyl Butyl Ketone	32.58	6.27	70	9.2	5.91	3.01	2.85	-	>11.77	-
Tetrahydrofuran	31.86	6.30	55	26.7	<0.10	0.08	0.31	0.07	<0.56	262

*MCP containing 32 percent P_2O_5 was a slurry while MCP containing 47 percent P_2O_5 was a solid material.

**"P_2O_5 Yield" and "Percent Impurity" represent the time averages over all dissociation reaction periods investigated for experimental runs using a certain set of conditions while "Filtration Rate" represents the time average for those experimental runs made using not more than one hour of dissociation reaction time.

Table 6. Average P_2O_5 Yield, Average Impurity Concentration and Average Filtration Rate for Phosphoric Acid from the Dissociation of Crude Monocalcium Phosphate with Methanol and Acetone. (The Crude Monocalcium Phosphate was Prepared from North Carolina Phosphate Rock).

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent per Pound of Total P_2O_5 in Unreacted MCP	Reaction and Filtration Temperature, °C	Average P_2O_5 Yield in Product Acid**, Percent	Average Percent Impurity in Product Acid Containing 54% P_2O_5**					Average Filtration Rate**, lbs. of Filtrate P_2O_5/Hr/Sqft Filtration Area
					CaO	Fe_2O_3	Al_2O_3	MgO	Total Major Cations	
Methanol	46.60	1.59	55	11.2	0.80	2.25	1.05	-	>4.10	<1
Methanol	46.60	3.16	55	24.1	-	0.39	0.35	0.17	>0.91	7
Methanol	46.60	6.30	55	31.1	0.66	0.10	0.26	0.50	1.52	6
Acetone	46.60	1.60	55	15.6	<0.07	0.97	0.32	0.08	<1.44	24

*MCP Containing 46.60 percent P_2O_5 was a solid material.

**"P_2O_5 Yield" and "Percent Impurity" represent the time averages over all dissociation reaction periods investigated for experimental runs using a certain set of conditions while "Filtration Rate" represents the time average for those experimental runs made using not more than one hour of dissociation reaction time.

monocalcium phosphate prepared from Florida phosphate rock. The dissociation reactions for which data are summarized in Tables 5 and 6 used as reactants either monocalcium phosphate containing approximately 32 percent P_2O_5 or monocalcium phosphate containing approximately 47 percent P_2O_5. The crude monocalcium phosphate containing 32 percent P_2O_5 was a slurry composed of a solid and a liquid phase whereas the crude monocalcium phosphate containing 47 percent P_2O_5 was a solid material which had to be pulverized prior to dissociation.

The average P_2O_5 yields which appear in Tables 5 and 6 represent the percentage of monocalcium phosphate reactant P_2O_5 that resulted as product phosphoric acid P_2O_5 with all such P_2O_5 yields having been time-averaged over the dissociation reaction periods investigated using a certain set of reaction conditions. The average concentrations of major cation impurities (CaO, Fe_2O_3, Al_2O_3, MgO and total major cations) that appear in Tables 5 and 6 represent the weight percentage of these species in product phosphoric acid containing 54 percent P_2O_5 with all such impurity concentrations having been time-averaged over the dissociation reaction periods investigated using a certain set of conditions. The average total major cation impurity concentration in product phosphoric acid is the sum of the average impurity concentrations of the CaO, Fe_2O_3, Al_2O_3 and MgO species. The average filtration rates appearing in Tables 5 and 6 represent the rate of filtration of dissociation slurry with the filtration rates having been time-averaged for those experimental runs made using not more than one hour of dissociation reaction time. The P_2O_5 yields, product acid impurity concentrations and filtration rates were time-averaged in order to condense the data to a form such that a

comparison of the relative merits of the organic solvents when used to dissociate crude commercial monocalcium phosphate would be facilitated. It was determined that the reaction time parameter for a dissociation reaction period of 15 minutes or more when using a given solvent is a relatively minor factor when compared to the reaction parameters of dissociation temperature, solvent/P_2O_5 ratio and reactant monocalcium phosphate P_2O_5 concentration (see Appendix B).

In general, when using an alcohol as the dissociation solvent for monocalcium phosphate prepared from Florida phosphate rock the product phosphoric acid P_2O_5 yield decreased as the molecular weight of the alcohol increased (see Table 5). The two ketones investigated, acetone and methyl butyl ketone, showed the same general trend with the use of methyl butyl ketone. The use of methanol as the dissociation solvent resulted in a product phosphoric acid P_2O_5 yield of over 30 percent, the highest yield for any alcohol evaluated. Acetone when used as the dissociation solvent also resulted in a high product phosphoric acid yield of a little less than 30 percent. Other organic solvents used as dissociation solvents which resulted in high product phosphoric acid P_2O_5 yields were ethanol, normal propanol, normal butanol and tetrahydrofuran.

It may be seen from Table 6 that the use of methanol as the dissociation solvent for crude monocalcium phosphate prepared from North Carolina phosphate rock resulted in a reasonably high product phosphoric acid P_2O_5 yield when a ratio of 6.3 pounds of methanol per pound of monocalcium phosphate P_2O_5 was used. Although the product phosphoric acid P_2O_5 yield decreased when a lower methanol solvent/P_2O_5 ratio was used, the yield is still fairly high for a ratio of 3.2 pounds of methanol per

pound of crude monocalcium phosphate P_2O_5. Of the organic solvents which appeared to be most promising with regard to product phosphoric acid P_2O_5 yield (methanol, ethanol, normal propanol, normal butanol, acetone and tetrahydrofuran), the least expensive were methanol and acetone (see Table 2) with methanol being cheaper than acetone.

Table 5 also shows that the CaO concentration was less than 0.3 weight percent in product phosphoric acid containing 54 percent P_2O_5 which resulted from the dissociation of crude monocalcium phosphate prepared from Florida phosphate rock while using an alcoholic solvent with less than six carbon atoms except for methanol. The use of methanol as a dissociation solvent resulted in a higher CaO concentration in the product phosphoric acid. Product phosphoric acid prepared by dissociating with normal hexanol exhibited a relatively low CaO concentration of around 0.2 weight percent but, in general, when the alcohols of a molecular weight higher than pentanol were used as dissociation solvents, the CaO concentration in the product phosphoric acid was higher than one weight percent. This compares very unfavorably with the 0.1 weight percent CaO content of commercial merchant grade phosphoric acid produced from Florida phosphate rock by the conventional wet process (see Table 1). The use of acetone and tetrahydrofuran as solvents for dissociating crude monocalcium phosphate prepared from Florida phosphate rock resulted in a product phosphoric acid which contained less than 0.1 weight percent CaO.

The Fe_2O_3 concentration was 0.1 weight percent or less in product phosphoric acid containing 54 percent P_2O_5 which resulted from the dissociation of crude monocalcium phosphate prepared from Florida phosphate rock while using an alcoholic solvent with less than six carbon atoms (see

Table 5). Product phosphoric acid prepared by the dissociation of crude monocalcium phosphate with hexanol and alcohols of higher molecular weight than hexanol exhibited, in general, Fe_2O_3 concentrations of around 0.5 weight percent or higher. While this Fe_2O_3 content is lower than the 1.2 weight percent Fe_2O_3 concentration found in commercial merchant grade phosphoric acid produced from Florida phosphate rock by the conventional wet process (see Table 1), the use of alcohols with less than six carbon atoms appears more promising from a viewpoint of Fe_2O_3 rejection during the dissociation reaction. The use of acetone and tetrahydrofuran as solvents for dissociating crude monocalcium phosphate prepared from Florida phosphate rock resulted in a product phosphoric acid which contained less than 0.1 weight percent Fe_2O_3.

The Al_2O_3 concentration was approximately 0.3 weight percent or less in product phosphoric acid containing 54 percent P_2O_5 which resulted from the dissociation of crude monocalcium phosphate prepared from Florida phosphate rock while using an alcohol solvent with less than six carbon atoms (see Table 5). The use of acetone and tetrahydrofuran as solvents for dissociating crude monocalcium phosphate prepared from Florida phosphate rock resulted in a product phosphoric acid which contained approximately 0.3 weight percent Al_2O_3. Product phosphoric acid prepared by the dissociation of crude monocalcium phosphate with hexanol and alcohols of higher molecular weight than hexanol generally exhibited Al_2O_3 concentrations of greater than 0.6 weight percent. While a merchant grade phosphoric acid Al_2O_3 concentration of 0.6 weight percent represents an improvement over the 1.3 weight percent Al_2O_3 concentration found in commercial merchant grade phosphoric acid produced from Florida phosphate rock by the conventional wet process (see Table 1), the use of

alcohols with less than six carbon atoms or the use of acetone or tetrahydrofuran appears more promising with regard to Al_2O_3 rejection during the dissociation reaction.

Table 5 also shows that the concentration of MgO in product phosphoric acid resulting from the dissociation of crude monocalcium phosphate prepared from Florida phosphate rock decreased with increasing alcoholic solvent molecular weight for methanol through pentanol. A substantial reduction in product phosphoric acid MgO content when compared to the 0.6 weight percent MgO concentration found in commercial merchant grade phosphoric acid (see Table 1) was realized when using ethanol, normal propanol, normal butanol, and pentanol as dissociation solvents. The use of acetone and tetrahydrofuran as solvents for dissociating crude monocalcium phosphate prepared from Florida phosphate rock also resulted in very good MgO rejection from the product phosphoric acid. Even though the data for methanol at the two sets of dissociation reaction conditions in Table 5 indicate methanol to be a poor choice of a dissociation solvent with regard to MgO rejection in the product phosphoric acid, further experimentation uncovered dissociation reaction conditions at which the use of methanol resulted in much better MgO rejection. These data are presented later in this work.

It was estimated that the sulfate content of the product phosphoric acid resulting from the dissociation of crude monocalcium phosphate was less than 0.0005 weight percent regardless of the solvent used. The chemical analysis for P_2O_5 of the product phosphoric acid that resulted from a dissociation reaction routinely required the addition of a certain amount of barium chloride solution during the analysis. At no time could a precipitate of barium sulfate be discerned while analyzing

product phosphoric acid samples. The upper limit of sulfate concentration was calculated from the solubility product constant for barium sulfate. Since the production of merchant grade phosphoric acid by the conventional wet process requires a two to three weight percent free sulfate concentration for efficient processing (81), production of a sulfate-free product phosphoric acid by the dissociation of crude monocalcium phosphate with an organic solvent represents a substantial decrease in sulfuric acid losses in the product phosphoric acid for the case when the dried dicalcium phosphate residue is recycled.

It may be seen from Table 5 that the concentration of total major cation impurities (CaO, Fe_2O_3, Al_2O_3, and MgO) for product phosphoric acid containing 54 percent P_2O_5 resulting from the dissociation of crude monocalcium phosphate prepared from Florida phosphate rock was lower than the approximately three weight percent total major cation impurity concentration of typical commercial merchant grade phosphoric acid (see Table 1) when acetone, tetrahydrofuran, or alcohols with six carbon atoms or less were used as dissociation solvents. Even though the data for methanol at the two sets of dissociation reaction conditions in Table 5 indicate methanol to be a poor choice of a dissociation solvent with regard to total major cation impurity rejection in the product phosphoric acid, further experimentation uncovered dissociation reaction conditions at which the use of methanol resulted in much better rejection of the major cation impurities. These data are presented later in this work.

It may be seen from Table 6 that the use of acetone for dissociating crude monocalcium phosphate prepared from North Carolina phosphate rock resulted in a product phosphoric acid that contained less than 0.1

weight percent CaO. The CaO concentration in typical commercial merchant grade phosphoric acid produced from North Carolina phosphate rock by the conventional wet process is approximately 0.1 weight percent (see Table 1). The CaO content of the product phosphoric acid resulting from the dissociation with methanol of crude monocalcium phosphate prepared from North Carolina phosphate rock was higher than the CaO content found in typical merchant grade phosphoric acid.

It may be seen from Table 6 that fairly good rejection of Fe_2O_3 and Al_2O_3 impurities resulted when methanol was used to dissociate crude monocalcium phosphate prepared from North Carolina phosphate rock. The Fe_2O_3 concentration was less than 0.4 weight percent and the Al_2O_3 concentration was approximately 0.3 weight percent in the product phosphoric acid containing 54 percent P_2O_5 when using the two highest solvent/P_2O_5 ratios of methanol. The Fe_2O_3 and Al_2O_3 concentrations in the product phosphoric acid resulting from these two experiments were lower than the typical 1.4 weight percent Fe_2O_3 and 1.0 weight percent Al_2O_3 concentrations found in commercial merchant grade phosphoric acid produced from North Carolina phosphate rock by the conventional wet process. The Fe_2O_3 and Al_2O_3 concentrations in product phosphoric acid resulting from the use of acetone as the dissociation solvent were higher than the Fe_2O_3 and Al_2O_3 concentrations in product phosphoric acid resulting from the use of methanol at the two highest solvent/P_2O_5 ratios but were lower than the Fe_2O_3 and Al_2O_3 concentrations of commercial merchant grade phosphoric acid produced from North Carolina phosphate rock.

The MgO concentration was less than 0.1 weight percent in product acid containing 54 percent P_2O_5 which resulted from the dissociation of

crude monocalcium phosphate prepared from North Carolina phosphate rock when using acetone as the dissociation solvent (see Table 6). This represents a substantial reduction in phosphoric acid MgO content when compared to the typically high 1.1 weight percent MgO concentration found in commercial merchant grade phosphoric acid produced from North Carolina phosphate rock by the conventional wet process (see Table 1). Even though the MgO content of the product phosphoric acid resulting from the dissociation with methanol of crude monocalcium phosphate prepared from North Carolina phosphate rock was higher than the MgO content of product phosphoric acid resulting from the use of acetone as the dissociation solvent, the MgO content of phosphoric acid resulting from methanol dissociation was still lower than the MgO content of typical commercial merchant grade phosphoric acid.

Table 6 also shows that the concentration of total major cation impurities (CaO, Fe_2O_3, Al_2O_3 and MgO) for product phosphoric acid containing 54 percent P_2O_5 resulting from the dissociation of crude monocalcium phosphate prepared from North Carolina phosphate rock was lower than the 3.6 weight percent total major cation impurity content of typical commercial North Carolina merchant grade phosphoric acid (see Table 1) when acetone and methanol (at the two highest solvent/P_2O_5 ratios) were used as dissociation solvents.

The organic solvents which appeared to be most promising with regard to rejecting cation impurities from the product phosphoric acid resulting from the dissociation of crude monocalcium phosphate prepared from either Florida or North Carolina phosphate rock were methanol, ethanol, normal propanol, normal butanol, pentanol, acetone and

tetrahydrofuran. The least expensive of these organic solvents were methanol and acetone (see Table 2) with methanol being cheaper than acetone.

The highest filtration rates occurred during the filtration of dissociation slurries resulting from the dissociation of crude monocalcium phosphate prepared from Florida phosphate rock when acetone or tetrahydrofuran were used (see Table 5). The filtration rates when the alcohols were used as the dissociation solvents were generally much lower than when acetone or tetrahydrofuran were used. The filtration rate when using alcohol solvents ranged widely from 15 to 121 pounds of filtrate P_2O_5 per hour per square foot of filtration area. The filtration rate was highest when using a given solvent at the highest filtration temperature. This was expected since the liquid phase flow rate through the filtration medium increases as its viscosity decreases.

The filtration rate of the slurry resulting from the dissociation of crude monocalcium phosphate prepared from North Carolina phosphate rock was highest when using acetone as the dissociation solvent (see Table 6). However, the filtration rates for slurries resulting from the dissociation of crude North Carolina monocalcium phosphate appear to be generally lower than the slurries resulting from the dissociation of crude monocalcium phosphate prepared from Florida phosphate rock when using methanol and acetone.

In Table 7 the dissociation of crude monocalcium phosphate prepared from Florida phosphate rock is compared with the dissociation of crude monocalcium phosphate prepared from North Carolina phosphate rock at various reaction conditions while using methanol and acetone. The average P_2O_5 yields and the average impurity concentrations in the product

Table 7. Comparison of the Dissociation at 55°C of Crude Monocalcium Phosphate Prepared from Florida Phosphate Rock and North Carolina Phosphate Rock.

Solvent	Source of Phosphate Rock Used for MCP Preparation	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent per Pound of Total P_2O_5 in Unreacted MCP	Average P_2O_5 Yield in Product Acid**, Percent	Average Percent Impurity in Product Acid Containing 54% P_2O_5**					Average Filtration Rate**, lbs. of Filtrate P_2O_5/Hr/Sqft Filtration Area
					CaO	Fe_2O_3	Al_2O_3	MgO	Total Major Cations	
Methanol	Florida	47.00	3.11	24.4	0.57	0.25	0.29	0.30	1.41	19
Methanol	North Carolina	46.60	3.16	24.1	-	0.39	0.35	0.17	>0.91	7
Methanol	Florida	47.00	6.19	29.3	0.55	0.06	0.09	0.14	0.84	18
Methanol	North Carolina	46.60	6.30	31.1	0.66	0.10	0.26	0.50	1.52	6
Acetone	Florida	47.17	1.57	17.0	0.29	1.14	0.59	0.04	2.06	423
Acetone	North Carolina	46.60	1.60	15.6	<0.07	0.97	0.32	0.08	<1.44	24

*MCP Containing 47 percent P_2O_5 was a solid material.

**"P_2O_5 Yield" and "Percent Impurity" represent the time averages over all dissociation reaction periods investigated for experimental runs using a certain set of conditions while "Filtration Rate" represents the time average for those experimental runs made using not more than one hour of dissociation reaction time.

phosphoric acid are presented along with the average dissociation slurry filtration rates that resulted during these experiments. The product acid P_2O_5 yields and the product acid impurity concentrations were time-averaged over all the dissociation reaction periods investigated using a certain set of reaction conditions whereas the dissociation slurry filtration rates were time-averaged for those experimental runs made using not more than one hour of dissociation reaction time.

The P_2O_5 yields in the filtrates resulting from the dissociation with methanol or acetone at 55°C of crude monocalcium phosphate containing approximately 47 percent P_2O_5 prepared from Florida phosphate rock agree closely with the P_2O_5 yields in phosphoric acid resulting from the dissociation of crude North Carolina monocalcium phosphate at similar reaction conditions. The total major cation impurity concentration in the product phosphoric acid resulting from the methanol or acetone dissociation of crude monocalcium phosphate appeared to be about the same when similar reaction conditions were used regardless of the source of the phosphate rock. The filtration rate of the slurry resulting from the dissociation of crude Florida monocalcium phosphate appears to be higher than the filtration rate of slurry resulting from the dissociation of crude North Carolina monocalcium phosphate when similar reaction conditions are used. As had been noted before, the dissociation slurry filtration rate when using acetone was higher than when using methanol.

Methanol and acetone are the best of the organic solvents which appeared to be most promising with regard to product acid P_2O_5 yield and product acid impurity content (methanol, ethanol, normal propanol, normal butanol, acetone and tetrahydrofuran). Methanol and acetone are

the cheapest solvents of those investigated in the exploratory study (see Table 2). Methanol and acetone when used as dissociation solvents produce a product phosphoric acid with a high P_2O_5 yield and low impurity content relative to the other solvents. The dissociation slurry resulting from using acetone has one of the highest filtration rates of those organic solvents investigated. Both methanol and acetone are relatively low boiling solvents which will facilitate solvent stripping from the dissociation filtrate with the use of low quality heat.

Further Experimentation with Methanol and Acetone Dissociation Solvents

Further experimentation was performed to determine the effect of certain process parameters on the yield of phosphoric acid and impurity rejection from the purified acid product while using the most promising dissociation solvents, methanol and acetone. The effect of the following process parameters were investigated: 1) dissociation reaction time, 2) dissociation reaction temperature, 3) amount of free water present in the crude monocalcium phosphate reactant and 4) proportion of organic solvent present during the dissociation. Near-optimum dissociation operating conditions were determined from these studies.

Crude monocalcium phosphate prepared from Florida phosphate rock was used exclusively for these studies in order to eliminate any possible effect on the results which might be attributable to the introduction of another variable (phosphate rock source). However, it is believed that the results obtained for product acid P_2O_5 yield and product acid impurity rejection also apply to the dissociation of crude monocalcium phosphate prepared from North Carolina phosphate rock (see Table 7).

It was determined (see Appendix B) from a two-way analysis of

variance scheme that the parameters of dissociation reaction temperature, solvent/monocalcium phosphate P_2O_5 ratio, and monocalcium phosphate P_2O_5 content had a statistically significant effect on P_2O_5 yield when methanol and acetone were used as dissociation solvents. Dissociation reaction time, however, was not a statistically significant factor and had no effect on product acid P_2O_5 yield at the levels investigated for methanol and acetone solvents. The same product acid P_2O_5 yield resulted after 15 minutes of reaction time that resulted after four hours of reaction time and any differences in the data are apparently due to experimental error alone.

Methanol Solvent

The effect of dissociation reaction temperature on product acid P_2O_5 yield, product acid impurity concentration and filtration rate when methanol was used as the dissociation solvent is shown in Table 8. The product acid P_2O_5 yields and the product acid impurity concentrations were time-averaged over all the dissociation reaction periods investigated using a certain set of reaction conditions whereas the dissociation slurry filtration rates were time-averaged for those experimental runs made using not more than one hour of dissociation reaction time.

The P_2O_5 yield in the phosphoric acid product resulting from the dissociation of crude Florida monocalcium phosphate containing 32 percent total P_2O_5 in the presence of 6.2 pounds of methanol per pound of monocalcium phosphate P_2O_5 increased as the dissociation reaction temperature was increased. The total major cation impurity content of the product phosphoric acid generally appeared to decrease with increasing dissociation temperature. The filtration rate of the dissociation slurry increased

Table 8. Average P_2O_5 Yield, Average Impurity Concentration and Average Filtration Rate for Phosphoric Acid from the Dissociation of Crude Monocalcium Phosphate with Methanol at Different Reaction and Filtration Temperatures. (The Crude MCP Slurry Prepared from Florida Phosphate Rock Contained 32 percent P_2O_5. A Constant Solvent Ratio of 6.2 Pounds of Methanol per Pound of MCP Total P_2O_5 was Used).

Reaction and Filtration Temperature, °C	Average P_2O_5 Yield in Product Acid*, Percent	Average Percent Impurity in Product Acid Containing 54% P_2O_5*					Average Filtration Rate*, Pounds of Filtrate P_2O_5 per Hour per Square Foot of Filtration Area
		CaO	Fe_2O_3	Al_2O_3	MgO	Total Major Cations	
25	31.8	0.99	0.08	0.28	0.80	2.15	15
40	34.2	0.52	0.10	0.25	0.71	1.58	21
55	34.9	0.73	0.08	0.18	0.70	1.69	29

*"P_2O_5 Yield" and "Percent Impurity" represent the time averages over all dissociation reaction periods investigated for experimental runs using a certain set of conditions while "Filtration Rate" represents the time average for those experimental runs made using not more than one hour of dissociation reaction time.

with increasing dissociation temperature on account of the faster flow rate through the filtration medium of the filtrate due to its decreased viscosity. A high dissociation reaction temperature appears to be best for methanol because a higher dissociation P_2O_5 yield, a higher dissociation slurry filtration rate and better impurity rejection from the product phosphoric acid occur at high temperature. A high dissociation temperature is also desirable in the continuous process since hot recovered solvent will be recycled to the dissociation stage after having been condensed from the overhead stream of the fractionation stage. Crude monocalcium phosphate will also enter the dissociation stage at a temperature above ambient.

The effect of solvent/P_2O_5 ratio on product acid P_2O_5 yield, product acid impurity concentration and filtration rate when methanol was used as the dissociation solvent is shown in Table 9. The product acid P_2O_5 yields and the product acid impurity concentrations were time-averaged over all the dissociation reaction periods investigated using a certain set of reaction conditions whereas the dissociation slurry filtration rates were time-averaged for those experimental runs made using not more than one hour of dissociation reaction time. The data in Table 9 resulted from experimental runs involving the dissociation with methanol of crude Florida monocalcium phosphate containing 32 percent P_2O_5 at 55°C using different solvent ratios.

These results are summarized in Figure 2. Also shown in Figure 2 are the results for the dissociation with methanol at 55°C of crude Florida monocalcium phosphate containing 47 percent P_2O_5 using different solvent/P_2O_5 ratios (see Table 7). The P_2O_5 yield in the product

Table 9. Average P_2O_5 Yield, Average Impurity Concentration and Average Filtration Rate for Phosphoric Acid from the Dissociation of Crude Monocalcium Phosphate with Methanol at Different Solvent Ratios. (The Crude MCP Slurry Prepared from Florida Phosphate Rock Contained 32 Percent P_2O_5. Reaction and Filtration Temperature was 55°C).

Pounds of Anhydrous Methanol per Pound of Total P_2O_5 in Unreacted MCP	Average P_2O_5 Yield in Product Acid*, Percent	Average Percent Impurity in Product Acid Containing 54% P_2O_5*					Average Filtration Rate*, lbs. of Filtrate P_2O_5/Hr/Sqft of Filtration Area
		CaO	Fe_2O_3	Al_2O_3	MgO	Total Major Cations	
3.16	30.1	1.25	0.24	0.24	0.79	2.52	50
4.78	35.2	0.89	0.10	0.19	0.72	1.90	61
6.30	34.9	0.73	0.08	0.18	0.70	1.69	29
12.62	37.9	0.27	0.04	0.27	0.42	1.00	20
24.63	36.1	<0.12	0.11	0.25	0.28	<0.76	15

*"P_2O_5 Yield" and "Percent Impurity" represent the time averages over all dissociation reaction periods investigated for experimental runs using a certain set of conditions while "Filtration Rate" represents the time average for those experimental runs made using not more than one hour of dissociation reaction time.

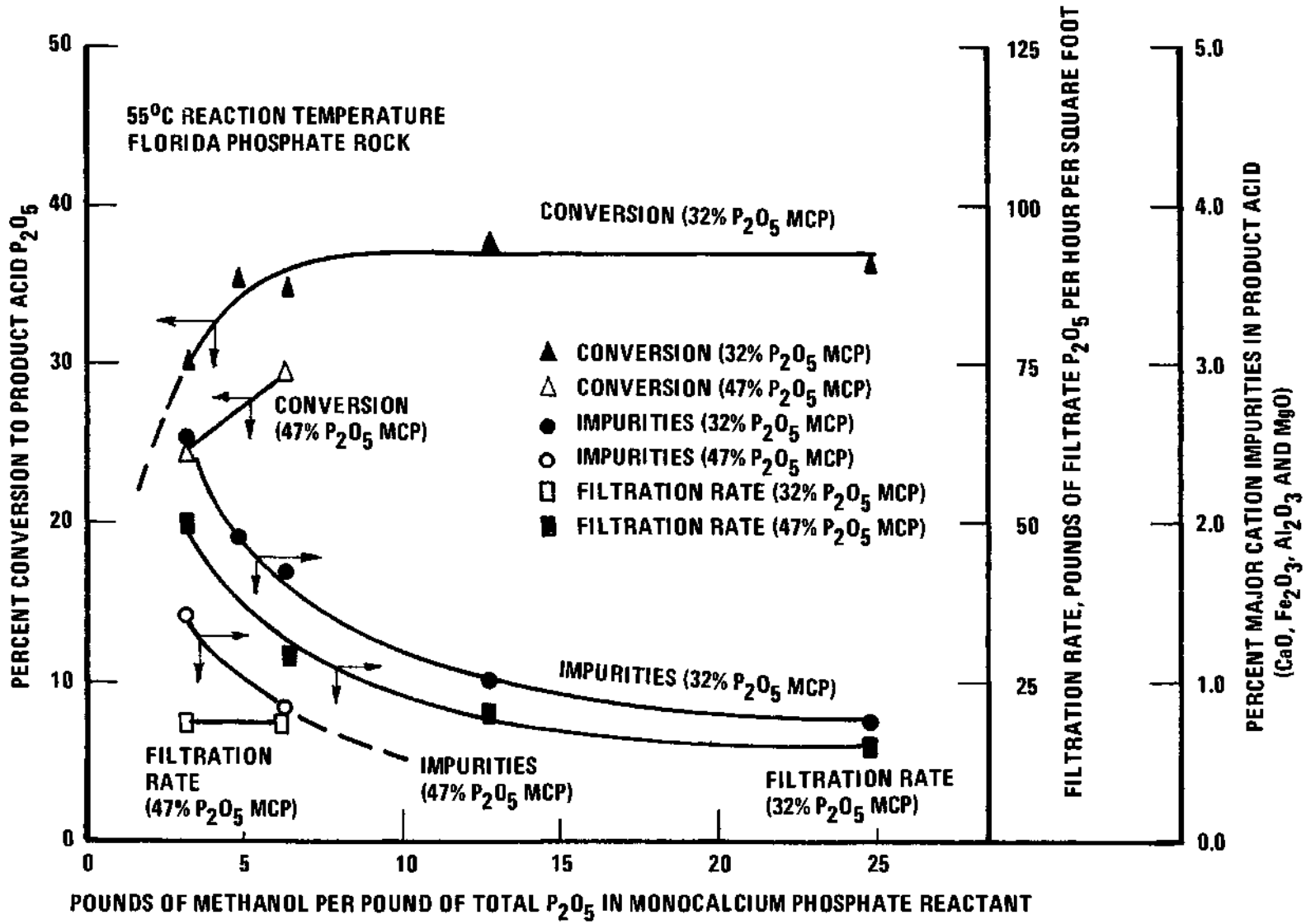

Figure 2. Filtrate P_2O_5 Yield, Impurity Concentration and Filtration Rate Versus Methanol/Monocalcium Phosphate P_2O_5 Ratio

acid resulting from the dissociation of crude Florida monocalcium phosphate containing 32 percent P_2O_5 increased rapidly with increasing solvent/P_2O_5 ratio up to approximately six pounds of methanol per pound of monocalcium phosphate P_2O_5. This increase in P_2O_5 yield is probably caused by an increase in phosphoric acid-solvent association due to the larger proportion of solvent present thus enhancing the monocalcium phosphate dissociation reaction by hindering the reverse reaction. As the ratio was increased above six pounds of methanol per pound of monocalcium phosphate P_2O_5, the product phosphoric acid P_2O_5 yield became relatively constant at approximately 37 percent conversion to product acid P_2O_5. The product phosphoric acid yield resulting from the dissociation of crude Florida monocalcium phosphate containing 47 percent P_2O_5 increased as the solvent/P_2O_5 ratio was increased from 3.1 to 6.2 pounds of methanol per pound of monocalcium phosphate P_2O_5. Although the product phosphoric acid yield resulting from the dissociation of crude monocalcium phosphate containing 47 percent P_2O_5 was lower than that resulting from dissociation of crude monocalcium phosphate containing 32 percent P_2O_5, the P_2O_5 yield was a reasonably high 29 percent when six pounds of methanol per pound of monocalcium phosphate P_2O_5 were used.

Figure 2 also shows the total major cation impurity (CaO, Fe_2O_3, Al_2O_3 and MgO) concentration at different methanol solvent/P_2O_5 ratios in the product phosphoric acid resulting from the dissociation at 55° C of crude Florida monocalcium phosphate containing 32 percent and 47 percent P_2O_5. The total major cation impurity concentration in product phosphoric acid resulting from the dissociation of 47 percent P_2O_5 monocalcium phosphate was considerably lower than the total major cation impurity

concentration in the product phosphoric acid resulting from the dissociation of 32 percent P_2O_5 monocalcium phosphate. This phenomenon probably occurred as a result of the lower amount of water in 47 percent P_2O_5 monocalcium phosphate thus allowing only lower amounts of water soluble impurities to be rendered soluble during dissociation.

The total major cation impurity concentration in the product phosphoric acid resulting from dissociation of monocalcium phosphate containing 32 percent and 47 percent P_2O_5 decreased as the methanol solvent/P_2O_5 ratio was increased. The total major cation impurity concentration in the product phosphoric acid resulting from the dissociation of 32 percent P_2O_5 monocalcium phosphate decreased rapidly as the ratio was increased up to approximately six pounds of methanol per pound of monocalcium phosphate P_2O_5. As the ratio was increased above six pounds of methanol per pound of monocalcium phosphate P_2O_5, the decrease of the total major cation concentration in the product phosphoric acid resulting from the dissociation of 32 percent P_2O_5 monocalcium phosphate was not as pronounced. When using a ratio of six pounds of methanol per pound of monocalcium phosphate reactant P_2O_5, the product phosphoric acid resulting from the dissociation of 32 percent P_2O_5 monocalcium phosphate contained approximately 1.6 percent total major cation impurities while the product phosphoric acid resulting from the dissociation of 47 percent P_2O_5 monocalcium phosphate contained approximately 0.9 percent total major cation impurities.

Figure 2 also shows the filtration rate at different methanol solvent/P_2O_5 ratios of the slurry resulting from the dissociation at 55°C of crude Florida monocalcium phosphate containing 32 percent and 47

percent P_2O_5. The filtration rates are expressed in terms of pounds of filtrate P_2O_5 that resulted per hour per square foot of filtration area. The filtration rate of the slurry resulting from the dissociation of 32 percent P_2O_5 monocalcium phosphate decreased as the methanol solvent/P_2O_5 ratio was increased. Even though the filtration rate of the slurry resulting from the dissociation of 47 percent P_2O_5 monocalcium phosphate was somewhat lower than the filtration rate of the 32 percent P_2O_5 monocalcium phosphate dissociation slurry, the filtration rate of the 47 percent P_2O_5 monocalcium phosphate dissociation slurry was relatively constant for the methanol solvent/P_2O_5 ratios investigated.

The effect of crude monocalcium phosphate P_2O_5 content on product acid P_2O_5 yield, product acid impurity concentration and filtration rate when methanol was used as the dissociation solvent is shown in Table 10. The product acid P_2O_5 yields and the product acid impurity concentrations were time-averaged over all the dissociation reaction periods investigated using a certain set of reaction conditions whereas the dissociation slurry filtration rates were time-averaged for those experimental runs made using not more than one hour of dissociation reaction time. The data in Table 10 resulted from experimental runs involving the dissociation at 55°C of crude Florida monocalcium phosphate containing different percentages of P_2O_5 using a ratio of 6.2 pounds of methanol per pound of reactant monocalcium phosphate P_2O_5.

These results are summarized in Figure 3. The P_2O_5 yield in the product phosphoric acid resulting from the dissociation at 55°C of crude Florida monocalcium phosphate using 6.2 pounds of methanol per pound of monocalcium phosphate P_2O_5 decreased from 35 percent to 26 percent as

Table 10. Average P_2O_5 Yield, Average Impurity Concentration and Average Filtration Rate for Phosphoric Acid from the Dissociation of Crude Monocalcium Phosphate with Methanol at Different Monocalcium Phosphate P_2O_5 Concentrations. (The Crude MCP was Prepared from Florida Phosphate Rock. Reaction and Filtration Temperature was 55°C. A Constant Solvent Ratio of 6.2 Pounds of Methanol per Pound of MCP Total P_2O_5 was Used).

Percent Total P_2O_5 in Unreacted MCP*	Average P_2O_5 Yield in Product Acid**, Percent	Average Percent Impurity in Product Acid Containing 54% P_2O_5**					Average Filtration Rate*, lbs. of Filtrate P_2O_5/Hr/Sqft of Filtration Area
		CaO	Fe_2O_3	Al_2O_3	MgO	Total Major Cations	
31.86	34.9	0.73	0.08	0.18	0.70	1.69	29
34.97	31.9	0.76	0.07	0.21	0.68	1.72	28
38.04	32.5	0.68	0.09	0.15	0.40	1.32	28
41.17	29.2	0.47	0.11	0.14	0.23	0.95	30
43.97	32.1	0.54	0.10	0.11	0.12	0.87	22
47.00	29.3	0.55	0.06	0.09	0.14	0.84	18
49.97	25.8	0.42	0.06	0.19	0.14	0.81	12
52.55	3.2	<0.40	-	-	-	-	-
53.74	2.8	<0.40	-	-	-	-	-
56.08	1.7	<1.00	-	-	-	-	-

*MCP Containing 32 and 35 percent P_2O_5 was a slurry while MCP containing 38 and 41 percent P_2O_5 was a pasty material, MCP containing 44 percent P_2O_5 or greater was a solid material.

**"P_2O_5 Yield" and "Percent Impurity" represent the time averages over all dissociation reaction periods investigated for experimental runs using a certain set of conditions while "Filtration Rate" represents the time averages for those experimental runs made using not more than one hour of dissociation reaction time.

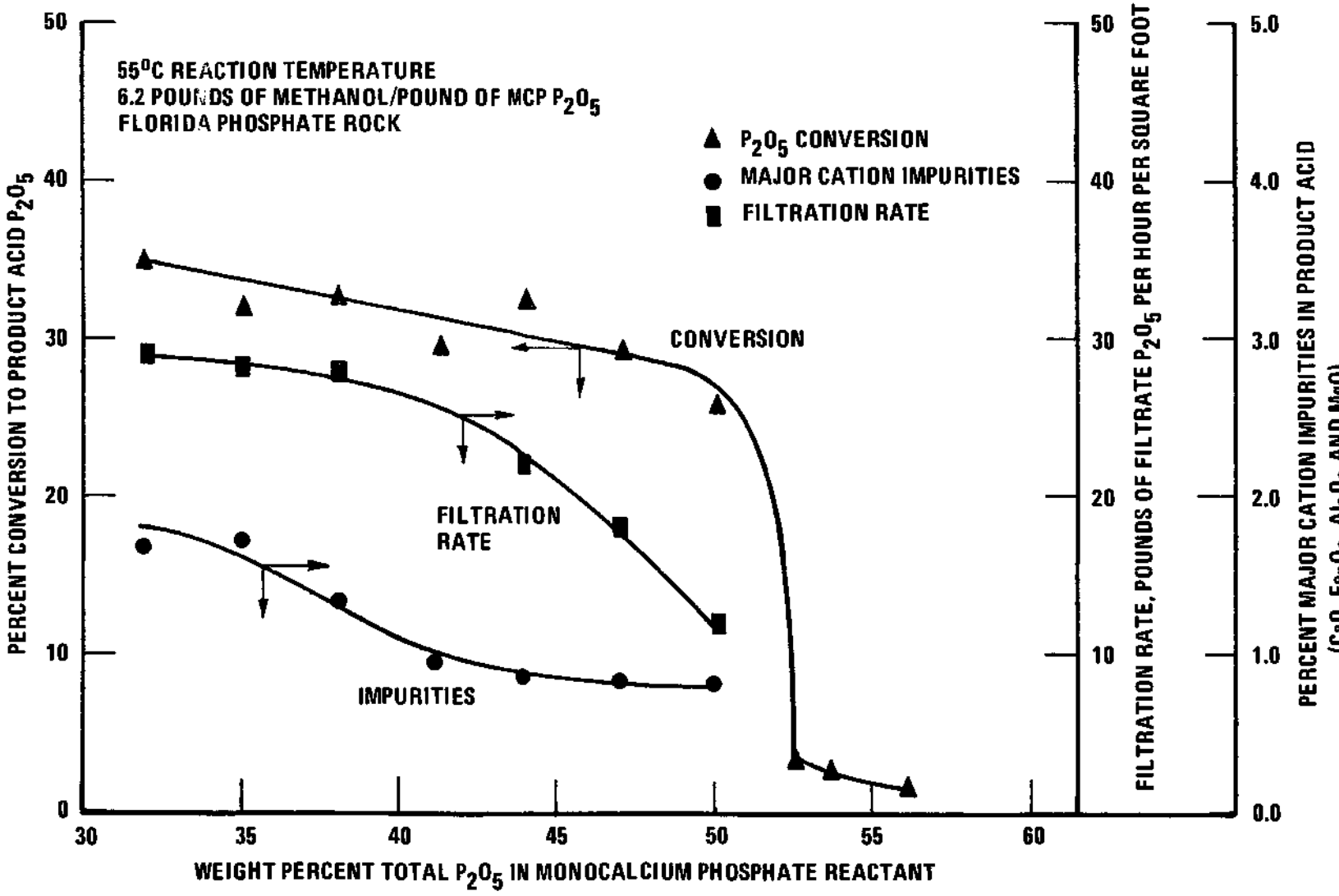

Figure 3. Filtrate P_2O_5 Yield, Impurity Concentration and Filtration Rate Versus Monocalcium Phosphate P_2O_5 Concentration Using Methanol

the reactant monocalcium phosphate P_2O_5 concentration was increased from 32 percent to 50 percent P_2O_5. Above a concentration of 50 percent P_2O_5 in the reactant monocalcium phosphate, the product phosphoric acid P_2O_5 yield decreased very rapidly so that the P_2O_5 yield of the product phosphoric acid resulting from the dissociation of 52.6 percent P_2O_5 monocalcium phosphate was only three percent. It can be seen from Table 3 that the crude 50 percent P_2O_5 Florida monocalcium phosphate contained no free water and only one percent water of crystallization while the crude Florida monocalcium phosphate reactants more concentrated than 50 percent P_2O_5 contained no free water and no water of crystallization. Therefore, very poor P_2O_5 yields result from the dissociation with methanol of crude Florida monocalcium phosphate that contains no free water and no hydrated monocalcium orthophosphate.

Figure 3 also shows the total major cation impurity (CaO, Fe_2O_3, Al_2O_3 and MgO) concentration in the product phosphoric acid resulting from the dissociation at 55°C of crude Florida monocalcium phosphate containing different percentages of P_2O_5 using 6.2 pounds of methanol per pound of monocalcium phosphate P_2O_5. The total major cation impurity concentration in the product phosphoric acid decreased when crude monocalcium phosphate with a higher P_2O_5 content was used as the dissociation reactant. This phenomenon probably occurred as a result of the lower amount of water in more concentrated monocalcium phosphate which thus allowed only lower amounts of the water soluble impurities to be rendered soluble during dissociation. The total major cation impurity concentration was less than one percent in the product phosphoric acid that resulted from the dissociation of crude monocalcium phosphate containing 41 percent P_2O_5

or more.

Figure 3 also shows the filtration rate of the slurry resulting from the dissociation at 55°C of crude Florida monocalcium phosphate containing different percentages of P_2O_5 when using 6.2 pounds of methanol per pound of monocalcium phosphate P_2O_5. The filtration rates are expressed in terms of pounds of filtrate P_2O_5 that resulted per hour per square foot of filtration area. The filtration rate of the dissociation slurry was reasonably constant for the dissociation of crude monocalcium phosphate containing up to approximately 40 percent P_2O_5 above which it decreased with increasing monocalcium phosphate P_2O_5 content above 40 percent P_2O_5 monocalcium phosphate.

Acetone Solvent

The effect of solvent/P_2O_5 ratio on product acid P_2O_5 yield, product acid impurity concentration and filtration rate when acetone was used as the dissociation solvent is shown in Table 11. These data resulted from experimental runs involving the dissociation with acetone of crude Florida monocalcium phosphate containing 47 percent P_2O_5 at 55°C using different solvent/P_2O_5 ratios. The product phosphoric acid P_2O_5 yields and the product acid impurity concentrations were time-averaged over all the dissociation reaction periods investigated using a certain set of reaction conditions. The dissociation slurry filtration rates are reported for the samples filtered after 15 minutes of reaction time and do not represent time averages as do the filtration rates reported previously for methanol. The filtration rates for the dissociation slurry that resulted when acetone solvent was used decreased with increasing dissociation reaction time while the filtration rates for the dissociation slurry

Table 11. Average P_2O_5 Yield, Average Impurity Concentration and Average Filtration Rate for the Phosphoric Acid from the Dissociation of Crude Monocalcium Phosphate with Acetone at Different Solvent Ratios. (The Crude Solid MCP Prepared from Florida Phosphate Rock Contained 47 Percent P_2O_5. Reaction and Filtration Temperature was 55°C.).

Pounds of Acetone per Pound of Total P_2O_5 in Unreacted MCP	Average P_2O_5 Yield in Product Acid*, Percent	Average Percent Impurity in Product Acid Containing 54% P_2O_5*					Filtration Rate After Fifteen Minutes, Pounds of Filtrate P_2O_5 per Hour per Square Foot of Filtration Area
		CaO	Fe_2O_3	Al_2O_3	MgO	Total Major Cations	
1.57	17.0	0.29	1.14	0.59	0.04	2.06	423
3.11	18.3	<0.06	0.57	0.44	0.04	<1.11	167
4.69	26.8	<0.07	0.43	0.61	0.02	<1.13	128
6.22	32.8	<0.07	0.32	0.44	0.03	<0.86	74

*"P_2O_5 Yield" and "Percent Impurity" represent the time averages over all dissociation reaction periods investigated for experimental runs using a certain set of conditions.

that resulted when using methanol solvent were relatively constant during the first hour of dissociation (see Appendix C).

The data presented in Table 11 are also summarized in Figure 4. The P_2O_5 yield in the product phosphoric acid resulting from the dissociation of crude Florida monocalcium phosphate containing 47 percent P_2O_5 increased with increasing solvent/P_2O_5 ratio and a plot of the P_2O_5 yield as it varied with acetone solvent ratio was reasonably linear for the range 1.6 to 6.2 pounds of acetone per pound of monocalcium phosphate P_2O_5. This increase in P_2O_5 yield can probably be attributed to an increase in phosphoric acid-acetone association due to the larger proportion of solvent present which enhances the monocalcium phosphate dissociation reaction by hindering the reverse reaction. It is not know above what solvent/P_2O_5 ratio the P_2O_5 yield begins to become constant although a theoretical upper limit of 50 percent product acid P_2O_5 yield can be predicted from the overall dissociation reaction:

$$Ca(H_2PO_4)_2 = H_3PO_4 + CaHPO_4 \qquad \text{(III-1)}$$

Figure 4 also shows the total major cation impurity (CaO, Fe_2O_3, Al_2O_3 and MgO) concentration at different acetone solvent/P_2O_5 ratios in the product phosphoric acid resulting from the dissociation at 55°C of crude Florida monocalcium phosphate containing 47 percent P_2O_5. The total major cation impurity concentration in the product phosphoric acid decreased rapidly as the solvent/P_2O_5 ratio was increased from 1.6 to 3.1 pounds of acetone per pound of monocalcium phosphate P_2O_5. However, above a ratio of 3.1 pounds of acetone per pound of monocalcium phosphate P_2O_5, the total major cation impurity concentration in the product

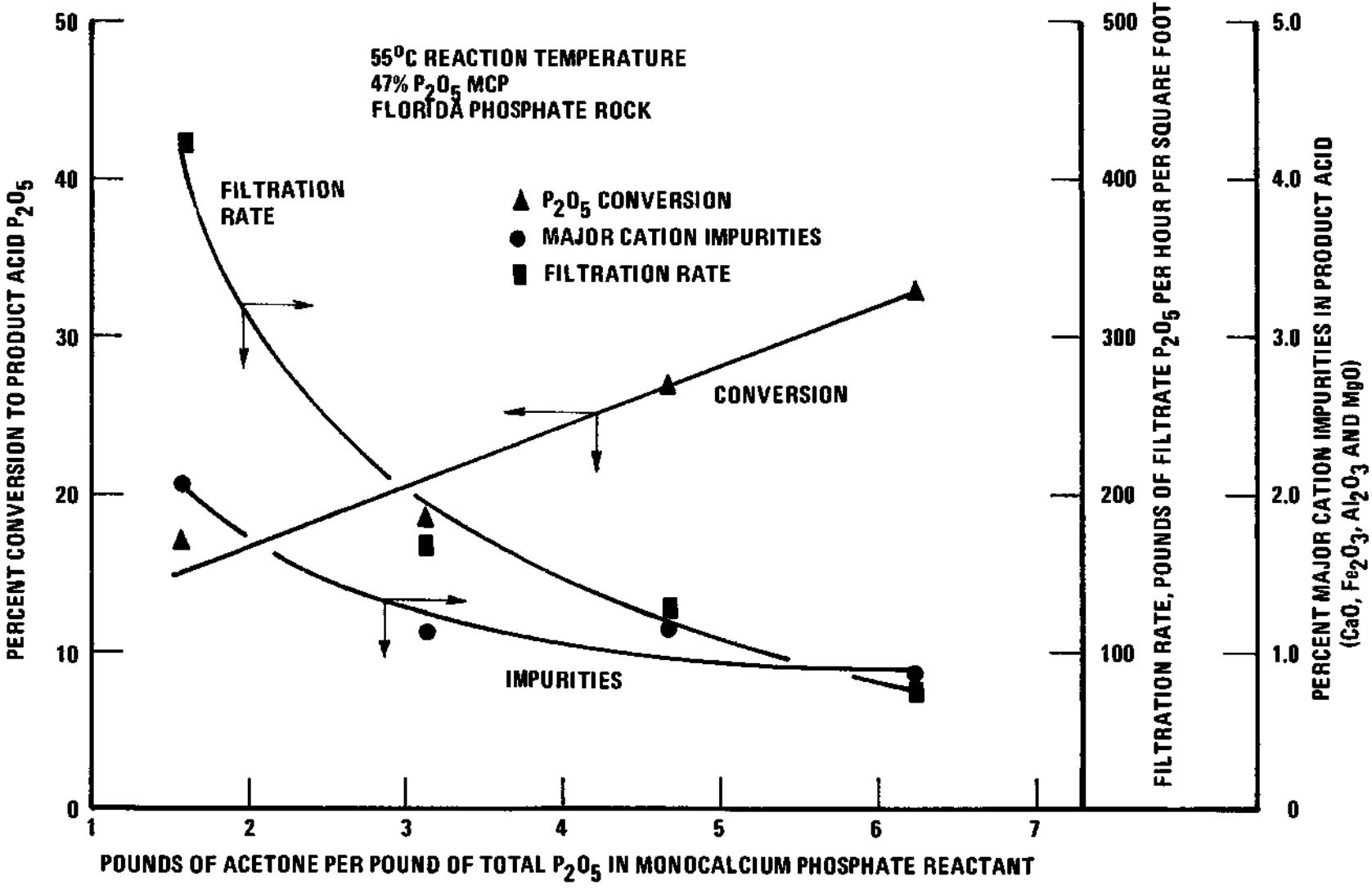

Figure 4. Filtrate P_2O_5 Yield, Impurity Concentration and Filtration Rate Versus Acetone/Monocalcium Phosphate P_2O_5 Ratio

phosphoric acid was relatively constant at approximately one percent.

When the data concerned with the product acid impurity concentrations when using methanol solvent (see Tables 8, 9 and 10) are compared with those when using acetone solvent (see Table 11), it can be seen that the choice of solvent dictated which major cation impurities were preferentially rejected from the product phosphoric acid. When methanol was used as the dissociation solvent, the concentrations of Fe_2O_3 and Al_2O_3 in the product phosphoric acid were generally much lower than when acetone was the dissociation solvent. However, when acetone was used as the dissociation solvent, the concentrations of CaO and MgO were generally much lower than when methanol was the dissociation solvent. However, even though methanol rejects iron and aluminum impurities better than acetone and acetone rejects calcium and magnesium impurities better than methanol, the total major cation impurity concentration in the product phosphoric acid is approximately the same when dissociating with methanol or acetone using similar reaction conditions.

Figure 4 also shows the filtration rate at different acetone solvent/P_2O_5 ratios of the slurry resulting from the dissociation at 55°C of crude Florida monocalcium phosphate containing 47 percent P_2O_5. The filtration rates are expressed in terms of pounds of filtrate P_2O_5 that resulted per hour per square foot of filtration area. The dissociation slurry filtration rate after 15 minutes of reaction time decreased rapidly as the solvent/P_2O_5 ratio was increased up to approximately three pounds of acetone per pound of monocalcium phosphate P_2O_5. As the ratio was increased above three pounds of acetone per pound of monocalcium phosphate P_2O_5, the decrease of the dissociation slurry filtration rate was

not as pronounced. As discussed previously, the dissociation slurry filtration rate while using acetone as the dissociation solvent was much higher than when using methanol. For example, the filtration rate of the slurry resulting from the dissociation at 55°C of crude 47 percent P_2O_5 Florida monocalcium phosphate using 3.1 pounds of solvent per pound of monocalcium phosphate P_2O_5 was 167 pounds of filtrate P_2O_5 per hour per square foot for acetone compared with 19 pounds of filtrate P_2O_5 per hour per square foot for methanol (see Tables 7 and 11).

Batchwise Simulation of Chemical Process Using Methanol and Acetone

A number of experiments were performed in the laboratory to simulate the steady-state process conditions that would occur in a continuous commercial plant producing low impurity phosphoric acid by the process discussed in this work in the case when only the low impurity phosphoric acid product and no dicalcium phosphate is produced. These process simulation experiments were carried out chiefly to determine the appearance and chemical composition of the low impurity phosphoric acid product after fractionation of the dissociation solvent, to determine whether impurity build-up would occur in a continuous process due to recycle of the dissociation filter cake containing most of the rejected impurities and to determine whether crude phosphoric acid could be successfully produced by sulfuric acid attack on the dried dissociation filter cake using the conventional wet process method.

The experimental procedure used was to simulate three cycles of the continuous process in the laboratory. Crude phosphoric acid containing approximately 28 percent P_2O_5 prepared from Florida phosphate rock by the conventional wet process method was reacted with more Florida

phosphate rock using the theoretical acid/phosphate rock ratio (P_2O_5/CaO mole ratio equals 1.0) for producing monocalcium phosphate. This monocalcium phosphate slurry containing approximately 30 percent P_2O_5 was oven dried at 105°C until the weight of the dried material corresponded to that of 47 percent P_2O_5 monocalcium phosphate as determined by a P_2O_5 balance. After pulverizing the dried monocalcium phosphate with a mortar and pestle so that the largest particle passed through a U. S. Standard 18 mesh screen (1.00 millimeter diameter), the screened material was dissociated for 15 minutes with either methanol or acetone at 55°C using a certain solvent/P_2O_5 ratio and filtered through Whatman Number 42 filter paper using water aspiration to provide a vacuum in the filtrate receiver. The filter cake was then washed with a small amount of the dissociation solvent corresponding to approximately five percent of the solvent used for dissociation. A more detailed description of the dissociation and filtration procedures may be found in Chapter II.

The solvent and low impurity phosphoric acid product were separated by fractionation using a Vigreaux column to provide sharp rectification. The procedure utilized for the batch distillation is outlined in more detail in Chapter II.

The filter cake resulting from the crude monocalcium phosphate dissociation was oven dried for 24 hours at 105°C and then pulverized with a mortar and pestle so that the largest particle passed through a U. S. Standard 18 mesh screen (1.00 millimeter diameter). The screened filter cake residue was then reacted with sulfuric acid in order to produce crude wet process phosphoric acid, thus completing one cycle of the process simulation. A more detailed description of the acidulation procedure is given in Chapter II of this work. This crude phosphoric acid

was used to prepare another batch of crude monocalcium phosphate by reaction with Florida phosphate rock, thus initiating the second cycle of the process simulation. Altogether three complete cycles of the chemical process simulation were carried out with each of the dissociation solvents, methanol and acetone. During the second and third simulation cycles, the solvent which had been recovered from the previous cycle by fractionation was used as the dissociation solvent.

Tables 12 and 13 summarize the results of the process simulation experiments. The chemical compositions of the crude phosphoric acid and the low impurity phosphoric acid product are shown in Table 12 along with the P_2O_5 yield in the product acid for the three simulation cycles when using 6.2 pounds of methanol per pound of monocalcium phosphate P_2O_5 and when using 1.6 pounds of acetone per pound of monocalcium phosphate P_2O_5. The dissociation slurry filtration rate and the chemical composition of the dried filter cake are shown in Table 13 along with the wet filter cake solids content and the solvent recovery by fractionation for the three simulation cycles using either methanol or acetone.

It is believed that a fairly good approximation of the chemical compositions of the process flow streams in the steady-state continuous process was acquired during the third process simulation cycle for both methanol and acetone solvents since during the second and third simulation cycles the chemical compositions of the crude phosphoric acid, the low impurity phosphoric acid product and the dried filter cake agreed reasonably well. The P_2O_5 yields, the filtration rates, the filter cake solids contents and the distilled solvent recoveries also agreed reasonably well during the second and third simulation cycles when using

Table 12. Crude and Product Phosphoric Acid Compositions and P_2O_5 Yields for Process Simulations Using Methanol and Acetone. (Crude Florida MCP Containing 47 Percent P_2O_5 was Dissociated at 55°C for 15 Minutes Using the Same Solvent Ratio for the Three Simulation Runs).

Process Simulation	Crude Phosphoric Acid Composition, Weight Percent						Product Phosphoric Acid Composition, Weight Percent						P_2O_5 Yield in Product Acid, Percent
	P_2O_5	CaO	Fe_2O_3	Al_2O_3	MgO	F	P_2O_5	CaO	Fe_2O_3	Al_2O_3	MgO	F	
Solvent Ratio: 6.2 Pounds of Methanol per Pound of MCP P_2O_5													
First*	28.30	0.04	1.16	0.43	0.28	1.81	54.41	0.49	0.07	0.08	0.26	0.35	32.3
Second**	27.17	0.00	1.42	1.16	0.33	1.73	55.03	0.37	0.09	0.13	0.23	0.27	28.8
Third**	30.01	0.11	1.41	1.18	0.34	1.64	54.00	0.45	0.08	0.10	0.23	0.31	29.5
Solvent Ratio: 1.6 Pounds of Acetone per Pound of MCP P_2O_5													
First*	28.30	0.04	1.16	0.43	0.28	1.81	51.61	0.04	0.87	0.39	0.19	0.16	15.0
Second**	29.93	0.16	1.32	1.18	0.37	1.83	52.46	0.04	0.95	0.43	0.24	0.19	15.8
Third**	29.79	0.15	1.51	1.32	0.31	1.73	52.82	0.05	0.79	0.34	0.18	0.17	17.0

*The crude phosphoric acids used in the first process simulations were prepared from sulfuric acid acidulation of Florida phosphate rock.

**The crude phosphoric acids used in the second and third process simulations were prepared from sulfuric acid acidulations of the dried filter cakes from the previous process simulations.

Table 13. Filtration Rates, Filter Cake Compositions and Solvent Fractionation Duties for Process Simulations Using Methanol and Acetone. (Crude Florida MCP Containing 47 percent P_2O_5 was Dissociated at 55°C for 15 Minutes Using the Same Solvent Ratio for the Three Simulation Runs).

Process Simulation	Filtration Rate		Dried Filter Cake Composition, Weight Percent				Pounds of Dry Filter Cake per Pound of Wet Filter Cake	Pounds of Distilled Solvent per Pound of Dissociation Solvent Reactant and Cake Wash
	lbs. of Filtrate P_2O_5/Hr. per SqFt	Gal. of Filtrate per Hr. per Sqft.	Total P_2O_5	Citrate Insoluble P_2O_5	Water Soluble P_2O_5	CaO		
		Solvent Ratio: 6.2 Pounds of Methanol per Pound of MCP P_2O_5						
First	-	-	45.23	0.13	28.47	25.13	0.564	0.830
Second	18	62	45.78	0.87	34.77	23.71	0.602	0.840
Third	17	60	45.97	0.18	27.65	24.00	0.580	0.792
		Solvent Ratio: 1.6 Pounds of Acetone per Pound of MCP P_2O_5						
First	336	579	51.27	0.73	37.08	23.47	0.694	0.645
Second	309	521	51.13	0.62	37.78	24.06	0.663	0.517
Third	373	556	50.76	0.49	36.90	23.31	0.665	0.554

either methanol or acetone.

The data indicate that the total recycle in a continuous process of the dried filter cake which results from dissociation with methanol or acetone does not produce the undesirable effect of a gradual increase in product phosphoric acid impurity concentration due to an accumulation of impurities in the system (see Table 12). The concentration of the major impurities (CaO, Fe_2O_3, Al_2O_3, MgO and F) in the product phosphoric acid remained reasonably constant with no noticeable increase during the three process simulation cycles when using methanol and acetone. The effect of filter cake recycle on the product phosphoric acid P_2O_5 yield was negligible since the P_2O_5 yield remained reasonably constant during the three simulation cycles when using methanol or acetone.

The concentration of the product phosphoric acid that resulted after fractionation of the dissociation solvent was close to 54 percent P_2O_5, the concentration of commercial merchant grade phosphoric acid, when using either methanol or acetone. This product phosphoric acid concentration is a function of the relative amounts of P_2O_5 and water which result in the filtrate after dissociation. Therefore, the product phosphoric acid concentration is a function of both the product phosphoric acid P_2O_5 yield and the proportion of water in crude monocalcium phosphate reactant. The production of low impurity phosphoric acid containing 54 percent P_2O_5 directly as a result of the solvent fractionation step without the necessity of a subsequent acid concentration step using vacuum evaporation would be highly desirable from an economic standpoint.

The color of the product phosphoric acid resulting from the use of uncalcined phosphate rock after fractionation of the methanol or

acetone dissociation solvent was brown and resembled the appearance of commercial merchant grade brown acid prepared from uncalcined phosphate rock. During fractionation in one experiment, the temperature of the product phosphoric acid was allowed to rise well above 100°C after most of the methanol solvent had been vaporized and recovered. This product phosphoric acid was a black color which probably resulted from the thermal decomposition of a small amount of residual organic solvent remaining in the acid. The methanol in the filtrate resulting from the dissociation of 47 percent P_2O_5 monocalcium phosphate made from calcined North Carolina phosphate rock was separated by evaporation at ambient temperature using water aspiration vacuum. This product acid contained approximately 54 percent P_2O_5 and was light green in color similar to the commercial merchant grade phosphoric acid produced from calcined North Carolina phosphate rock.

It may be seen from Table 12 that the dissociation of crude monocalcium phosphate containing 47 percent P_2O_5 resulted in producing a phosphoric acid product that was not only more concentrated but also contained substantially reduced amounts of calcium, iron, aluminum, magnesium and fluorine impurities when compared to the crude phosphoric acid reactant. As had been noted earlier in this work, the use of methanol as the dissociation solvent resulted in producing a product phosphoric acid that was low in iron and aluminum content while the use of acetone resulted in producing a product phosphoric acid that was low in calcium and magnesium content. The fluorine impurity content was substantially reduced when using either solvent, but was lower in the product phosphoric acid produced by dissociation with acetone. Because no precipitation occurred

upon addition of barium chloride to product acid samples, the sulfate content of the product phosphoric acid resulting from the methanol and acetone process simulation experiments was estimated to be less than 0.0005 weight percent.

The product acid P_2O_5 yields and the CaO, Fe_2O_3, Al_2O_3, and MgO concentrations in the product acids resulting from the process simulations when using methanol agreed very well with analogous data that resulted from dissociating 47 percent P_2O_5 crude Florida monocalcium phosphate at 55°C with 6.2 pounds of methanol per pound of monocalcium phosphate P_2O_5 during the earlier experimentation (compare Tables 10 and 12). The product acid P_2O_5 yields and the Fe_2O_3 and Al_2O_3 concentrations in the product acids resulting from the process simulations when using acetone agreed reasonably well with analogous data that resulted from dissociating 47 percent P_2O_5 crude Florida monocalcium phosphate at 55°C with 1.6 pounds of acetone per pound of monocalcium phosphate P_2O_5 during the earlier experimentation (compare Tables 11 and 12). However, the product acid CaO content was somewhat lower and the MgO content was somewhat higher in the acetone process simulation experiments than had resulted during the earlier experimentation.

The filtration rates of the dissociation slurry resulting from the process simulations when using methanol or acetone agreed reasonably well with the filtration rates that had been observed during earlier experimentation when dissociating 47 percent P_2O_5 crude monocalcium phosphate at 55°C (see Tables 10, 11 and 13). As has been observed earlier in this work, the filtration rate of the dissociation slurry when using acetone was much greater than when using methanol. This observation is true when

expressing filtration rate on a basis of gallons per hour per square foot of filtration area as well as on a basis of pounds of filtrate P_2O_5 per hour per square foot of filtration area.

The dried filter cake consists chiefly of a mixture of monocalcium phosphate and dicalcium phosphate. The CaO/P_2O_5 mole ratios for the dried filter cakes resulting from the process simulations were approximately 1.3 when using methanol and approximately 1.2 when using acetone based on the chemical analyses in Table 13. The mole ratio was closer to that for monocalcium phosphate and the total P_2O_5 concentration was higher for the filter cakes resulting from the acetone process simulations than for the methanol simulations because the P_2O_5 conversion to phosphoric acid and dicalcium phosphate was lower in the case when using acetone solvent. The water soluble P_2O_5 concentration, which is indicative of monocalcium phosphate content, in the filter cakes resulting from the acetone process simulations was higher than in those filter cakes resulting from the methanol process simulations because of the lower conversion of monocalcium phosphate to dicalcium phosphate and phosphoric acid.

It was observed during pulverization of the dried filter cakes resulting from crude monocalcium phosphate dissociation with a mortar and pestle, that the cakes resulting from dissociation with acetone were very easily ground while the cakes resulting from dissociation with methanol were pulverized only with difficulty. The ease of dried filter cake pulverization would be a definite advantage in a chemical process because less sophisticated and less expensive grinding equipment would be required.

The gypsum filter cakes which resulted from the sulfuric acid

digestion of the minus 18 mesh dissociation filter cake residues were leached with copious amounts of distilled water in order to separate any remaining water soluble P_2O_5. The leached gypsum cakes were then dried, weighed and chemically analyzed for P_2O_5. The P_2O_5 remaining in the gypsum was found to be a range of 0.3 to 0.4 percent of the total P_2O_5 in the dissociation filter cake reactant. Therefore, typical P_2O_5 substitution losses and P_2O_5 losses as unreacted dissociation filter cake are less than 0.4 percent based on the P_2O_5 in the reactant dissociation filter cake when using conventional wet process conditions for the conversion of the phosphate in dried minus 18 mesh dissociation filter cake to crude phosphoric acid. Since typical insoluble P_2O_5 losses in the range of two to three percent normally occur as a result of the sulfuric acid digestion of Florida phosphate rock in a conventional wet process plant (81), it is believed that crude phosphoric acid can be successfully produced by sulfuric acid attack on the dried dissociation filter cake using the conventional wet process method with a fair degree of efficiency.

Table 13 also shows the pounds of dissociation filter cake after drying at 105°C that resulted per pound of wet dissociation filter cake. Since the weight loss during drying is indicative of the amount of solvent evaporated from the filter cake, it can be seen that, generally, more solvent was occluded per pound of filter cake when methanol was used than when acetone was used.

The pounds of solvent that were recovered from the filtrate by fractionation for each simulation cycle while using methanol and acetone are shown in Table 13. The weight of distilled solvent is reported as a proportion of the total amount of solvent used as a dissociation reactant and as a filter cake wash. However, these data do not represent the overall solvent recovery efficiency since a substantial amount of

solvent was occluded in the wet filter cake to be recovered during cake drying. The proportion of solvent recovered during fractionation is indicative only of the proportion of total solvent used that remained in the filtrate after slurry filtration and was then later separated from the product phosphoric acid by fractionation. The proportion of acetone recovered by fractionation was substantially lower than the proportion of distilled methanol because a greater portion of the total acetone charge was occluded in the wet filter cake due to the lower reactant solvent ratio and a subsequently lower solvent/solids ratio in the dissociation slurry.

Methanol and acetone which have been recovered by fractionation from the dissociation filtrate may be successfully recycled for use as solvent for the dissociation of fresh crude monocalcium phosphate without undesirable effects on the filtrate P_2O_5 yield or the impurity rejection from product phosphoric acid. No significant difference in the P_2O_5 yield or product phosphoric acid impurity concentrations could be detected when using fresh or recovered acetone and methanol solvents.

Hydration States of Mono- and Dicalcium Phosphate After Dissociation

The product phosphoric acid concentrations that resulted from the experiments involving dissociation of 47 percent P_2O_5 monocalcium phosphate with methanol indicate that the wet filter cake is composed chiefly of a mixture of anhydrous monocalcium phosphate and anhydrous dicalcium phosphate. Water balances around the dissociation reaction of monocalcium phosphate containing 47 percent P_2O_5 were made assuming the formation of four different product mixtures in the resultant filter cake. The reactant crude monocalcium phosphate was assumed to be in the monohydrate form and

and was assumed to contain 0.50 weight percent free water which is typical for 47 percent P_2O_5 crude monocalcium phosphate (see Table 3). During reaction, the dissociated monocalcium phosphate monohydrate was assumed to yield its water of crystallization to the filtrate. Thirty percent conversion of the monocalcium phosphate P_2O_5 to phosphoric acid was assumed and dilution of the product phosphoric acid by impurities was neglected in the calculations. The four different cases of resultant filter cake products which were assumed during calculation of the water balances were as follows: 1) formation of anhydrous unreacted monocalcium phosphate and anhydrous dicalcium phosphate, 2) formation of unreacted monocalcium phosphate monohydrate and anhydrous dicalcium phosphate, 3) formation of anhydrous unreacted monocalcium phosphate and dicalcium phosphate dihydrate and 4) formation of unreacted monocalcium phosphate monohydrate and dicalcium phosphate dihydrate. The theoretical product phosphoric acid concentrations calculated from water balances assuming the formation of these four different filter cake products were 54.4, 64.8, 75.1 and 96.6 percent P_2O_5, respectively. It may be seen from Table 12 that the P_2O_5 concentration of the product phosphoric acid after fractionation which resulted from the dissociation of 47 percent P_2O_5 monocalcium phosphate with 6.2 pounds of methanol per pound of monocalcium phosphate P_2O_5 at 55°C fell in a range of 54.00 to 55.03 percent P_2O_5. This range agreed well with the 54.4 percent P_2O_5 concentration predicted by the water balance assuming the formation of anhydrous unreacted monocalcium phosphate and anhydrous dicalcium phosphate in the filter cake. An advantage which arises from the formation of anhydrous calcium phosphates in the filter cake is the ability to recycle evaporated

solvent to the dissociation step directly without the necessity of an additional step to separate water which has been also vaporized during cake drying.

Table 14 shows the theoretical product phosphoric acid P_2O_5 concentrations which would result from monocalcium phosphate dissociations at different P_2O_5 yields and different monocalcium phosphate compositions calculated assuming the formation of anhydrous unreacted monocalcium phosphate and anhydrous dicalcium phosphate in the wet filter cake. The reactant crude monocalcium phosphate was assumed to be in the monohydrate form except for the 50 percent P_2O_5 material and, during reaction, the dissociated monocalcium phosphate monohydrate was assumed to yield its water of crystallization to the filtrate. Dilution of the product acid by impurities was neglected in the calculations. The monocalcium phosphate containing 47 percent P_2O_5 was assumed to contain a typical 0.50 percent free water. The free water content for the other compositions was calculated on this basis.

It may be seen that, as stated above, the theoretical product phosphoric acid P_2O_5 concentration resulting from dissociation of 47 percent P_2O_5 monocalcium phosphate with 30 percent P_2O_5 yield in the filtrate after fractionation was 54.4 percent P_2O_5. This was experimentally verified during the dissociation of 47 percent P_2O_5 monocalcium phosphate with 6.2 pounds of methanol per pound of monocalcium phosphate P_2O_5 at 55°C (see Table 12). It may be seen that the product phosphoric acid concentration varies greatly as the monocalcium phosphate composition is varied within a range of 32 to 50 percent P_2O_5 and as the filtrate P_2O_5 yield is varied within a range of 20 to 35 percent. In order to produce

Table 14. Product Phosphoric Acid Concentration Resulting from Monocalcium Phosphate Dissociations at Different P_2O_5 Yields and Different Monocalcium Phosphate Compositions. (The Calculated Product Acid Concentrations Assume that the Monocalcium Phosphate and Dicalcium Phosphate in the Filter Cake are both in the Anhydrous Forms and that the Free Water and Water of Crystallization Originally in the Crude MCP Reactant Remain in the Product Acid after Dissociation. Dilution of the Product Acid by Impurities was Neglected in the Calculations).

Calculated Reactant Monocalcium Phosphate Composition, Weight Percent			Calculated Product Phosphoric Acid P_2O_5 Content at Various Dissociation P_2O_5 Yields, Weight Percent P_2O_5			
Total P_2O_5	Free Water*	Water of Crystallization**	20 Percent Yield	25 Percent Yield	30 Percent Yield	35 Percent Yield
32	32.26	4.06	14.2	16.9	19.4	21.6
35	25.90	4.44	17.5	20.6	23.4	25.9***
38	19.55	4.82	21.8	25.3	28.4	31.1***
41	13.20	5.20	27.6	31.5	34.8	37.6***
44	6.85	5.58	35.8	39.8	43.1	45.7***
47	0.50	5.97	48.3	51.8	54.4****	56.4***
50	0.00	0.49	69.9	70.4	70.7***	71.0***

*The 47 percent P_2O_5 MCP was assumed to contain a typical 0.50 percent free water. The free water content for the other MCP compositions was calculated on this basis.

**Reactant monocalcium phosphate was assumed to be in the monohydrate form except for the 50 percent P_2O_5 MCP. Crude monocalcium phosphate monohydrate with no free water would correspond to 6.00 percent water of crystallization.

***Not within experimental range studied.

****This is the only experiment in which the P_2O_5 content of the product acid was experimentally determined.

merchant strength product phosphoric acid (54 percent P_2O_5) without subsequent water evaporation after dissociation, the reactant monocalcium phosphate should be dried to a P_2O_5 composition of 47 percent prior to dissociation when the crude monocalcium phosphate is dissociated using conditions which promote a 30 percent filtrate P_2O_5 yield.

Table 14 also indicates that the P_2O_5 concentration in the product phosphoric acid resulting from the dissociation of crude monocalcium phosphate containing 50 percent P_2O_5 is approximately 70 percent P_2O_5 when a filtrate P_2O_5 yield of 20 percent or more is realized. Although this product acid concentration has not been verified experimentally, an earlier experiment resulted in a 26 percent filtrate P_2O_5 yield when methanol was used to dissociate crude Florida monocalcium phosphate containing 50 percent P_2O_5 (see Table 10). Since commercial phosphoric acid of higher P_2O_5 concentration than conventional merchant grade acid is desirable for some applications, it is recommended that further study be initiated to investigate more completely the production of phosphoric acid by the dissociation of crude monocalcium phosphate containing more than 47 percent P_2O_5.

Near Optimum Dissociation Conditions Using Methanol and Acetone

Processing conditions for a chemical process are optimized in order to produce a desired product at the cheapest production cost. The process investigated in this work produces a phosphoric acid which is intermediate in impurity content between commercial wet process phosphoric acid and commercial furnace grade phosphoric acid essentially by treating a crude wet process phosphoric acid raw material with certain processing steps which will probably add to the cost of the finished product. During

optimization, the cheapest processing cost per unit of product is determined. The low impurity phosphoric acid resulting from the process might be expected to have a price intermediate between commercial wet process and commercial furnace grade phosphoric acids since its impurity content is lower than that of wet process acid, but higher than that of furnace acid. The present marketing prices (19) for tank car quantities of wet process phosphoric and furnace grade phosphoric acids containing 54 percent P_2O_5 are approximately $145 per ton and $61 per ton, respectively. It may be seen that there exists a reasonably large difference between the prices of the two grades of phosphoric acid so that the low impurity acid could probably be successfully sold at an intermediate value to pay for any increased production cost above that for wet process acid.

Methanol and acetone appear to be the best organic solvents of those studied for dissociating crude monocalcium phosphate to produce low impurity phosphoric acid and a solid residue containing dicalcium phosphate. Not only are methanol and acetone the cheapest solvents but they also result in reasonably high filtrate P_2O_5 yields and reasonably good impurity rejection from the filtrates when used to dissociate crude monocalcium phosphate. The dissociation slurry resulting from the use of acetone has one of the highest filtration rates of those organic solvents investigated. Both methanol and acetone are relatively low boiling solvents which will facilitate solvent stripping from the dissociation filtrate with the use of low quality heat. The effect of total filter cake recycle on filtrate P_2O_5 yield and product phosphoric acid impurity concentration is negligible when using methanol or acetone to dissociate crude Florida monocalcium phosphate containing 47 percent P_2O_5. The

production of crude phosphoric acid by the sulfuric acid attack of recycled filter cake resulting from monocalcium phosphate dissociation with methanol or acetone appears to be entirely feasible.

The data indicate that no more than 15 minutes of dissociation reaction time is required when using methanol or acetone solvent. No significant difference could be detected between the filtrate P_2O_5 yields and product phosphoric acid impurity concentrations resulting from dissociation reaction periods of 15 minutes and four hours. However, the dissociation slurry filtration rate while using acetone was highest for 15 minute reaction periods and decreased with increasing reaction time.

The data indicate that crude monocalcium phosphate containing 47 percent P_2O_5 appears to be a near optimum dissociation reactant when using methanol and acetone. Reasonably high filtrate P_2O_5 yields are possible and lower product phosphoric acid impurity concentrations result when dissociating 47 percent P_2O_5 monocalcium phosphate than occur when dissociating crude monocalcium phosphate containing less than 47 percent P_2O_5. The product phosphoric acid after solvent fractionation is approximately merchant grade concentration (54 percent P_2O_5) without subsequent concentration using expensive vacuum evaporation when crude monocalcium phosphate containing 47 percent P_2O_5 is dissociated with methanol or acetone.

A high dissociation reaction temperature should be utilized as higher filtrate P_2O_5 yields occur at higher temperatures when using either methanol or acetone. A dissociation temperature close to the normal boiling point of the solvent is probably near optimum when operating at atmospheric pressure because high filtrate P_2O_5 yields occur at

high temperatures, because the recycled solvent having been condensed just prior to recycle will be near its boiling temperature and because the dried and pulverized crude monocalcium phosphate reactant will be hot unless expensive cooling is effected prior to dissociation. The dissociation reaction temperatures which have been studied using methanol and acetone with the closest proximity to the normal boiling point of these solvents is 55°C. A 55°C dissociation temperature is recommended when using acetone and, due to lack of data at higher temperatures, a 55°C dissociation temperature is also recommended for methanol. Further work should be initiated to study crude monocalcium phosphate dissociation with methanol at a temperature closer to its normal boiling point than 55°C.

Based on presently existing data, solvent/P_2O_5 ratio of six pounds of methanol per pound of P_2O_5 in crude 47 percent P_2O_5 monocalcium phosphate is near optimum. Product phosphoric acid containing 54 percent P_2O_5 (merchant grade concentration) results after methanol fractionation directly without the need for subsequent concentration when this solvent/P_2O_5 ratio is used (see Tables 12 and 14). At this ratio, the resulting product phosphoric acid contains less than one weight percent total major cation impurities; i.e., calcium, iron, aluminum and magnesium (see Table 12 and Figure 2). However, at ratios much lower than six pounds of methanol per pound of monocalcium phosphate P_2O_5, the resultant product phosphoric acid contains impurities at concentrations substantially higher than one percent total major cations. Since the plot of major cation impurity concentration as a function of methanol solvent/P_2O_5 ratio while dissociating 47 percent P_2O_5 monocalcium phosphate has a reasonably

steep slope at six pounds of methanol per pound of crude monocalcium phosphate P_2O_5, it is believed that dissociation with methanol at higher solvent/P_2O_5 ratios should be investigated.

The filtrate P_2O_5 yield is a reasonably high 30 percent while dissociating 47 percent P_2O_5 monocalcium phosphate with six pounds of methanol per pound of monocalcium phosphate P_2O_5 and is substantially higher than when dissociating with three pounds of methanol per pound of monocalcium phosphate P_2O_5 (see Figure 2). Since the plot of filtrate P_2O_5 yield as a function of methanol solvent/P_2O_5 ratio when dissociating 47 percent P_2O_5 monocalcium phosphate has a reasonably steep slope at six pounds of methanol per pound of crude monocalcium phosphate P_2O_5, it is believed that dissociation with methanol at higher solvent/P_2O_5 ratios should be investigated. The filtration rate of the slurry resulting from the methanol dissociation of 47 percent P_2O_5 monocalcium phosphate is approximately the same (around 20 pounds of filtrate P_2O_5 per hour per square foot) regardless of whether three or six pounds of methanol per pound of monocalcium phosphate P_2O_5 are used (see Figure 2).

When using acetone to dissociate crude monocalcium phosphate containing 47 percent P_2O_5, ratio of three pounds of acetone per pound of monocalcium phosphate P_2O_5 is near optimum based on presently existing data. At this solvent/P_2O_5 ratio, the resulting product phosphoric acid contains approximately one weight percent total major cation impurities; i.e., calcium, iron, aluminum and magnesium (see Figure 4). However, at higher solvent/P_2O_5 ratios the data indicate that further decrease in product acid cation impurities is small. A reasonably good filtrate P_2O_5 yield of approximately 20 percent results when three pounds of acetone

per pound of monocalcium phosphate are used. At this solvent/P_2O_5 ratio the dissociation slurry filtration rate is very good (approximately 200 pounds of filtrate P_2O_5 per hour per square foot) but the use of a higher solvent/P_2O_5 ratio would result in a substantial decrease in filtration rate (see Figure 4). Therefore, a ratio of three pounds of acetone per pound of monocalcium phosphate P_2O_5 is recommended for the process in the case when both low impurity phosphoric acid product and the solid product containing dicalcium phosphate are produced and in the case when only the solid product containing dicalcium phosphate is produced with the low impurity phosphoric acid being recycled.

However, when considering the process variation during which low impurity phosphoric acid is the sole product with the dried dissociation filter cake being recycled, material balances around the CaO and P_2O_5 constituents require that the process be operated with a minimum dissociation filtrate P_2O_5 yield of 23 percent in order to produce crude monocalcium phosphate with a CaO/P_2O_5 mole ratio of 1.0. At filtrate P_2O_5 yields of less than the minimum 23 percent, the crude monocalcium phosphate CaO/P_2O_5 mole ratio will be less than 1.0 thus allowing unreacted crude phosphoric acid to be present in the monocalcium phosphate effluent stream. In order to achieve a 23 percent filtrate P_2O_5 yield when dissociating crude monocalcium phosphate containing 47 percent P_2O_5 at 55°C, a solvent/P_2O_5 ratio of 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 must be used (see Figure 4). Although the impurity content in the low impurity phosphoric acid resulting from the use of either 3.0 or 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 is approximately the same, the dissociation slurry filtration rate

when using a ratio of 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 is approximately 150 pounds of filtrate P_2O_5 per hour per square foot compared with 200 pounds of filtrate P_2O_5 per hour per square foot at a ratio of 3.0 pounds of acetone per pound of monocalcium phosphate P_2O_5. When producing a sole product of low impurity phosphoric acid, a solvent/P_2O_5 ratio of 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 is recommended.

Although the actual P_2O_5 concentration of the product acid after solvent fractionation when dissociating 47 percent P_2O_5 monocalcium phosphate with 3.0 or 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 has not been determined, it is believed that the P_2O_5 concentration is approximately that of merchant grade acid (54 percent P_2O_5) based on the process simulation experiments using 1.6 pounds of acetone per pound of monocalcium phosphate P_2O_5. The P_2O_5 concentration of the product phosphoric acid when dissociating with 3.0 and 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 should be experimentally determined using the process simulation technique. The phosphoric acid products resulting from the dissociation of crude 47 percent P_2O_5 monocalcium phosphate at 55°C with either 6.0 pounds of methanol or 3.0 or 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 are both approximately merchant grade (54 percent P_2O_5) after solvent fractionation without subsequent concentration. The phosphoric acid products resulting from dissociation with these solvents at their respective ratios both contain approximately one weight percent major cation impurities (CaO, Fe_2O_3, Al_2O_3 and MgO). However, the use of six pounds of methanol per pound of monocalcium phosphate P_2O_5 results in product phosphoric acid

which is very low in iron and aluminum impurities while the use of 3.0 or 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 results in product phosphoric acid which is very low in calcium and magnesium impurities. Dissociation with 6.0 pounds of methanol per pound of monocalcium phosphate P_2O_5 results in a phosphoric acid product containing approximately 0.3 weight percent fluorine. The actual fluorine concentration of the product acid resulting from dissociation with 3.0 or 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 has not been determined but is believed to be lower than the approximately 0.2 weight percent fluorine concentration in the acid product resulting from dissociation with 1.6 pounds of acetone per pound of monocalcium phosphate P_2O_5. The fluorine content in the acid product while dissociating with 3.0 and 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 should be experimentally determined using the process simulation technique.

The use of 6.0 pounds of methanol per pound of monocalcium phosphate P_2O_5 (the recommended ratio) to dissociate crude 47 percent P_2O_5 monocalcium phosphate results in a higher (30 percent) filtrate P_2O_5 yield than when using the recommended 3.0 or 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 (20 and 23 percent yield). However, dissociation with 6.0 pounds of methanol per pound of monocalcium phosphate P_2O_5 produces a slurry which filters approximately one-tenth as rapidly as the dissociation slurry resulting from the use of 3.0 or 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 (20 pounds of filtrate P_2O_5 per hour per square foot versus 200 or 150 pounds of filtrate P_2O_5 per hour per square foot).

Methanol is a cheaper solvent, on a weight basis, than acetone.

Methanol is less volatile and, consequently, lower losses attributed to solvent vaporization would probably result with the use of methanol solvent in the process.

The use of acetone as dissociation solvent results in the production of a dried filter cake which is much more easily pulverized than when using methanol solvent. Therefore, it is anticipated that the use of acetone would require a less sophisticated, cheaper mill for pulverizing dried filter cake than when using methanol. The dissociation slurry produced by the use of acetone filters much more rapidly than that corresponding to the use of methanol resulting in a lower capital cost required for filtration equipment. The data indicate that less solvent is occluded in the wet filter cake when using acetone resulting in the requirement of a lower cake dryer duty. Because the boiling point of acetone is lower than that of methanol, easier rectification of solvent and acid product should result in a fractionator when acetone solvent is used. Also, the use of lower pressure steam for fractionation and filter cake drying should result when acetone is used. Since the enthalpy of vaporization of acetone is approximately one-half that of methanol, on a weight basis, the use of acetone would require a much lower energy duty for solvent fractionation and cake drying per pound of solvent used.

In general, at equal solvent/P_2O_5 ratios and equal dissociation temperatures methanol and acetone produce approximately the same filtrate P_2O_5 yield when dissociating crude monocalcium phosphate containing 47 percent P_2O_5. Approximately the same total cation impurity concentrations in the product phosphoric acid result when acetone and methanol are used to dissociate crude 47 percent P_2O_5 monocalcium phosphate using

equal solvent/P_2O_5 ratios and equal dissociation temperatures. However, the use of methanol results in preferential rejection of iron and aluminum impurities whereas the use of acetone results in the preferential rejection of calcium and magnesium impurities.

It is recommended that a very comprehensive economic study be made to determine whether methanol or acetone is the better dissociation solvent to use. Each solvent has its relative merits and a close economic study is needed to determine the better solvent for the process.

To summarize, methanol and acetone are considered to be the best organic dissociation solvents to be used in the chemical process under consideration. It is recommended that the crude monocalcium phosphate be dried to contain 47 percent P_2O_5 and then dissociated in the presence of either methanol or acetone using 15 minutes contact time at 55°C. Using these dissociation conditions and the recommended solvent/P_2O_5 ratio, the resulting filtrate yields and filtration rates are as follows:

Solvent	Recommended Pounds of Solvent per lb. of Total P_2O_5 in Unreacted MCP	P_2O_5 Yield in Product Acid, %	Filtration Rate: Pounds of Filtrate P_2O_5 per Hour per Square Foot	Filtration Rate: Gals. of Filtrate per Hour per Square Foot
Methanol	6.0	30	20	60
Acetone	3.0	20	200	460
Acetone	3.7	23	150	370

The product phosphoric acid, which results after fractionation and recovery of the dissociation solvent when the recommended dissociation conditions are used, has the following chemical analysis:

Solvent	Lbs. of Solvent per lb. of MCP P_2O_5	Chemical Analysis of Product Acid, Weight Percent P_2O_5	CaO	Fe_2O_3	Al_2O_3	MgO	F	$SO_4^=$
Methanol	6.0	54	0.4	0.08	0.10	0.25	0.3	0.00
Acetone	3.0	54	0.05	0.5	0.4	0.05	<0.2	0.00
Acetone	3.7	54	0.05	0.5	0.4	0.05	<0.2	0.00

A ratio of 3.0 pounds of acetone per pound of monocalcium phosphate P_2O_5 is recommended for the process in the case when both low impurity phosphoric acid product and the solid product containing dicalcium phosphate are produced and in the case when only the solid product containing dicalcium phosphate is produced with the low impurity phosphoric acid being recycled. A ratio of 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 is recommended when producing low impurity phosphoric acid alone with the dried dissociation filter cake being recycled.

Experimentation Concerned with Overall Process Variations

Some experimentation was performed which was concerned with determining the feasibility of using certain variations in the overall chemical process that has been previously described for producing low impurity phosphoric acid and/or a solid product containing dicalcium phosphate by the dissociation of crude monocalcium phosphate with an organic solvent.

Production of Solid Product Containing Dicalcium Phosphate and Gypsum

As an alternative mode of operation of the phosphoric acid-dicalcium phosphate process described earlier in this work, the possibility of producing a solid fertilizer product containing both dicalcium phosphate and gypsum was investigated. In this proposed alternative, the

filtration of gypsum and impurities (Step B in Figure 1) is omitted and the digestion and reaction Steps A and C are combined into one reaction step so that the gypsum leaves the process mixed with the dried solid containing dicalcium phosphate. The phosphoric acid is recycled to the combined reaction and digestion Steps A and C so that the sole product is a solid material chiefly composed of gypsum, dicalcium phosphate and unreacted monocalcium phosphate. Such a product would be suitable as a fertilizer, although lower in P_2O_5 concentration than the mixture of dicalcium phosphate and monocalcium phosphate alone; for some applications it would be preferable to the mixture of dicalcium phosphate and monocalcium phosphate because of its sulfur content.

With all the phosphoric acid from the dissociation and separation steps recycled, the net result of the process is the production of a dicalcium phosphate-monocalcium phosphate-gypsum product with much less sulfuric acid than required to convert the same amount of phosphate rock into triple superphosphate or normal superphosphate (a commercial mixture composed chiefly of gypsum and monocalcium phosphate). For example, if the dissociation step went to completion resulting in a dicalcium phosphate-gypsum product containing no unreacted monocalcium phosphate, then this product would theoretically require the usage of one-half the amount of sulfuric acid to produce a unit of available P_2O_5 as that required to produce a unit of available P_2O_5 in either normal or triple superphosphate.

An experiment simulating the process variation described above was performed during which methanol was used as the dissociation solvent. A slurry containing a mixture of crude monocalcium phosphate and gypsum

was prepared by reacting predetermined amounts of ground Florida phosphate rock, technical grade sulfuric acid, water and previously prepared crude wet process phosphoric acid containing approximately 30 percent P_2O_5. The amounts of these reactants were calculated assuming 30 percent P_2O_5 in the acid recycled from the dissociation step where a 30 percent P_2O_5 yield in the recycle acid occurred and assuming a CaO/P_2O_5 mole ratio of 1.0 in the resulting monocalcium phosphate after precipitation of the sulfate as gypsum. These four reactants were agitated at 70°C to 80°C for 90 minutes and then agitated with 6.1 pounds of methanol per pound of P_2O_5 in the initial reactants at 55°C for 15 minutes. After filtration of this dissociation slurry the resultant filtrate and solid product were subjected to chemical analysis.

It was determined that the dried filter cake product contained 30.81 percent CaO and 17.23 percent total P_2O_5 with water soluble and citrate insoluble P_2O_5 contents of 8.47 percent and 2.81 percent, respectively. The P_2O_5 yield in the filtrate was 50.5 percent of the P_2O_5 in the initial reactants. Although this high filtrate P_2O_5 yield indicates that the dissociation reaction went to completion, it is believed that, in fact, the dissociation reaction was somewhat less than complete and that the high filtrate P_2O_5 yield was caused by a portion of the initial crude phosphoric acid reactant washing through with the filtrate without reacting with the phosphate rock to form crude monocalcium phosphate. This is supported by the higher than desired citrate insoluble P_2O_5 content of the cake which indicates that conversion of the phosphate rock to monocalcium phosphate was less than complete and is also supported by the water soluble P_2O_5 content of the cake which indicates

that at least a portion of the crude monocalcium phosphate remained undissociated. However, a substantial amount of monocalcium phosphate dissociation did occur since the citrate soluble content of the cake, indicative of dicalcium phosphate, was 5.95 percent by difference.

The wet filter cake contained 0.603 pounds of dry cake per pound of wet cake after drying. This indicates that the amount of methanol solvent occluded in the wet cake is approximately the same amount of solvent occluded in the wet filter cake resulting from the dissociation of crude monocalcium phosphate with methanol (see Table 13).

The data resulting from this one experiment indicate that this proposed variation of the chemical process is feasible. Although a lower P_2O_5 availability than desired occurred in the solid product resulting from this one experiment, it is believed that a longer reaction period to produce crude monocalcium phosphate and gypsum would decrease the citrate insoluble P_2O_5 content of the final product. It is recommended that a study be initiated to study this process alternate in more detail concentrating on determining optimum reaction conditions to produce the crude monocalcium phosphate-gypsum reactant and on determining the best solvent to use for dissociation along with optimum dissociation conditions. Methanol and acetone are two solvents which are especially recommended for further study in this process variation.

Combination of Crude Monocalcium Phosphate Preparation and Dissociation Steps

The feasibility of combining the crude monocalcium phosphate preparation and dissociation steps was experimentally investigated as a variation of operating the phosphoric acid-dicalcium phosphate process.

In this alternative the reaction of phosphate rock and crude phosphoric acid and the dissociation of crude monocalcium phosphate (Steps C and E in Figure 1) are combined into one reaction step so that crude phosphoric acid, phosphate rock and solvent all react to form dicalcium phosphate, undissociated monocalcium phosphate and purified phosphoric acid. The crude monocalcium phosphate drying Step D is omitted and water removal from the system occurs either during a crude phosphoric acid concentration step which takes place immediately after gypsum filtration or during a purified phosphoric acid concentration step which takes place immediately after gypsum filtration or during a purified phosphoric acid concentration step which takes place immediately after separation of solvent and dissociation phosphoric acid. In addition to the obvious advantage of equipment elimination and overall process simplification that such a variation offers, another reason for undertaking the study of this process alternate was to determine whether the formation and dissociation of crude monocalcium phosphate in the presence of an organic solvent would occur in the same processing step.

A number of experiments simulating the process variation described above were performed during which five organic solvents were used as dissociation media, i.e., methanol, normal propanol, normal butanol, isoamyl alcohol and acetone. Weighed amounts of ground Florida phosphate rock, crude phosphoric acid prepared from Florida phosphate rock and solvent were vigorously agitated at a controlled temperature. The crude phosphoric acid reactant was either unconcentrated wet process acid containing approximately 30 percent P_2O_5 or wet process acid which had been concentrated to 52 percent P_2O_5 by vacuum evaporation. The amounts

of crude phosphoric acid and phosphate rock reacted were calculated using various CaO/P_2O_5 mole ratios including a CaO/P_2O_5 mole ratio of 1.0. Samples of the agitated slurry were filtered after certain reaction periods and the resulting filtrates and filter cakes were chemically analyzed for various materials.

Condensed data which resulted from these experiments are presented in Table 15. The detailed results are given in Appendix D. Table 15 shows, at various reaction conditions, the average P_2O_5 yields in the product phosphoric acid and the average concentrations of CaO, Fe_2O_3 and Al_2O_3 impurities in product phosphoric acid containing 54 percent P_2O_5. The solvent, solvent/P_2O_5 ratio, reactant acid P_2O_5 concentration, reaction temperature and the reactant acid P_2O_5/total reactant P_2O_5 ratio are shown in Table 15. For the raw materials used in this set of experiments, 0.726 pounds of reactant acid P_2O_5 per pound of P_2O_5 in the reactants corresponds to a CaO/P_2O_5 mole ratio of 1.0. It can be seen that CaO/P_2O_5 mole ratios above and below 1.0 were used in the experiments.

The average P_2O_5 yields that appear in Table 15 represent the percentage of reactant P_2O_5 that resulted as product phosphoric acid P_2O_5 with all such P_2O_5 yields having been time-averaged over the dissociation reaction periods investigated using a certain set of reaction conditions. The average concentrations of product acid CaO, Fe_2O_3 and Al_2O_3 that appear in Table 15 represent the weight percentage of these species in product phosphoric acid containing 54 percent P_2O_5 with all such impurity concentrations having been time-averaged over the dissociation reaction periods investigated using a certain set of conditions. The P_2O_5 yields and product acid impurity concentrations were time-averaged in order

Table 15. Average P_2O_5 Yield and Average Impurity Concentration for Phosphoric Acid from the Combination of Crude Monocalcium Phosphate Formation and Dissociation Steps Using Various Organic Solvents. (Florida Phosphate Rock and Acid Prepared from Florida Phosphate Rock were Used as Reactants).

Solvent	Pounds Solvent per Pound P_2O_5 in Reactants	Total P_2O_5 in Reactant Acid, Weight Percent	Pounds Reactant Acid P_2O_5 Per Pound P_2O_5 in Reactants	Reaction Temperature, °C	Average P_2O_5 Yield in Product Acid*, Percent	Average Percent Impurity in Product Acid Containing 54% P_2O_5*		
						CaO	Fe_2O_3	Al_2O_3
Methanol	1.57	34.28	0.726	55	77.4	0.37	2.28	1.07
Methanol	3.14	34.28	0.726	55	80.4	0.23	2.42	2.15
Methanol	6.28	34.28	0.726	55	74.4	0.18	2.63	1.71
Methanol	12.57	34.28	0.726	55	78.2	0.69	2.04	1.29
Normal Propanol	6.28	34.28	0.726	70	75.4	0.15	0.87	0.11
Normal Butanol	6.28	34.28	0.725	70	64.8	0.60	0.61	0.20
Isoamyl Alcohol (85%)	6.28	34.28	0.725	70	62.6	4.39	2.21	1.81
Acetone	6.28	34.28	0.726	51	75.7	0.14	1.28	0.46
Methanol	3.16	52.11	0.498	55	55.1	0.13	2.25	1.45
Methanol	3.15	52.11	0.666	55	73.1	0.20	1.55	2.67
Methanol	3.15	52.11	0.726	55	71.3	0.04	1.97	1.89

Table 15. (Continued)

Solvent	Pounds Solvent per Pound P_2O_5 in Reactants	Total P_2O_5 in Reactant Acid, Weight Percent	Pounds Reactant Acid P_2O_5 Per Pound P_2O_5 in Reactants	Reaction Temperature, °C	Average P_2O_5 Yield in Product Acid*, Percent	Average Percent Impurity in Product Acid Containing 54% P_2O_5*		
						CaO	Fe_2O_3	Al_2O_3
Methanol	3.13	52.11	0.749	55	77.2	0.12	2.05	1.99
Methanol	3.13	52.11	0.799	55	82.5	<0.1	2.18	2.03
Methanol	3.15	52.11	0.833	55	86.2	0.01	2.22	1.40
Methanol	6.39	52.11	0.500	55	50.0	<0.01	1.96	1.90
Methanol	6.29	52.11	0.666	55	73.3	0.05	2.13	1.24
Methanol	6.64	52.11	0.726	55	75.4	0.08	2.14	1.50
Methanol	6.30	52.11	0.749	55	81.1	<0.01	2.02	1.43
Methanol	6.29	52.11	0.799	55	85.7	<0.01	2.17	1.44
Methanol	6.28	52.11	0.833	55	85.9	0.21	2.18	1.73
Methanol	12.61	52.11	0.666	55	73.6	0.06	2.46	1.87
Methanol	12.64	52.11	0.725	55	79.7	0.03	1.53	1.85

*"P_2O_5 Yield" and "Percent Impurity" represent the time averages over all dissociation reaction periods investigated for experimental runs using a certain set of conditions.

to condense the data to a form such that determination of the feasibility of combining the crude monocalcium phosphate formation and dissociation steps would be facilitated.

The filtrate P_2O_5 yield resulting from these experiments was generally above 50 percent and much higher than the filtrate P_2O_5 yields observed when dissociating crude monocalcium phosphate with the same solvent. The fraction of reactant P_2O_5 which resulted as filtrate P_2O_5 agrees reasonably well with the pounds of reactant phosphoric acid P_2O_5 that were used per pound of P_2O_5 in the reactants in almost every case. Therefore, it is believed that virtually no reaction between crude phosphoric acid and phosphate rock occurs when the monocalcium phosphate formation and dissociation steps are combined in the presence of an organic solvent.

Although high filtrate P_2O_5 yields were realized during these experiments, the resultant product acid impurity concentrations were also high; in most instances the product acid impurity concentrations were higher than those in commercial merchant grade phosphoric acid produced by the conventional wet process (see Table 1). Therefore, it is concluded that the combination of the crude monocalcium phosphate formation and dissociation steps is a poor method of process operation.

Dissociation of Highly Dried Monocalcium Phosphate With Methanol and Water

Dissociation of highly dried crude monocalcium phosphate in the presence of methanol and small amounts of water was studied. Crude monocalcium phosphate prepared from Florida phosphate rock was dried at 200°C until all free water, all hydrated water and some water of

constitution were expelled. After grinding the dried material to pass a U. S. Standard 18 mesh screen (1.00 millimeter diameter), the crude monocalcium phosphate contained 57.41 percent P_2O_5.

It had been established that dissociation of crude monocalcium phosphate containing 52.6 percent P_2O_5 or greater with anhydrous methanol resulted in very low filtrate P_2O_5 yields (see Table 10 and Figure 3). However, it was hoped that dissociation of highly dried crude monocalcium phosphate in the presence of methanol to which a small amount of water had been added to aid the dissociation mechanism might result in better filtrate P_2O_5 yields. It was hoped that, in addition to high filtrate P_2O_5 yields, lower product phosphoric acid impurity concentrations would result when using this method of dissociation as opposed to the dissociation of crude monocalcium phosphate dried to contain lower concentrations of P_2O_5.

Consequently, experiments were performed during which the minus 18 mesh crude monocalcium phosphate was treated at 55°C with anhydrous methanol to which small amounts of distilled water had been added to hopefully promote dissociation. The amount of distilled water added to the reaction slurry was that amount necessary to dilute the highly dried crude monocalcium phosphate to a P_2O_5 concentration in the range 32 to 47 percent so that the results of these experiments could be compared to the methanol dissociation of monocalcium phosphate containing 47 percent P_2O_5 or less. The methanol, water and highly dried monocalcium phosphate were vigorously agitated at 55°C and samples of the agitated slurry were filtered after certain reaction periods up to four hours. The resulting filtrates and filter cakes were chemically analyzed for various materials.

Condensed data which resulted from these experiments are presented in Table 16. The detailed results are given in Appendix E. Table 16 shows, at various reaction conditions, the average filtrate P_2O_5 yields and the average concentrations of CaO, Fe_2O_3 and Al_2O_3 impurities in the product phosphoric acid containing 54 percent P_2O_5. The calculated monocalcium phosphate P_2O_5 content after water dilution and the solvent/P_2O_5 ratio, which was approximately 6.2 pounds of anhydrous methanol per pound of crude monocalcium phosphate P_2O_5, are also shown in Table 16.

The average filtrate P_2O_5 yields that appear in Table 16 represent the percentage of reactant P_2O_5 that resulted as product phosphoric acid P_2O_5 with all such P_2O_5 yields having been time-averaged over the dissociation reaction periods investigated using a certain set of reaction conditions. The average concentrations of product acid CaO, Fe_2O_3 and Al_2O_3 that appear in Table 16 represent the weight percentage of these species in product phosphoric acid calculated to a 54 percent P_2O_5 basis with all such impurity concentrations having been time-averaged over the dissociation reaction periods investigated using a certain set of conditions. The P_2O_5 yields and product acid impurity concentrations were time-averaged in order to condense the data to a form such that the practicality of this dissociation variation might be more easily discerned.

Very little P_2O_5 was converted to phosphoric acid (less than 3 percent yields for the conditions studied) even when enough free water was added to dilute the dried monocalcium phosphate to an effective P_2O_5 content of 32 percent. Also, when no free water was added to aid dissociation, crude monocalcium phosphate containing 56.08 percent P_2O_5 dissociated with anhydrous methanol resulted in a filtrate P_2O_5

Table 16. Average P_2O_5 Yield and Average Impurity Concentration for Phosphoric Acid from the Dissociation with Methanol at 55°C of Dried Crude Monocalcium Phosphate to which Water was Added to Aid Reaction. (The Crude Solid MCP Prepared from Florida Phosphate Rock was Dried to Contain 57.41 percent P_2O_5).

Equivalent Percent Total P_2O_5 in MCP After Water Addition	Pounds of Methanol per Pound of Total P_2O_5 in Unreacted MCP	Average P_2O_5 Yield in Product Acid*, Percent	Average Percent Impurity in Product Acid Calculated to 54% P_2O_5*		
			CaO	Fe_2O_3	Al_2O_3
32.0	6.16	2.7	<0.70	0.51	1.87
35.0	6.17	1.7	<1.27	1.88	5.55
38.0	6.20	1.2	<1.36	2.00	4.79
41.0	6.23	2.2	<1.60	2.42	5.11
47.0	6.18	1.5	<2.18	2.06	3.26

*"P_2O_5 Yield" and "Percent Impurity" represent the time averages over all dissociation reaction periods investigated for experimental runs using a certain set of conditions.

yield of only 1.7 percent (see Table 10). The product phosphoric acid impurity content was high, in most cases being higher than that found in commercial merchant grade wet process acid (see Table 1). It is therefore concluded that dissociation of highly dried monocalcium phosphate with methanol to which water is added to promote dissociation is a poor method of process operation.

CHAPTER IV

CHEMICAL PROCESS FLOW DIAGRAMS

Flow diagrams are presented in Figures 5, 6 and 7 for three variations of the chemical process which produces low impurity phosphoric acid and/or a solid fertilizer containing dicalcium phosphate utilizing the dissociation of crude monocalcium phosphate in the presence of an organic solvent. The three variations discussed include: 1) the case during which low impurity phosphoric acid alone is produced with recycle of the solid containing dicalcium phosphate, 2) the case during which only a solid product containing dicalcium phosphate is produced with recycle of the low impurity phosphoric acid and 3) the case during which both a low impurity phosphoric acid product and a solid product containing dicalcium phosphate are produced. These flow diagrams are presented along with the total mass flow rates and the compositions of the main flow streams for each process variation based on a total production of 1000 tons per day of product P_2O_5. Flow rates were calculated assuming process operation at the recommended processing conditions discussed in Chapter III using the best dissociation solvents, methanol and acetone.

It should be reiterated that the processing conditions recommended in Chapter III and used in the material balances for the flow sheets presented below are based on data presently available and are not necessarily optimum. The data need to be subjected to an extensive economic study in order to establish true optimum processing conditions,

especially the optimum solvent/P_2O_5 ratio. However, when considering solvent/reactant monocalcium phosphate P_2O_5 ratio, it should be observed that the following advantages are generally realized when the ratio is increased: 1) higher filtrate P_2O_5 yield and higher proportion of dicalcium phosphate in the dissociation filter cake, 2) lower impurity content in the low impurity phosphoric acid and 3) slightly lower sulfuric acid usage per unit of product P_2O_5 for the process variations when recycle of one of the dissociation products occurs. Conversely, the following advantages are generally realized when the solvent/monocalcium phosphate P_2O_5 ratio is decreased: 1) lower solvent losses (assuming solvent losses are proportional to the solvent volume inventory in the process), 2) lower energy requirements for solvent separation from the dissociation products per unit of product P_2O_5 3) higher dissociation slurry filtration rate while using acetone with a corresponding lower filtration expense per unit of P_2O_5, 4) lower amount of working capital required for the solvent inventory in the process and 5) smaller process flow volumes per unit of P_2O_5 product in the process due to the smaller volume of solvent required with a corresponding lower equipment capital cost.

The list of the assumptions used in calculating the material balances which are presented below are given here. The process produces 1000 tons per day of product P_2O_5 resulting from the dissociation at 55°C for 15 minutes of dried crude monocalcium phosphate containing 47 percent total P_2O_5. The dried monocalcium phosphate contains 2.5 percent fluorine. Three percent P_2O_5 losses in the waste gypsum stream are assumed (based on total P_2O_5 in the digestion step) while producing the crude phosphoric

acid. The CaO/P_2O_5 mole ratio in the crude monocalcium phosphate is 1.0. The chemical analysis of the ground phosphate rock reactant is as follows: 33 percent P_2O_5, 50 percent CaO, 1.3 percent Fe_2O_3, 1.3 percent Al_2O_3, 0.4 percent MgO and 3.8 percent F. The chemical analysis of the crude phosphoric acid produced by sulfuric acid digestion after filtration is as follows: 30 percent P_2O_5, 0.5 percent CaO, 1.1 percent Fe_2O_3, 0.8 percent Al_2O_3, 0.3 percent MgO, 2.0 percent F and 2 percent free sulfate. The phosphoric acid resulting during dissociation contains no sulfate. Solvent losses and impurities in the recycled solvent are assumed negligible. When using methanol, a solvent/monocalcium phosphate P_2O_5 ratio of 6.0 tons of methanol per ton of P_2O_5 results in a 30 percent filtrate P_2O_5 yield during dissociation. The dissociation slurry filtration rate is 60 gallons or 20 pounds of filtrate P_2O_5 per hour per square foot. Chemical analysis of the phosphoric acid which results after fractionation of the methanol is as follows: 54 percent P_2O_5, 0.4 percent CaO, 0.08 percent Fe_2O_3, 0.10 percent Al_2O_3, 0.25 percent MgO, 0.3 percent F and 0.0 percent sulfate. The solvent content of the wet dissociation filter cake is 0.4 tons of methanol per ton of wet filter cake. When using acetone, a solvent/P_2O_5 ratio of 3.0 tons of acetone per ton of monocalcium phosphate P_2O_5 is assumed for the case when the solid product containing dicalcium phosphate alone is produced or for the case when both low impurity phosphoric acid product and the solid product containing dicalcium phosphate are produced. When using this ratio, a 20 percent filtrate P_2O_5 yield results during dissociation. The dissociation slurry filtration rate is 460 gallons of filtrate or 200 pounds of filtrate P_2O_5 per hour per square foot. A solvent/P_2O_5 ratio of 3.7 tons of acetone per

ton of monocalcium phosphate P_2O_5 is assumed when a sole product of low impurity phosphoric acid is produced by the process. When using this ratio, a 23 percent filtrate P_2O_5 yield results during dissociation. The dissociation slurry filtration rate is 370 gallons of filtrate or 150 pounds of filtrate P_2O_5 per hour per square foot. Chemical analysis of the phosphoric acid which results after fractionation of the acetone using either solvent/P_2O_5 ratio is as follows: 54 percent P_2O_5, 0.05 percent CaO, 0.5 percent Fe_2O_3, 0.4 percent Al_2O_3, 0.05 percent MgO, 0.2 percent F and 0.0 percent sulfate. The solvent content of the wet dissociation filter cake is 0.35 tons of acetone per ton of wet filter cake when operating at either solvent/monocalcium phosphate P_2O_5 ratio.

Low Impurity Phosphoric Acid Product Only

A flow diagram showing the major processing steps and the major flow streams in the process when producing low impurity phosphoric acid alone with recycle of the solid containing dicalcium phosphate is presented in Figure 5. This figure shows the chief constituents in the streams entering and leaving each of the major processing steps. Each flow stream is labeled with a number to facilitate cross-reference with Tables 17 and 18. Total mass flow rates and compositions of the main process flow streams when producing low impurity phosphoric acid (1000 tons per day of product P_2O_5 output) by dissociation with 6.0 tons of methanol per ton of dried monocalcium phosphate P_2O_5 are shown in Table 17 while the total mass flow rates and compositions of the main process flow streams when producing low impurity phosphoric acid (1000 tons per day of product P_2O_5 output) by dissociation with 3.7 tons of acetone per ton of dried monocalcium phosphate P_2O_5 are shown in Table 18.

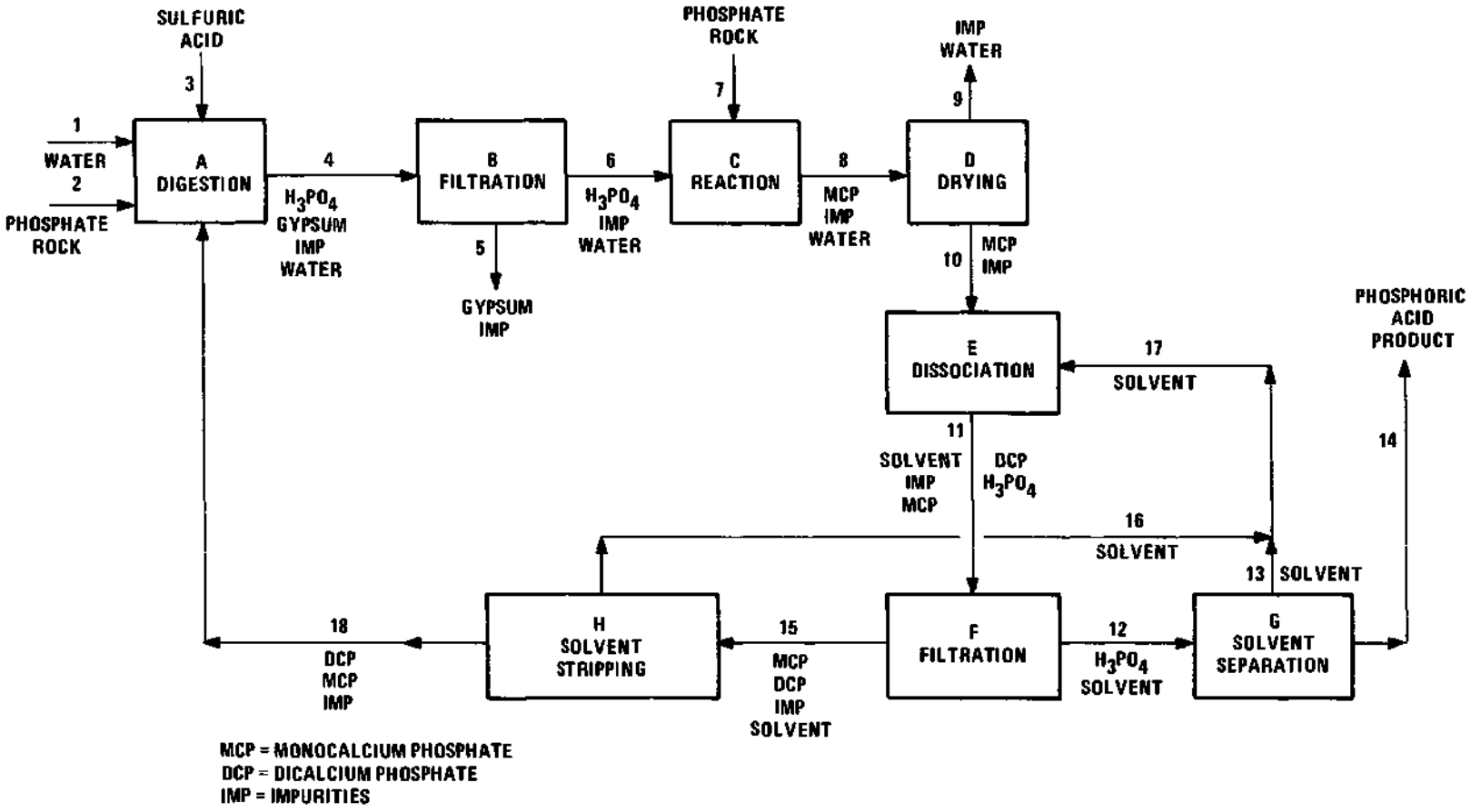

Figure 5. Schematic Diagram for Process with Low Impurity Phosphoric Acid Product and with Recycle of Solid Containing Dicalcium Phosphate

Table 17. Process Flow Rates for the Production of Low Impurity Phosphoric Acid Product With Recycle of Solid Containing Dicalcium Phosphate Using Methanol.
(The process produces 1000 tons per day of product P_2O_5 resulting from the dissociation at 55°C for 15 minutes of dried MCP containing 47 percent P_2O_5 with 6.0 tons of methanol per ton of MCP P_2O_5. Three percent P_2O_5 losses in the waste gypsum stream are assumed while producing the crude phosphoric acid. The crude phosphoric acid is assumed to contain 2.0 percent free $SO_4^=$. The CaO/P_2O_5 mole ratio in the crude MCP is 1.0. During dissociation, a filtrate P_2O_5 yield of 30 percent results. Solvent losses and impurities in the recycled solvent are assumed negligible. The solvent content of the wet dissociation filter cake is assumed to be 0.4 tons of methanol per ton of wet filter cake.)

Process Stream	Process Stream Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per Day							
			P_2O_5	CaO	$SO_4^=$	Fe_2O_3	Al_2O_3	MgO	F	Solvent
1	Water	4486	0	0	0	0.0	0.0	0.0	0.0	0
2	Ground Phosphate Rock	713	235	356	0	9.3	9.3	2.9	27.1	0
3	93 Percent Sulfuric Acid	3053	0	0	2781	0.0	0.0	0.0	0.0	0
4	Wet Process Acid Slurry	13493	2568	1665	2947	132.4	107.0	33.4	198.8	0
5	Waste Gypsum	5187	78	1624	2781	41.0	40.6	8.5	32.7	0
6	Crude Phosphoric Acid	8306	2490	41	166	91.4	66.4	24.9	166.1	0
7	Ground Phosphate Rock	2550	843	1275	0	33.2	33.2	10.2	96.9	0
8	Monocalcium Phosphate Slurry	10856	3333	1316	166	124.6	99.6	35.1	263.0	0
9	Dryer Effluent	3763	0	0	0	0.0	0.0	0.0	85.7	0

Table 17. (Continued)

Process Stream	Process Stream Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per Day							
			P_2O_5	CaO	$SO_4^{=}$	Fe_2O_3	Al_2O_3	MgO	F	Solvent
10	Dried Monocalcium Phosphate	7093	3333	1316	166	124.6	99.6	35.1	177.3	0
11	Dissociation Slurry	27901	3333	1316	166	124.6	99.6	35.1	177.3	19998
12	Dissociation Filtrate	18356	1000	7.4	0	1.5	1.9	4.6	5.6	16504
13	Fractionated Solvent	16504	0	0	0	0.0	0.0	0.0	0.0	16504
14	Low Impurity Phosphoric Acid	1852	1000	7.4	0	1.5	1.9	4.6	5.6	0
15	Dissociation Filter Cake	8735	2333	1309	166	123.1	97.7	30.5	171.7	3494
16	Stripped Solvent	3494	0	0	0	0.0	0.0	0.0	0.0	3494
17	Dissociation Solvent Reactant	19998	0	0	0	0.0	0.0	0.0	0.0	19998
18	Dried Dissociation Residue	5241	2333	1309	166	123.1	97.7	30.5	171.7	0

Table 18. Process Flow Rates for the Production of Low Impurity Phosphoric Acid Product With Recycle of Solid Containing Dicalcium Phosphate Using Acetone
(The process produces 1000 tons per day of product P_2O_5 resulting from the dissociation at 55°C for 15 minutes of dried MCP containing 47 percent P_2O_5 with 3.7 tons of acetone per ton of MCP P_2O_5. Three percent P_2O_5 losses in the waste gypsum stream are assumed while producing the crude phosphoric acid. The crude phosphoric acid is assumed to contain 2.0 percent free $SO_4^=$. The CaO/P_2O_5 mole ratio in the crude MCP is 1.0. During dissociation, a filtrate P_2O_5 yield of 23 percent results. Solvent losses and impurities in the recycled solvent are assumed negligible. The solvent content of the wet dissociation filter cake is assumed to be 0.35 tons of acetone per ton of wet filter cake.)

Process Stream	Process Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per day							
			P_2O_5	CaO	SO_4	Fe_2O_3	Al_2O_3	MgO	F	Solvent
1	Water	5611	0	0	0	0.0	0.0	0.0	0.0	0
2	Ground Phosphate Rock	0	0	0	0	0.0	0.0	0.0	0.0	0
3	93 Percent Sulfuric Acid	3135	0	0	2856	0.0	0.0	0.0	0.0	0
4	Wet Process Acid Slurry	16169	3359	1721	3073	153.6	122.9	45.0	228.2	0
5	Waste Gypsum	5308	101	1667	2856	34.1	36.0	12.4	11.0	0
6	Crude Phosphoric Acid	10861	3258	54	217	119.5	86.9	32.6	217.2	0
7	Ground Phosphate Rock	3335	1101	1668	0	43.4	43.4	13.3	126.7	0
8	Monocalcium Phosphate Slurry	14196	4359	1722	217	162.9	130.3	45.9	343.9	0
9	Dryer Effluent	4921	0	0	0	0.0	0.0	0.0	112.0	0

Table 18. (Continued)

Process Stream	Process Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons per day							
			P_2O_5	CaO	$SO_4^{=}$	Fe_2O_3	Al_2O_3	MgO	F	Solvent
10	Dried Monocalcium Phosphate	9275	4359	1722	217	162.9	130.3	45.9	231.9	0
11	Dissociation Slurry	25403	4359	1722	217	162.9	130.3	45.9	231.9	16128
12	Dissociation Filtrate	13983	1000	0.9	0	9.3	7.4	0.9	3.7	12131
13	Fractionated Solvent	12131	0	0	0	0.0	0.0	0.0	0.0	12131
14	Low Impurity Phosphoric Acid	1852	1000	0.9	0	9.3	7.4	0.9	3.7	0
15	Dissociation Filter Cake	11420	3359	1721	217	153.6	122.9	45.0	228.2	3997
16	Stripped Solvent	3997	0	0	0	0.0	0.0	0.0	0.0	3997
17	Dissociation Solvent Reactant	16128	0	0	0	0.0	0.0	0.0	0.0	16128
18	Dried Dissociation Residue	7423	3359	1721	217	153.6	122.9	45.0	228.2	0

The assumptions used in calculating the material balances for Tables 17 and 18 were discussed above.

The sulfuric acid usage and phosphate rock requirement per unit of product P_2O_5 are slightly higher when dissociating with acetone than when dissociating with methanol because of a difference in conversion in the dissociation step. The cause for this stems from the assumption that P_2O_5 losses in the waste gypsum stream are directly proportional to the amount of P_2O_5 in the digestion step. The lower filtrate P_2O_5 yield when dissociating with acetone requires the recycle of a larger amount of dissociation filter cake P_2O_5 to the sulfuric acid digestion step per unit of low impurity phosphoric acid P_2O_5 produced. Hence, a larger P_2O_5 loss in the waste gypsum stream occurs when using 3.7 tons of acetone per ton of monocalcium phosphate P_2O_5 than when using 6.0 tons of methanol per ton of monocalcium phosphate P_2O_5. This larger P_2O_5 loss necessitates a slightly larger total phosphate rock requirement along with a corresponding slightly higher sulfuric acid usage to precipitate the additional CaO in the system as gypsum. Although the higher phosphate rock and sulfuric acid raw material usages while dissociating with acetone could be lowered by increasing the dissociation filtrate P_2O_5 yield by means of a corresponding increase in solvent/monocalcium phosphate P_2O_5 ratio, the savings in lowered phosphate rock and sulfuric acid usages would be at least partially offset by a probable increased solvent loss, higher solvent separation energy requirement and a higher equipment depreciation debit due to the larger equipment required for processing the increased volume of dissociation slurry and the larger filtration equipment required for the slower filtering dissociation slurry.

Solid Product Containing Dicalcium Phosphate Only

A flow diagram showing the major processing steps and the major flow streams in the process when producing only the solid product containing dicalcium phosphate with recycle of the low impurity phosphoric acid is presented in Figure 6. This figure shows the chief constituents in the streams entering and leaving each of the major processing steps. Each flow stream is labeled with a number to facilitate cross-reference with Tables 19 and 20. Total mass flow rates and compositions of the main process flow streams when producing the solid product containing dicalcium phosphate (1000 tons per day of product P_2O_5 output) by dissociation with 6.0 tons of methanol per ton of dried monocalcium phosphate P_2O_5 are shown in Table 19 while the total mass flow rates and compositions of the main process flow streams when producing the solid product containing dicalcium phosphate (1000 tons per day of product P_2O_5 output) by dissociation with 3.0 tons of acetone per ton of dried monocalcium phosphate P_2O_5 are shown in Table 20. The assumptions used in calculating the material balances for Tables 19 and 20 were discussed above.

Although the sulfate content of the solid product and the phosphate rock requirement per unit of product P_2O_5 are approximately the same regardless of whether methanol or acetone is used for dissociation, the sulfuric acid usage is slightly higher when dissociating with acetone. Since a lower conversion of crude monocalcium phosphate to phosphoric acid and dicalcium phosphate occurs when dissociating with 3.0 tons of acetone per ton of monocalcium phosphate P_2O_5 than when dissociating with 6.0 tons of methanol per ton of monocalcium phosphate P_2O_5, the resultant solid product will contain less dicalcium phosphate and will have

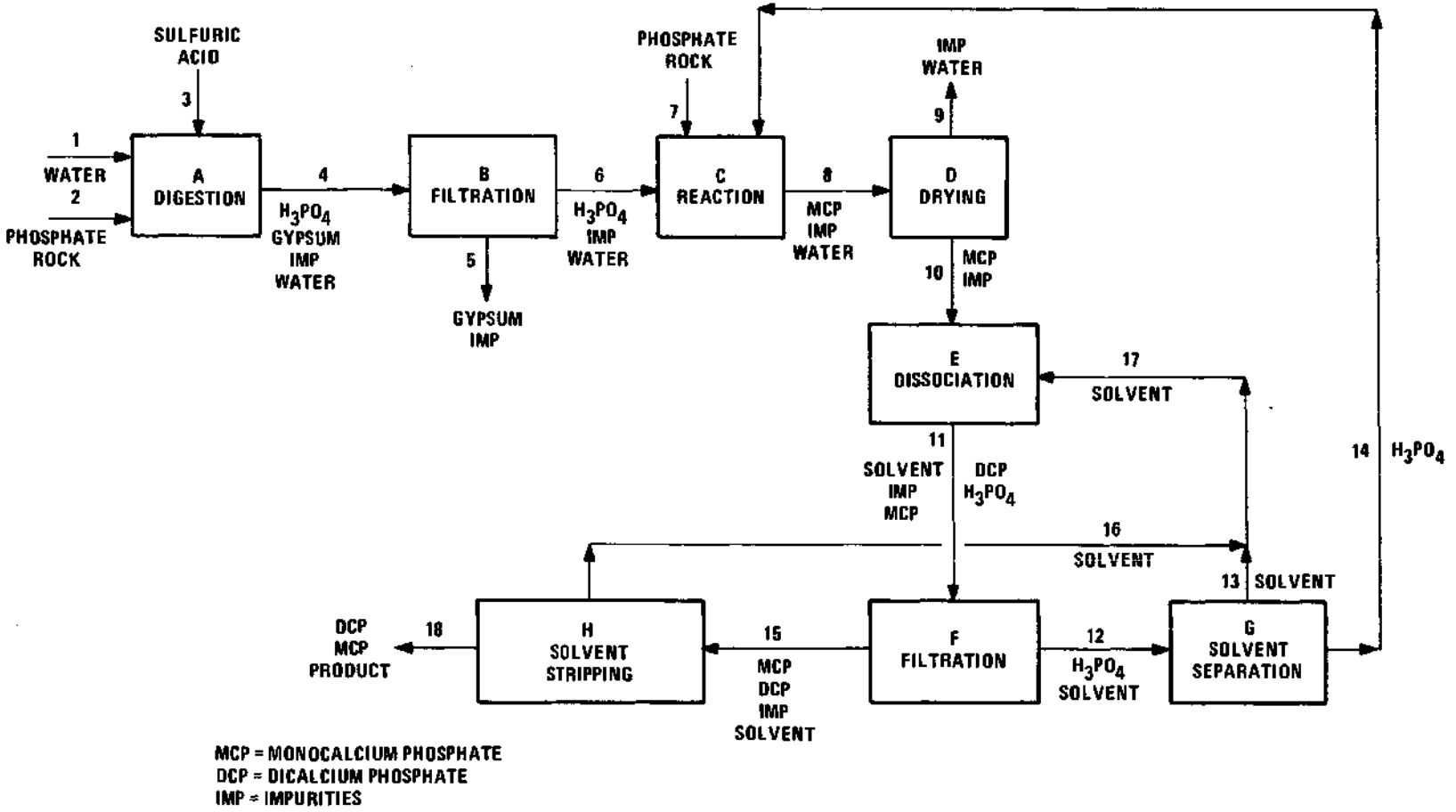

Figure 6. Schematic Diagram for Process with Solid Product Containing Dicalcium Phosphate and with Recycle of Low Impurity Phosphoric Acid

Table 19. Process Flow Rates for the Production of Solid Product Containing Dicalcium Phosphate with Recycle of Low Impurity Phosphoric Acid Using Methanol.
(The process produces 1000 tons per day of product P_2O_5 resulting from the dissociation at 55°C for 15 minutes of dried MCP containing 47 percent P_2O_5 with 6.0 tons of methanol per ton of MCP P_2O_5. Three percent P_2O_5 losses in the waste gypsum stream are assumed while producing the crude phosphoric acid. The crude phosphoric acid is assumed to contain 2.0 percent free $SO_4^=$. The CaO/P_2O_5 mole ratio in the crude MCP is 1.0. During dissociation a filtrate P_2O_5 yield of 30 percent results. Solvent losses and impurities in the recycled solvent are assumed negligible. The solvent content of the wet dissociation filter cake is assumed to be 0.4 tons of methanol per ton of wet filter cake.

Process Stream	Process Stream Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per Day							
			P_2O_5	CaO	$SO_4^=$	Fe_2O_3	Al_2O_3	MgO	F	Solvent
1	Water	1322	0	0	0	0.0	0.0	0.0	0.0	0
2	Ground Phosphate Rock	1988	656	994	0	25.8	25.8	8.0	75.5	0
3	93 Percent Sulfuric Acid	1896	0	0	1727	0.0	0.0	0.0	0.0	0
4	Wet Process Acid Slurry	5206	656	994	1727	25.8	25.8	8.0	75.5	0
5	Waste Gypsum	3088	20	983	1684	2.5	8.9	1.7	33.1	0
6	Crude Phosphoric Acid	2118	636	11	43	23.3	16.9	6.3	42.4	0
7	Ground Phosphate Rock	1103	364	551	0	14.3	14.3	4.4	41.9	0
8	Monocalcium Phosphate Slurry	4015	1429	565	43	38.2	32.0	12.7	86.7	0
9	Dryer Effluent	975	0	0	0	0.0	0.0	0.0	10.7	0

Table 19. (Continued)

Process Stream	Process Stream Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per Day							
			P_2O_5	CaO	$SO_4^{=}$	Fe_2O_3	Al_2O_3	MgO	F	Solvent
10	Dried Monocalcium Phosphate	3040	1429	565	43	38.2	32.0	12.7	76.0	0
11	Dissociation Slurry	11610	1429	565	43	38.2	32.0	12.7	76.0	8570
12	Dissociation Filtrate	7866	429	3.2	0	0.6	0.8	2.0	2.4	7072
13	Fractionated Solvent	7072	0	0	0	0.0	0.0	0.0	0.0	7072
14	Low Impurity Phosphoric Acid	794	429	3.2	0	0.6	0.8	2.0	2.4	0
15	Dissociation Filter Cake	3744	1000	562	43	37.6	31.2	10.7	73.6	1498
16	Stripped Solvent	1498	0	0	0	0.0	0.0	0.0	0.0	1498
17	Dissociation Solvent Reactant	8570	0	0	0	0.0	0.0	0.0	0.0	8570
18	Dried Dissociation Residue	2246	1000	562	43	37.6	31.2	10.7	73.6	0

Table 20. Process Flow Rates for the Production of Solid Product Containing Dicalcium Phosphate with Recycle of Low Impurity Phosphoric Acid Using Acetone
(The process produces 1000 tons per day of product P_2O_5 resulting from the dissociation at 55°C for 15 minutes of dried MCP containing 47 percent P_2O_5 with 3.0 tons of acetone per ton of MCP P_2O_5. Three percent P_2O_5 losses in the waste gypsum stream are assumed while producing the crude phosphoric acid. The crude phosphoric acid is assumed to contain 2.0 percent free $SO_4^=$. The CaO/P_2O_5 mole ratio in the crude MCP is 1.0. During dissociation a filtrate P_2O_5 yield of 20 percent results. Solvent losses and impurities in the recycled solvent are assumed negligible. The solvent content of the wet dissociation filter cake is assumed to be 0.35 tons of acetone per ton of wet filter cake.)

Process Stream	Process Stream Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per Day							
			P_2O_5	CaO	$SO_4^=$	Fe_2O_3	Al_2O_3	MgO	F	Solvent
1	Water	1415	0	0	0	0.0	0.0	0.0	0.0	0
2	Ground Phosphate Rock	2126	703	1063	0	27.6	27.6	8.5	80.8	0
3	93 Percent Sulfuric Acid	2031	0	0	1850	0.0	0.0	0.0	0.0	0
4	Wet Process Acid Slurry	5572	703	1063	1850	27.6	27.6	8.5	80.8	0
5	Waste Gypsum	3302	22	1052	1803	2.6	9.4	1.7	35.4	0
6	Crude Phosphoric Acid	2270	681	11	47	25.0	18.2	6.8	45.4	0
7	Ground Phosphate Rock	966	319	483	0	12.5	12.5	3.9	36.6	0
8	Monocalcium Phosphate Slurry	3699	1250	494	47	39.8	32.6	10.9	82.9	0
9	Dryer Effluent	1039	0	0	0	0.0	0.0	0.0	16.4	0

Table 20. (Continued)

Process Stream	Process Stream Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per Day							
			P_2O_5	CaO	$SO_4^{=}$	Fe_2O_3	Al_2O_3	MgO	F	Solvent
10	Dried Monocalcium Phosphate	2660	1250	494	47	39.8	32.6	10.9	66.5	0
11	Dissociation Slurry	6410	1250	494	47	39.8	32.6	10.9	66.5	3750
12	Dissociation Filtrate	3030	250	0.2	0	2.3	1.9	0.2	0.9	2567
13	Fractionated Solvent	2567	0	0	0	0.0	0.0	0.0	0.0	2567
14	Low Impurity Phosphoric Acid	463	250	0.2	0	2.3	1.9	0.2	0.9	0
15	Dissociation Filter Cake	3380	1000	494	47	37.5	30.7	10.7	65.6	1183
16	Stripped Solvent	1183	0	0	0	0.0	0.0	0.0	0.0	1183
17	Dissociation Solvent Reactant	3750	0	0	0	0.0	0.0	0.0	0.0	3750
18	Dried Dissociation Residue	2197	1000	494	47	37.5	30.7	10.7	65.6	0

a lower CaO/P_2O_5 ratio. Since the CaO entering the process via phosphate rock is approximately the same regardless of which solvent is used, the waste gypsum stream must contain a greater amount of CaO per unit of P_2O_5 in the solid product during the case when acetone is used. Therefore, the sulfuric acid required to precipitate the CaO as gypsum in the waste gypsum stream is larger when dissociating with 3.0 tons of acetone per ton of monocalcium phosphate P_2O_5.

It may be desirable to use higher solvent/monocalcium phosphate P_2O_5 ratios than used in calculating the material balances in Tables 19 and 20 in order to produce a solid product containing a higher proportion of dicalcium phosphate and to decrease the sulfuric acid usage per unit of product P_2O_5. Such increased solvent/monocalcium phosphate P_2O_5 ratios, however, would also result in probably higher solvent losses, higher solvent separation energy requirements and higher equipment depreciation debits due to the larger equipment required for processing the increased volumes of dissociation slurry.

Low Impurity Phosphoric Acid Product and Solid Product Containing Dicalcium Phosphate

A flow diagram showing the major processing steps and the major flow streams in the process when producing both the low impurity phosphoric acid product and the solid product containing dicalcium phosphate is presented in Figure 7. This figure shows the chief constituents in the streams entering and leaving each of the major processing steps. Each flow stream is labeled with a number to facilitate cross-reference with Tables 21 and 22. Total mass flow rates and compositions of the main process flow streams when producing low impurity phosphoric acid and the

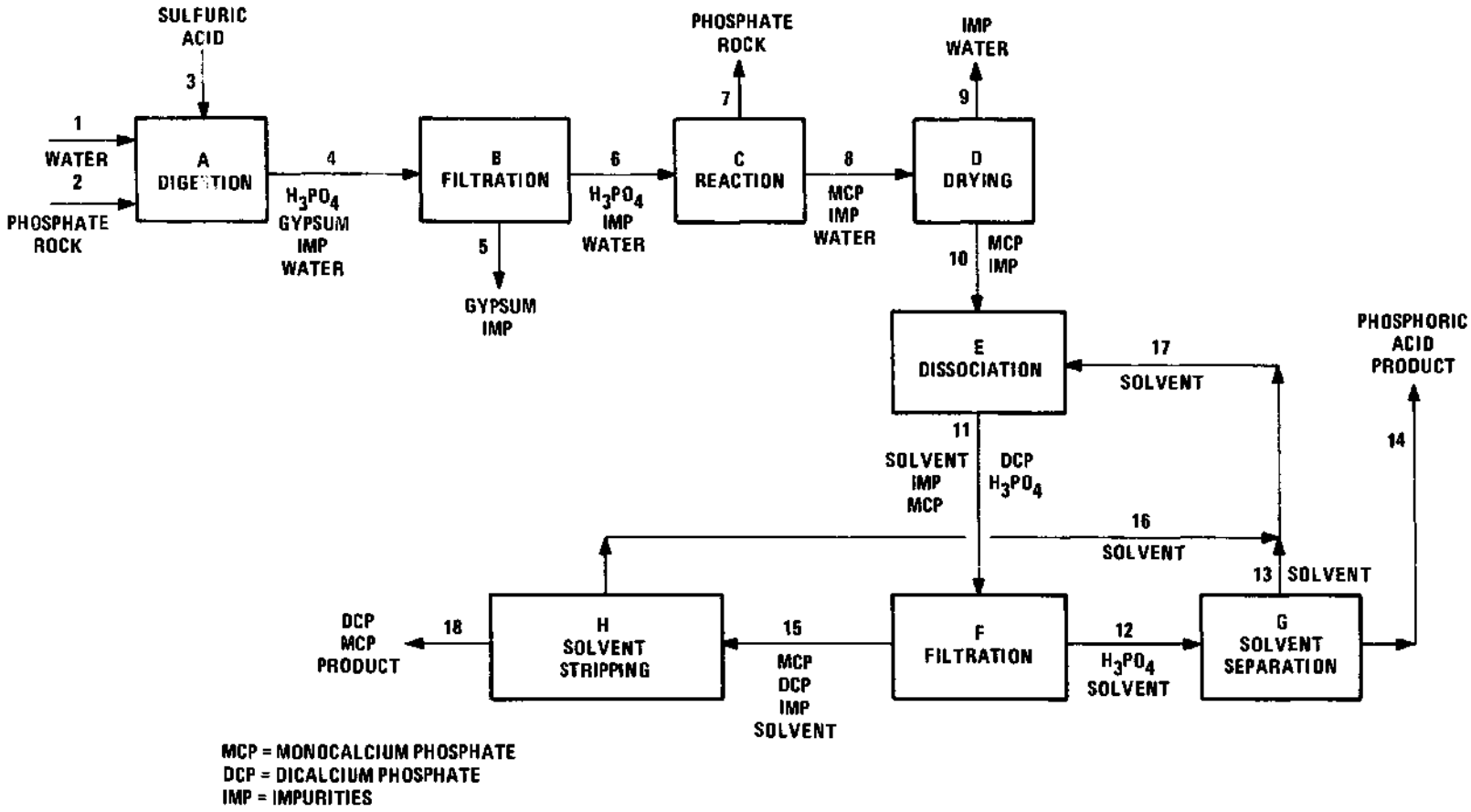

Figure 7. Schematic Diagram for Process with Low Impurity Phosphoric Acid Product and Solid Product Containing Dicalcium Phosphate

Table 21. Process Flow Rates for the Production of Low Impurity Phosphoric Acid Product and Solid Product Containing Dicalcium Phosphate Using Methanol
(The process produces 1000 tons per day of product P_2O_5 resulting from the dissociation at 55°C for 15 minutes of dried MCP containing 47 percent P_2O_5 with 6.0 tons of methanol per ton of MCP P_2O_5 . Three percent P_2O_5 losses in the waste gypsum stream are assumed while producing the crude phosphoric acid. The crude phosphoric acid is assumed to contain 2.0 percent free $SO_4^=$. The CaO/P_2O_5 mole ratio in the crude MCP is 1.0 During dissociation, a filtrate P_2O_5 yield of 30 percent results. Solvent losses and impurities in the recycled solvent are assumed negligible. The solvent content of the wet dissociation filter cake is assumed to be 0.4 tons of methanol per ton of wet filter cake.)

Process Stream	Process Stream Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per Day							
			P_2O_5	CaO	$SO_4^=$	Fe_2O_3	Al_2O_3	MgO	F	Solvent
1	Water	1553	0	0	0	0.0	0.0	0.0	0.0	0
2	Ground Phosphate Rock	2335	771	1168	0	30.4	30.4	9.3	88.7	0
3	93 Percent Sulfuric Acid	2228	0	0	2029	0.0	0.0	0.0	0.0	0
4	Wet Process Acid Slurry	6116	771	1168	2029	30.4	30.4	9.3	88.7	0
5	Waste Gypsum	3624	24	1156	1979	3.0	10.5	1.8	38.9	0
6	Crude Phosphoric Acid	2492	747	12	50	27.4	19.9	7.5	49.8	0
7	Ground Phosphate Rock	765	253	383	0	9.9	9.9	3.1	29.1	0
8	Monocalcium Phosphate Slurry	3257	1000	395	50	37.3	29.8	10.6	78.9	0
9	Dryer Effluent	1129	0	0	0	0.0	0.0	0.0	25.7	0

Table 21. (Continued)

Process Stream	Process Stream Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per Day							
			P_2O_5	CaO	$SO_4^{=}$	Fe_2O_3	Al_2O_3	MgO	F	Solvent
10	Dried Monocalcium Phosphate	2128	1000	395	50	37.3	29.8	10.6	53.2	0
11	Dissociation Slurry	8128	1000	395	50	37.3	29.8	10.6	53.2	6000
12	Dissociation Filtrate	5508	300	2.2	0	0.4	0.6	1.4	1.7	4952
13	Fractionated Solvent	4952	0	0	0	0.0	0.0	0.0	0.0	4952
14	Low Impurity Phosphoric Acid	556	300	2.2	0	0.4	0.6	1.4	1.7	0
15	Dissociation Filter Cake	2620	700	393	50	36.9	29.2	9.2	51.5	1048
16	Stripped Solvent	1048	0	0	0	0.0	0.0	0.0	0.0	1048
17	Dissociation Solvent Reaction	6000	0	0	0	0.0	0.0	0.0	0.0	6000
18	Dried Dissociation Residue	1572	700	393	50	36.9	29.2	9.2	51.5	0

Table 22. Process Flow Rates for the Production of Low Impurity Phosphoric Acid Product and Solid Product Containing Dicalcium Phosphate Using Acetone.
(The process produces 1000 tons per day of product P_2O_5 resulting from the dissociation at 55°C for 15 minutes of dried MCP containing 47 percent P_2O_5 with 3.0 tons of acetone per ton of MCP P_2O_5 . Three percent P_2O_5 losses in the waste gypsum stream are assumed while producing the crude phosphoric acid. The crude phosphoric acid is assumed to contain 2.0 percent free $SO_4^=$. The CaO/P_2O_5 mole ratio in the crude MCP is 1.0 During dissociation, a filtrate P_2O_5 yield of 20 percent results. Solvent losses and impurities in the recycled solvent are assumed negligible. The solvent content of the wet dissociation filter cake is assumed to be 0.35 tons of acetone per ton of wet filter cake.)

Process Stream	Process Stream Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per Day							
			P_2O_5	CaO	$SO_4^=$	Fe_2O_3	Al_2O_3	MgO	F	Solvent
1	Water	1553	0	0	0	0.0	0.0	0.0	0.0	0
2	Ground Phosphate Rock	2335	771	1168	0	30.4	30.4	9.3	88.7	0
3	93 Percent Sulfuric Acid	2228	0	0	2029	0.0	0.0	0.0	0.0	0
4	Wet Process Acid Slurry	6116	771	1168	2029	30.4	30.4	9.3	88.7	0
5	Waste Gypsum	3624	24	1156	1979	3.0	10.5	1.8	38.9	0
6	Crude Phosphoric Acid	2492	747	12	50	27.4	19.9	7.5	49.8	0
7	Ground Phosphate Rock	765	253	383	0	9.9	9.9	3.1	29.1	0
8	Monocalcium Phosphate Slurry	3257	1000	395	50	37.3	29.8	10.6	78.9	0
9	Dryer Effluent	1129	0	0	0	0.0	0.0	0.0	25.7	0

Table 22. (Continued)

Process Stream	Process Stream Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per Day							
			P_2O_5	CaO	$SO_4^{=}$	Fe_2O_3	Al_2O_3	MgO	F	Solvent
10	Dried Monocalcium Phosphate	2128	1000	395	50	37.3	29.8	10.6	53.2	0
11	Dissociation Slurry	5128	1000	395	50	37.3	29.8	10.6	53.2	3000
12	Dissociation Filtrate	2424	200	0.2	0	1.9	1.5	0.2	0.7	2054
13	Fractionated Solvent	2054	0	0	0	0.0	0.0	0.0	0.0	2054
14	Low Impurity Phosphoric Acid	370	200	0.2	0	1.9	1.5	0.2	0.7	0
15	Dissociation Filter Cake	2704	800	395	50	35.4	28.3	10.4	52.5	946
16	Stripped Solvent	946	0	0	0	0.0	0.0	0.0	0.0	946
17	Dissociation Solvent Reactant	3000	0	0	0	0.0	0.0	0.0	0.0	3000
18	Dried Dissociation Residue	1758	800	395	50	35.4	28.3	10.4	52.5	0

solid product containing dicalcium phosphate (1000 tons per day of total product P_2O_5 output) by dissociation with 6.0 tons of methanol per ton of dried monocalcium phosphate P_2O_5 are shown in Table 21. Total mass flow rates and compositions of the main process flow streams when producing low impurity phosphoric acid and the solid product containing dicalcium phosphate (1000 tons per day of total product P_2O_5 output) by dissociation with 3.0 tons of acetone per ton of monocalcium phosphate P_2O_5 are shown in Table 22. The assumptions used in calculating the material balances for Tables 21 and 22 were discussed above.

Exactly the same amounts of phosphate rock and sulfuric acid raw materials are required per unit of product P_2O_5 regardless of whether methanol or acetone is used for dissociation. The solvent used and the solvent/monocalcium phosphate P_2O_5 ratio, however, does determine the proportioning of product P_2O_5 between low impurity phosphoric acid and the solid containing dicalcium phosphate. If the solvent/monocalcium phosphate P_2O_5 ratio is increased, the proportion of product P_2O_5 resulting as low impurity phosphoric acid will increase along with the CaO/P_2O_5 ratio in the solid product (greater conversion of monocalcium phosphate to phosphoric acid and dicalcium phosphate).

In general, when using the same solvent and the same solvent/monocalcium phosphate P_2O_5 ratio for the three process variations, the highest sulfuric acid usage and the highest phosphate rock requirement per unit of product P_2O_5 are encountered in the variation which produces low impurity phosphoric acid alone with recyle of the solid product containing dicalcium phosphate. The cause for this stems from the assumption that P_2O_5 losses in the waste gypsum stream are directly proportional to

the amount of P_2O_5 in the digestion step. Due to the recycle of the solid containing dicalcium phosphate to the digestion step, the amount of P_2O_5 processed in the digestion step per unit of product P_2O_5 in this process variation is larger than the amounts of P_2O_5 processed in the digestion step in the other two process variations. Hence, a larger P_2O_5 loss in the waste gypsum stream per unit of product P_2O_5 occurs when producing low impurity phosphoric acid alone. This larger P_2O_5 loss necessitates a larger total phosphate rock requirement along with a corresponding higher sulfuric acid usage to precipitate the additional CaO in the system as gypsum.

In general, when using the same solvent and the same solvent/monocalcium phosphate P_2O_5 ratio, approximately the same amount of phosphate rock raw material is required per unit of product P_2O_5 for the process variation which produces only the solid product containing dicalcium phosphate with recycle of the low impurity phosphoric acid and for the process variation which produces both the low impurity phosphoric acid and the solid containing dicalcium phosphate. This phosphate rock requirement per unit of product P_2O_5 is lower than that for the process variation which produces low impurity phosphoric acid alone, as discussed above. However, the sulfuric acid usage per unit of product P_2O_5 is the lowest usage encountered in all three process variations when producing only the solid containing dicalcium phosphate with recycle of the low impurity phosphoric acid when using the same solvent and the same solvent/monocalcium phosphate P_2O_5 ratio. The cause for this is that this variation has the highest CaO/total product P_2O_5 ratio. Therefore, a high proportion of CaO which enters the process via phosphate rock leaves in the

product stream. Consequently, a low proportion of CaO which enters the process via phosphate rock leaves in the waste gypsum stream and a corresponding low amount of sulfuric acid is required to precipitate this existing CaO as gypsum.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The results of this investigation may be summarized as follows.

A chemical process for producing low impurity phosphoric acid and/or a solid material containing dicalcium phosphate by a method utilizing the dissociation in the presence of an organic solvent of crude monocalcium phosphate prepared from wet process phosphoric acid and phosphate rock is technically feasible. It has been demonstrated that phosphoric acid containing 54 percent P_2O_5 and lower amounts of impurities than found in conventional merchant grade wet process acid and a solid material composed of a mixture of mono- and dicalcium phosphates can be produced by a method involving the dissociation of crude monocalcium phosphate in the presence of an organic solvent. The dissociation reaction occurs in as little as 15 minutes reaction time in commercial monocalcium phosphate having a total P_2O_5 concentration ranging from 32 to 50 percent in the presence of methanol, ethanol, normal propanol, normal butanol, isoamyl alcohol, normal hexanol, 2-methyl pentanol, normal octanol, 2-ethyl hexanol, normal decanol, normal dodecanol, acetone, methyl butyl ketone and tetrahydrofuran.

In general, monocalcium phosphate conversion to phosphoric acid and dicalcium phosphate increases as: a) the number of carbon atoms in the organic solvent decreases, b) dissociation reaction temperature increases, c) solvent/monocalcium phosphate P_2O_5 ratio increases and

d) the water content of the crude monocalcium phosphate increases. The conversion to phosphoric acid and dicalcium phosphate in the presence of an organic solvent of monocalcium phosphate containing no free water and no water of crystallization is very low. Very little increase in dissociation filtrate P_2O_5 yield is observed after 15 minutes reaction when using either methanol or acetone. The data indicate that the filtrate P_2O_5 yields resulting from the dissociation in the presence of either methanol or acetone of crude monocalcium phosphate made from either uncalcined Florida phosphate rock or calcined North Carolina phosphate rock are approximately the same with all other dissociation reaction conditions held constant.

Methanol and acetone are the best solvents to use for the dissociation of crude monocalcium phosphate of those solvents investigated with regard to filtrate P_2O_5 yield, solvent cost and impurity rejection from the low impurity phosphoric acid. In addition, methanol and acetone are relatively low boiling solvents which will facilitate solvent recovery by vaporization from the low impurity phosphoric acid and the solid containing dicalcium phosphate. During dissociation of crude monocalcium phosphate containing 47 percent P_2O_5, methanol rejects iron and aluminum impurities from the resultant phosphoric acid better than acetone while acetone rejects calcium and magnesium impurities from the resultant phosphoric acid better than methanol. However, the total major cation impurity (CaO, Fe_2O_3, Al_2O_3 and MgO) concentration of the low impurity phosphoric acid and the filtrate P_2O_5 yield are approximately the same when dissociating with either methanol or acetone with all other dissociation reaction conditions held constant.

When dissociating with methanol instead of acetone, the following relative advantages occur. The rejection of iron and aluminum impurities from the low impurity phosphoric acid product is better. Methanol is a cheaper solvent. Methanol has a higher boiling point and, hence, solvent losses due to vaporization will be lower.

When dissociating with acetone instead of methanol, the following relative advantages occur. The rejection of calcium and magnesium impurities from the low impurity phosphoric acid product is better. The dissociation slurry filtration rate is much higher. Acetone has a lower boiling point and, hence, easier rectification of solvent and acid product will result in a fractionator. Also, the use of lower pressure steam for fractionation and filter cake drying will result when acetone is used. Since the enthalpy of vaporization for acetone is much lower than that of methanol, a much lower energy requirement for acetone vaporization during solvent recovery is needed. The dried dissociation filter cake is more easily pulverized. A lower amount of acetone occlusion in the wet dissociation filter cake occurs.

Although absolute optimum processing conditions need to be determined by a comprehensive economic analysis of the data, recommended near-optimum processing conditions for the dissociation step based on an intuitive analysis of presently existing data are as follows. Crude monocalcium phosphate produced from the reaction of phosphate rock and wet process 30 percent P_2O_5 phosphoric acid which has been dried to contain 47 percent total P_2O_5 should be dissociated at 55°C for 15 minutes in the presence of either methanol or acetone. When dissociating with methanol, 6.0 pounds of methanol per pound of monocalcium phosphate

P_2O_5 is recommended. A dissociation slurry filtration rate of 20 pounds of filtrate P_2O_5 per hour per square foot and a 30 percent filtrate P_2O_5 yield result. After fractionation of methanol from the dissociation filtrate, the resultant low impurity phosphoric acid has the following chemical analysis: 54 percent P_2O_5, 0.4 percent CaO, 0.08 percent Fe_2O_3, 0.10 percent Al_2O_3, 0.25 percent MgO, 0.3 percent F and 0.00 percent $SO_4^{=}$. The wet dissociation filter cake contains 0.6 pounds of dry residue per pound of wet filter cake. After drying, the resultant dry filter cake has the following chemical analysis: 46 percent total P_2O_5, 28 percent water soluble P_2O_5 and 24 percent CaO. The mono- and dicalcium phosphate in the filter cake contains no water of crystallization.

When dissociating with acetone, a ratio of 3.0 pounds of acetone per pound of monocalcium phosphate P_2O_5 is recommended for the process in the case when both low impurity phosphoric acid product and the solid product containing dicalcium phosphate are produced and in the case when only the solid product containing dicalcium phosphate is produced with the low impurity phosphoric acid being recycled. A dissociation filtration rate of 200 pounds of filtrate P_2O_5 per hour per square foot and a 20 percent filtrate P_2O_5 yield result. A ratio of 3.7 pounds of acetone per pound of monocalcium phosphate P_2O_5 is recommended when producing low impurity phosphoric acid alone with the dried dissociation filter cake being recycled. A dissociation filtration rate of 150 pounds of filtrate P_2O_5 per hour per square foot and a 23 percent filtrate P_2O_5 yield result. After fractionation of the acetone from the dissociation filtrate when using either of the recommended solvent/monocalcium phosphate P_2O_5 ratios, the resultant low impurity phosphoric acid has the following

chemical analysis: 54 percent P_2O_5, 0.05 percent CaO, 0.5 percent Fe_2O_3, 0.4 percent Al_2O_3, 0.05 percent MgO, no more than 0.2 percent F and 0.00 percent $SO_4^{=}$. The wet dissociation filter cake contains 0.65 pounds of dry residue per pound of wet filter cake.

Batch simulations of the continuous process indicate that total recycle of the dried filter cake which results from dissociation with methanol or acetone does not produce the undesirable effect of a gradual increase in product phosphoric acid impurity concentration due to an accumulation of impurities in the system. No noticeable effect of dissociation filter cake recycle on the product phosphoric acid P_2O_5 yield or dissociation slurry filtration rate is observed. Crude phosphoric acid can be successfully produced by sulfuric acid attack on the dried dissociation filter cake using the conventional wet process method. Methanol and acetone which have been recovered by fractionation from the dissociation filtrate may be successfully recycled for use as solvent for the dissociation of fresh crude monocalcium phosphate without undesirable effects on either filtrate P_2O_5 yield or impurity rejection from product phosphoric acid. No significant difference in the P_2O_5 yield or product phosphoric acid impurity concentrations can be detected when using either fresh or recovered acetone and methanol solvents.

Although combination of the crude monocalcium phosphate preparation and dissociation steps by agitating wet process phosphoric acid, phosphate rock and an organic solvent together results in a high filtrate P_2O_5 yield, the impurity concentrations in the resultant phosphoric acid are much too high for such a combination of processing

steps to be used in a commercial process for producing low impurity phosphoric acid.

Recommendations

It is recommended that the following items be given consideration in future investigations involved in the area of this study.

1. The range of existing data concerned with the dissociation of crude monocalcium phosphate in the presence of methanol and acetone should be extended. For example, solvent/monocalcium phosphate P_2O_5 ratios higher than 6.2 should be investigated when dissociating monocalcium phosphate containing 47 percent P_2O_5 with either methanol or acetone. The use of higher dissociation temperatures than previously studied should be investigated by operating at pressures higher than atmospheric pressure. Extension of existing dissociation data might reveal conditions where near quantitative yields of phosphoric acid and dicalcium phosphate occur. A near quantitative yield might be highly desirable for producing a solid fertilizer composed chiefly of dicalcium phosphate and little or no monocalcium phosphate.

2. The feasibility of using more than one reaction stage for dissociating monocalcium phosphate should be investigated. The filter cake from one dissociation stage would be treated with fresh dissociation solvent to increase the overall phosphoric acid and dicalcium phosphate yield.

3. The feasibility of producing low impurity phosphoric acid containing more than 54 percent P_2O_5 directly after solvent fractionation by dissociating crude monocalcium phosphate containing more than 47 percent P_2O_5 in the presence of methanol and acetone should be investigated.

4. The dissociation of crude calcium phosphate with CaO/P_2O_5 mole ratios other than 1.0 in the presence of an organic solvent should be investigated. For example, while dissociating calcium phosphate with a CaO/P_2O_5 mole ratio less than 1.0, the filtrate P_2O_5 yield might increase substantially with good impurity rejection in the product phosphoric acid still occurring.

5. The data concerned with dissociation in methanol and acetone of crude monocalcium phosphate prepared from types of phosphate rock other than Florida phosphate rock should be expanded.

6. Existing data concerned with the fluorine content of product phosphoric acid resulting from various dissociation conditions while using methanol and acetone should be expanded. Other properties of the product phosphoric acid such as viscosity and density should be investigated also.

7. The investigation should be extended on the process variation which produces a solid product containing monocalcium phosphate, dicalcium phosphate and gypsum by dissociating in the presence of an organic solvent a material prepared by reacting wet process phosphoric acid slurry including unfiltered gypsum with fresh phosphate rock.

8. A continuous pilot plant study of the different chemical process variations should be initiated to better determine optimum operating and processing conditions.

9. A comprehensive economic evaluation of the chemical process using the experimental data should be made to determine which of the two solvents, methanol and acetone, is best to use for dissociation and to determine optimum process operating conditions of a more refined nature.

APPENDICES

APPENDIX A

EXPERIMENTAL FILTRATE P_2O_5 YIELDS AND IMPURITY REJECTIONS IN VARIOUS ORGANIC SOLVENTS

The experimental procedures outlined in Chapter II were used to investigate the dissociation of crude monocalcium phosphate containing approximately 32 and 47 percent P_2O_5 in the presence of various organic solvents after different reaction time periods using different reaction temperatures. Solvent/monocalcium phosphate P_2O_5 ratios of approximately 6.2 were used during experimentation. The crude monocalcium phosphate was prepared from Florida ground phosphate rock.

Table 23 shows the P_2O_5 yields and the major cation impurity (CaO, Fe_2O_3, Al_2O_3 and MgO) concentrations in product phosphoric acid containint 54 percent total P_2O_5 resulting from these dissociation experiments. The solvent, solvent/monocalcium phosphate P_2O_5 ratio, reaction temperature, reaction time and percent total P_2O_5 in the reactant monocalcium phosphate are also shown in Table 23 for each experiment.

In order to facilitate comparison of the data resulting from monocalcium phosphate dissociation in the presence of the various organic solvents, the filtrate P_2O_5 yields and product acid impurity concentrations were time-averaged over all dissociation reaction periods investigated using a certain set of conditions. These summarized data were presented in Table 5.

Table 23. Variation of P_2O_5 Yield and Impurity Concentration with Reaction Time for Phosphoric Acid from the Dissociation of Crude Monocalcium Phosphate with Various Organic Solvents. (The crude MCP was prepared from Florida phosphate rock.)

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Temperature, °C	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5			
						CaO	Fe_2O_3	Al_2O_3	MgO
Methanol	31.86	6.35	25	0.25	32.9	1.16	0.07	0.21	0.80
				0.50	32.1	1.02	0.07	0.31	-
				2.00	32.9	0.82	0.09	0.32	-
				4.00	29.4	0.94	0.08	0.28	-
Methanol	31.86	6.30	55	0.25	36.5	0.83	0.06	0.19	0.70
				0.50	33.2	0.80	0.08	0.20	-
				1.00	33.4	0.67	0.08	0.15	-
				2.00	35.8	0.64	0.08	0.17	-
				4.00	35.7	0.71	0.08	0.17	-
Ethanol	31.86	6.15	55	0.25	26.7	<0.21	0.07	0.43	0.14
				0.50	27.3	<0.27	0.07	0.39	0.32
				1.00	27.9	<0.22	0.06	0.22	-
				2.00	26.5	<0.28	0.06	0.21	-
				7.00	30.3	<0.18	0.06	0.21	-
Ethanol	31.86	6.27	70	0.25	36.6	<0.23	0.07	0.32	0.21
				0.50	28.8	<0.22	0.13	0.57	0.25
				1.00	31.6	<0.17	0.30	0.36	-
				2.00	28.7	<0.18	0.04	0.24	-
				4.00	29.4	<0.17	0.04	0.23	-
				8.00	28.9	<0.16	0.04	0.29	-

Table 23. (Continued)

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Temperature, °C	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5			
						CaO	Fe_2O_3	Al_2O_3	MgO
Normal Propanol	31.86	6.29	25	0.25	33.8	<0.10	0.05	0.11	-
				0.50	30.7	<0.10	0.10	0.21	-
				2.00	29.1	<0.09	0.10	0.20	-
				8.00	29.1	<0.10	0.10	0.17	0.26
Normal Propanol	31.86	6.31	70	0.33	27.8	<0.11	0.09	0.26	0.15
				0.50	31.0	<0.10	0.06	0.26	-
				2.00	30.7	0.13	0.07	0.33	-
				9.00	27.3	0.11	0.06	0.33	-
Normal Butanol	31.86	6.28	25	0.25	23.6	<0.12	0.07	0.32	0.02
				0.50	24.7	<0.11	0.07	0.21	-
				4.00	24.8	<0.11	0.07	0.14	-
Normal Butanol	31.86	6.29	70	0.25	23.7	<0.12	0.05	0.29	0.04
				0.50	27.7	<0.12	0.16	0.19	0.05
				4.00	25.9	<0.11	0.03	0.32	-
Isoamyl Alcohol (85%)	31.86	6.29	40	0.25	14.9	<0.18	0.06	0.41	0.05
				0.50	15.7	<0.18	0.04	0.54	-
				4.00	15.1	<0.18	0.04	0.12	-

Table 23. (Continued)

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Temperature, °C	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5			
						CaO	Fe_2O_3	Al_2O_3	MgO
Normal Hexanol	31.86	6.31	70	0.25	9.9	<0.30	0.09	1.48	0.02
				0.50	11.1	<0.26	0.07	0.56	0.03
				1.00	13.1	<0.28	0.10	0.46	-
				2.00	12.2	<0.23	0.07	0.49	-
				4.00	14.1	<0.19	0.10	0.57	-
				11.00	20.6	<0.17	0.04	0.36	-
Normal Hexanol	47.00	6.17	70	0.25	11.1	0.19	0.54	0.38	0.28
				0.50	10.8	0.15	0.53	1.11	-
				1.00	12.8	0.15	0.43	0.58	-
				2.00	14.7	0.12	0.55	0.60	-
				4.00	12.3	0.11	0.52	0.85	-
2-Methyl Pentanol	32.58	6.16	70	2.00	1.7	5.76	3.04	3.54	-
Normal Octanol	31.86	6.31	70	5.00	10.5	3.54	0.84	0.55	0.55
Normal Octanol	47.00	6.19	70	0.25	18.2	2.19	0.43	0.37	0.20
				4.00	13.4	<0.11	0.60	0.52	-

Table 23. (Continued)

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Temperature, °C	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5			
						CaO	Fe_2O_3	Al_2O_3	MgO
2-Ethyl Hexanol	32.58	6.19 (First treatment)	70	2.00	2.6	<0.41	0.19	1.42	-
		6.23 (Second treatment)	70	2.00	2.5	<0.43	0.03	0.87	-
		6.20 (Third treatment)	70	2.00	4.4	<0.24	0.03	0.50	-
CO-898	32.58	6.28	70	4.00	15.1	1.45	0.45	0.63	0.23
Umbrex N	32.58	6.32	70	4.00	7.2	3.17	0.44	1.70	-
Normal Decanol	31.86	6.25	70	4.00	28.0	9.13	0.04	0.84	0.35
Normal Dodecanol	31.86	6.12	70	4.00	6.4	15.73	1.15	1.72	-
Acetone	31.86	6.30	25	0.25	25.5	<0.11	0.10	0.41	-
				0.50	26.9	<0.10	0.09	0.28	-
				2.00	26.2	<0.10	0.09	0.25	-
				4.00	25.3	<0.09	0.09	0.40	-
				9.00	27.1	<0.09	0.09	0.22	-

Table 23. (Concluded)

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Temperature, °C	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5			
						CaO	Fe_2O_3	Al_2O_3	MgO
Acetone	31.86	6.42	50	0.25	27.1	<0.12	0.12	0.29	0.17
				0.50	29.9	<0.09	0.11	0.22	-
				2.00	28.6	<0.10	0.10	0.34	-
				7.00	28.2	<0.10	0.08	0.20	-
Methyl Butyl Ketone	32.58	6.27	70	2.00	9.2	5.91	3.01	2.85	-
Tetrahydrofuran	31.86	6.30	55	0.25	29.0	<0.10	0.08	0.33	0.07
				0.50	25.4	<0.10	0.08	0.33	-
				4.00	25.6	<0.09	0.09	0.28	-

*MCP containing 32 percent P_2O_5 was a slurry whereas MCP containing 47 percent P_2O_5 was a solid material.

APPENDIX B

EXPERIMENTAL FILTRATE P_2O_5 YIELDS AND IMPURITY REJECTIONS IN METHANOL AND ACETONE

Further experimentation was performed to determine the effect of certain processing parameters on the yield of phosphoric acid and impurity rejection from the purified acid product while using methanol and acetone as dissociation solvents. Although most of the experiments used crude monocalcium phosphate prepared from Florida phosphate rock as the dissociation reactant, a few experiments were performed during which monocalcium phosphate made from North Carolina phosphate rock was the dissociation reactant. Results of the experiments involving North Carolina monocalcium phosphate were compared with analgous results involving the dissociation of Florida monocalcium phosphate. The experimental procedures outlined in Chapter II were used for these dissociation experiments.

Table 24 shows the filtrate P_2O_5 yields and major cation impurity (CaO, Fe_2O_3, Al_2O_3 and MgO) concentrations in product phosphoric acid containing 54 percent P_2O_5 resulting from the dissociation in the presence of methanol of crude monocalcium phosphate prepared from Florida phosphate rock. The crude monocalcium phosphate P_2O_5 concentration and methanol/monocalcium phosphate P_2O_5 ratio are shown along with the dissociation reaction temperature and time for each experiment.

Table 25 shows the filtrate P_2O_5 yields and major cation impurity (CaO, Fe_2O_3, Al_2O_3 and MgO) concentrations in product phosphoric

Table 24. Variation of P_2O_5 Yield and Impurity Concentration with Reaction Time for Phosphoric Acid from the Dissociation of Crude Monocalcium Phosphate Using Methanol. (The crude MCP was prepared from Florida phosphate rock.)

Percent Total P_2O_5 in Unreacted MCP*	Pounds of Anhydrous Methanol per Pound of Total P_2O_5 in Unreacted MCP	Reaction Temperature, °C	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5			
					CaO	Fe_2O_3	Al_2O_3	MgO
31.86	3.16	55	0.25	29.3	1.35	0.25	0.23	0.74
			0.50	30.9	1.28	0.24	0.22	0.83
			2.00	30.2	1.13	0.23	0.28	-
31.86	4.78	55	0.25	32.7	0.93	0.11	0.23	0.74
			0.50	34.4	0.87	0.10	0.21	0.70
			1.00	34.1	0.85	0.10	0.17	-
			2.00	37.0	0.91	0.10	0.18	-
			4.00	38.0	0.91	0.11	0.17	-
31.86	6.35	25	0.25	32.9	1.16	0.07	0.21	0.80
			0.50	32.1	1.02	0.07	0.31	-
			2.00	32.9	0.82	0.09	0.32	-
			4.00	29.4	0.94	0.08	0.28	-
31.86	6.17	40	0.25	35.4	0.76	0.08	0.13	0.71
			0.50	33.7	0.70	0.02	0.17	0.70
			1.00	34.8	0.72	0.07	0.20	-
			2.00	32.9	0.36	0.17	0.36	-
			4.00	34.2	<0.05	0.16	0.41	-
31.86	6.30	55	0.25	36.5	0.83	0.06	0.19	0.70
			0.50	33.2	0.80	0.08	0.20	-
			1.00	33.4	0.67	0.08	0.15	-
			2.00	35.8	0.64	0.08	0.17	-
			4.00	35.7	0.71	0.08	0.17	-

Table 24. (Continued)

Percent Total P_2O_5 in Unreacted MCP*	Pounds of Anhydrous Methanol per Pound of Total P_2O_5 in Unreacted MCP	Reaction Temperature, °C	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5			
					CaO	Fe_2O_3	Al_2O_3	MgO
31.86	12.62	55	0.25	37.4	0.48	0.05	0.42	0.45
			0.50	38.0	<0.12	0.04	0.14	0.39
			2.00	37.4	0.37	0.03	0.23	-
			4.00	38.6	<0.12	0.05	0.30	-
31.86	24.63	55	0.25	32.9	<0.13	0.05	0.13	-
			0.50	32.2	<0.13	0.03	0.13	0.28
			1.00	35.0	<0.12	0.03	0.29	-
			2.00	38.4	<0.12	0.13	0.47	-
			4.00	42.2	<0.10	0.32	0.21	-
34.97	6.19	55	0.25	31.1	0.48	0.06	0.20	0.68
			1.00	30.3	1.02	0.05	0.19	-
			2.00	28.3	1.14	0.07	0.17	-
			4.00	31.4	0.40	0.08	0.27	-
38.04	6.17	55	0.25	33.8	0.70	0.13	0.18	0.39
			0.50	30.8	0.72	0.10	0.17	0.40
			1.00	33.8	0.58	0.07	0.10	-
			2.00	31.9	0.76	0.07	0.12	-
			4.00	32.2	0.63	0.08	0.18	-
41.17	6.19	55	0.25	26.8	0.45	0.16	0.16	0.23
			0.50	32.2	0.55	0.12	0.16	-
			1.00	29.3	0.41	0.08	0.14	-
			2.00	27.9	0.55	0.10	0.09	-
			4.00	29.5	0.41	0.08	0.15	-

Table 24. (Continued)

Percent Total P_2O_5 in Unreacted MCP*	Pounds of Anhydrous Methanol per Pound of Total P_2O_5 in Unreacted MCP	Reaction Temperature, °C	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5			
					CaO	Fe_2O_3	Al_2O_3	MgO
43.97	6.17	55	0.50	32.4	0.55	0.14	0.13	0.12
			1.00	33.0	0.43	0.10	0.10	-
			2.00	33.3	0.50	0.08	0.12	-
			4.00	29.6	0.67	0.06	0.09	-
47.00	3.11	55	0.25	20.8	0.53	0.40	0.33	0.30
			0.50	27.1	-	0.22	0.28	-
			1.00	26.1	-	0.20	0.28	-
			4.00	23.4	0.61	0.17	0.28	-
47.00	6.19	55	0.25	25.9	0.38	0.06	0.13	0.10
			0.50	28.9	0.42	0.06	0.11	0.17
			1.00	30.9	0.57	0.05	0.10	-
			2.00	29.1	0.68	0.06	0.07	-
			4.00	31.9	0.69	0.05	0.06	-
49.97	6.19	55	0.25	27.3	0.40	0.04	0.19	0.14
			2.00	25.3	0.41	0.05	0.17	-
			4.00	25.1	0.45	0.08	0.20	-
52.55	6.17	55	0.25	2.0	<0.40	-	-	-
			0.50	2.4	<0.40	-	-	-
			1.00	3.0	<0.40	-	-	-
			2.00	5.4	<0.40	-	-	-
			4.00	3.4	<0.40	-	-	-

Table 24. (Concluded)

Percent Total P_2O_5 in Unreacted MCP*	Pound of Anhydrous Methanol per Pound of Total P_2O_5 in Unreacted MCP	Reaction Temperature, °C	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5			
					CaO	Fe_2O_3	Al_2O_3	MgO
53.74	6.17	55	0.25	1.3	<0.40	-	-	-
			0.50	3.8	<0.40	-	-	-
			1.00	1.3	<0.40	-	-	-
			2.00	3.4	<0.40	-	-	-
			4.00	4.3	<0.40	-	-	-
56.08	6.31	55	0.50	1.4	<1.00	-	-	-
			1.00	1.9	<1.00	-	-	-
			2.00	0.9	<1.00	-	-	-
			4.00	0.9	<1.00	-	-	-
			24.00	3.5	<1.00	-	-	-

*MCP containing 32 and 35 percent P_2O_5 was a slurry whereas MCP containing 38 and 41 percent P_2O_5 was a pasty material.
MCP containing 44 percent P_2O_5 or more was a solid material.

Table 25. Variation of P_2O_5 Yield and Impurity Concentration with Reaction Time for Phosphoric Acid from the Dissociation of Crude Monocalcium Phosphate Using Acetone. (The crude MCP was prepared from Florida phosphate rock.)

Percent Total P_2O_5 in Unreacted MCP*	Pounds of Acetone Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Temperature, °C	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5			
					CaO	Fe_2O_3	Al_2O_3	MgO
31.86	6.30	25	0.25	25.5	<0.11	0.10	0.41	--
			0.50	26.9	<0.10	0.09	0.28	-
			2.00	26.2	<0.10	0.09	0.25	-
			4.00	25.3	<0.09	0.09	0.40	-
			9.00	27.1	<0.09	0.09	0.22	-
31.86	6.42	50	0.25	27.1	<0.12	0.12	0.29	0.17
			0.50	29.9	<0.09	0.11	0.22	-
			2.00	28.6	<0.10	0.10	0.34	-
			7.00	28.2	<0.10	0.08	0.20	-
47.17	1.57	55	0.25	16.9	0.51	0.83	0.47	0.04
			0.50	19.0	-	0.85	0.47	-
			1.00	15.8	-	1.38	0.89	-
			2.00	16.7	-	1.25	0.70	-
			4.00	16.4	<0.06	1.37	0.44	-
47.17	3.11	55	0.25	17.8	<0.06	0.54	0.42	0.04
			0.50	18.3	-	0.67	0.53	-
			1.00	19.4	-	0.58	0.51	-
			2.00	18.1	-	0.53	0.38	-
			4.00	18.0	<0.05	0.52	0.34	-

Table 25. (Continued)

Percent Total P_2O_5 in Unreacted MCP*	Pounds of Acetone Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Temperature, °C	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5			
					CaO	Fe_2O_3	Al_2O_3	MgO
47.17	4.69	55	0.25	24.2	<0.07	0.43	0.50	0.02
			0.50	25.6	-	0.42	0.74	-
			1.00	29.1	-	0.47	0.48	-
			2.00	28.0	-	0.41	0.68	-
			4.00	27.0	<0.06	0.41	0.67	-
47.17	6.22	55	0.25	27.1	<0.08	0.28	0.46	0.03
			0.50	33.8	-	0.37	0.51	-
			1.00	30.9	-	0.32	0.32	-
			2.00	36.2	-	0.33	0.52	-
			4.00	36.1	<0.07	0.28	0.38	-

*MCP containing 32 percent P_2O_5 was a slurry whereas MCP containing 47 percent P_2O_5 was a solid material.

acid containing 54 percent P_2O_5 resulting from the dissociation in the presence of acetone of crude monocalcium phosphate prepared from Florida phosphate rock. The crude monocalcium phosphate P_2O_5 concentration and acetone/monocalcium phosphate P_2O_5 ratio are shown along with the dissociation reaction temperature and time for each experiment.

The filtrate P_2O_5 yields and major cation impurity (CaO, Fe_2O_3, Al_2O_3 and MgO) concentrations in product phosphoric acid containing 54 percent P_2O_5 resulting from the dissociation in the presence of methanol or acetone of crude monocalcium phosphate containing approximately 47 percent total P_2O_5 prepared from North Carolina phosphate rock are presented in Table 26. The solvent/monocalcium phosphate P_2O_5 ratio is shown along with the dissociation reaction temperature and time for each experiment.

In order to facilitate comparison of the data, the filtrate P_2O_5 yields and the product acid impurity concentrations were time-averaged over all dissociation reaction periods investigated using a certain set of conditions. The data which were time-averaged from the data in Table 24 were presented in Tables 8, 9 and 10 while the data, time-averaged from Table 25 concerning acetone, were presented in Table 11. Time-averaged data from Table 26 concerning dissociation of North Carolina monocalcium phosphate were given in Table 6. Time-averaged results concerned with North Carolina monocalcium phosphate dissociation were compared with analgous time-averaged results concerned with Florida monocalcium phosphate dissociation in Table 7.

Analysis of Variance

Analysis of variance calculations were performed on data

Table 26. Variation of P_2O_5 Yield and Impurity Concentration with Reaction Time for Phosphoric Acid from the Dissociation of Crude Monocalcium Phosphate Using Methanol and Acetone. (The crude solid MCP prepared from North Carolina phosphate rock contained 46.60 percent P_2O_5.)

Solvent	Pounds of Solvent per Pound of Total P_2O_5 in Unreacted MCP	Reaction Temperature, °C	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5			
					CaO	Fe_2O_3	Al_2O_3	MgO
Methanol	1.59	55	1.00	11.2	0.80	2.25	1.05	-
Methanol	3.16	55	0.25	21.6	-	0.61	0.40	0.17
			0.50	23.5	-	0.41	0.40	-
			1.00	23.7	-	0.36	0.37	-
			2.00	25.5	-	0.28	0.19	-
			4.00	26.0	-	0.30	0.37	-
Methanol	6.30	55	0.25	29.4	0.42	0.13	0.29	0.50
			0.50	28.2	-	0.10	0.28	-
			1.00	31.2	-	0.09	0.26	-
			2.00	33.7	-	0.07	0.22	-
			4.00	33.1	0.89	0.10	0.27	-
Acetone	1.60	55	0.25	15.0	<0.07	1.00	0.61	0.08
			0.50	16.0	-	1.07	0.27	-
			1.00	16.2	-	1.13	0.21	-
			2.00	15.5	-	0.88	0.30	-
			4.00	15.3	<0.06	0.78	0.22	-

dealing with the dissociation of Florida monocalcium phosphate with methanol (Table 24) and with acetone (Table 25) to determine whether a statistically significant effect on filtrate P_2O_5 yield exists when the dissociation parameters of reaction time, reaction temperature, solvent/monocalcium phosphate P_2O_5 ratio and monocalcium phosphate P_2O_5 content are varied. Two-factor analysis of variance calculations using one observation per cell were carried out using reaction time as one factor and either reaction temperature, solvent/monocalcium phosphate P_2O_5 ratio or monocalcium phosphate P_2O_5 content as the other factor. The theory and details of such analysis of variance calculations has been well described (21,34). The analysis of variance procedure basically involved statistically comparing, by means of an F test, the variance of filtrate P_2O_5 yield as a dissociation parameter was varied with an estimate of the variance of filtrate P_2O_5 yield expected due to procedural errors. The test F statistic was then compared with a tabulated value for the F statistic using an alpha value of 0.05 (the probability was 0.05 of concluding that a certain dissociation parameter had a significant effect on filtrate P_2O_5 yield when indeed there was no such significant effect).

When the effects on filtrate P_2O_5 yield of varying the reaction time between 0.25 and 4.0 hours and varying the reaction temperature between 25°C and 55°C for the dissociation with 6.2 pounds of methanol per pound of monocalcium phosphate P_2O_5 of Florida monocalcium phosphate containing 32 percent P_2O_5 were statistically tested, reaction time had no significant effect but reaction temperature did have a significant effect on filtrate P_2O_5 yield. When the effects on filtrate P_2O_5 yield

of varying the reaction time between 0.25 and 4.0 hours and varying the methanol/monocalcium phosphate P_2O_5 ratio for the dissociation of Florida monocalcium phosphate containing 32 percent P_2O_5 at 55°C were tested, reaction time had no significant effect but methanol/monocalcium phosphate P_2O_5 ratio had a highly significant effect on filtrate P_2O_5 yield. When the effects on filtrate P_2O_5 yield of varying the reaction time between 0.25 and 4.0 hours and varying the monocalcium phosphate P_2O_5 concentration between 32 and 50 percent P_2O_5 for the dissociation at 55°C of Florida monocalcium phosphate with 6.2 pounds of methanol per pound of monocalcium phosphate P_2O_5 were tested, reaction time had no significant effect but monocalcium phosphate P_2O_5 concentration had a highly significant effect on filtrate P_2O_5 yield.

When the effects on filtrate P_2O_5 yield of varying the reaction time between 0.25 and 4.0 hours and varying the acetone/monocalcium phosphate P_2O_5 ratio between 1.6 and 6.2 pounds of acetone per pound of monocalcium phosphate P_2O_5 for the dissociation at 55°C of Florida monocalcium phosphate containing 47 percent P_2O_5 were tested statistically, reaction time had no significant effect but acetone/monocalcium phosphate P_2O_5 ratio had a highly significant effect on filtrate P_2O_5 yield.

To summarize, during analysis of variance calculations performed on data arising from the dissociation of crude Florida monocalcium phosphate with either methanol or acetone, at no time did the variation of dissociation reaction time between 0.25 and 4.0 hours have a statistically significant effect on filtrate P_2O_5 yield using an alpha level of 0.05. However, variation of the dissociation reaction parameters of reaction temperature, solvent/monocalcium phosphate P_2O_5 ratio and

monocalcium phosphate P_2O_5 content all had statistically significant effects on the filtrate P_2O_5 yield when methanol was used. Variation of the acetone/monocalcium phosphate P_2O_5 ratio also had a statistically significant effect on filtrate P_2O_5 yield.

APPENDIX C

EXPERIMENTAL DISSOCIATION SLURRY FILTRATION RATES

The filtration rates of the slurries resulting from the dissociation of crude monocalcium phosphate at different reaction conditions in the presence of various organic solvents were measured. A sample of dissociation slurry was vacuum filtered using water aspiration to provide the vacuum through a filtration medium of known area as described in Chapter II. By measuring the time required to filter the slurry sample until the top portion of the cake appeared dry and after analyzing the resulting filtrate for P_2O_5, the filtration rate in units of pounds of filtrate P_2O_5 per hour per square foot of filtration area was then calculated. The filtration rate in units of gallons of filtrate per hour per square foot of filtration area was calculated assuming the density of the filtrate to be that of the pure dissociation solvent and assuming the volume of the resulting filtrate to be that of the solvent used in dissociation of the sample.

The filtration rates in units of pounds of filtrate P_2O_5 per hour per square foot and gallons of filtrate per hour per square foot that resulted during the dissociation at various conditions of crude monocalcium phosphate prepared from Florida phosphate rock are presented in Table 27. Similarly, the filtration rates in units of pounds of filtrate P_2O_5 per hour per square foot and gallons of filtrate per hour per square foot that resulted during the dissociation at various conditions of crude monocalcium phosphate prepared from North Carolina phosphate rock are

Table 27. Variation of Filtration Rate with Dissociation Reaction Time for Phosphoric Acid from the Dissociation of Crude Monocalcium Phosphate Prepared from Florida Phosphate Rock.

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent per Pound of Total P_2O_5 in Unreacted MCP	Reaction & Filtration Temp., °C	Reaction Time, Hours	Filtration Rate: Pounds of Filtrate P_2O_5 per Hour per Square Foot	Filtration Rate: Gallons of Filtrate per Hour per Square Foot
Methanol	31.86	3.16	55	0.25	46	75
				0.50	53	83
				2.00	47	74
Methanol	31.86	4.78	55	0.25	63	139
				0.50	66	138
				1.00	54	115
				2.00	51	100
				4.00	71	136
Methanol	31.86	6.35	25	0.25	15	44
				0.50	14	43
				2.00	15	45
				4.00	15	49
Methanol	31.86	6.17	40	0.25	22	59
				0.50	20	57
				1.00	22	59
				2.00	19	54
				4.00	22	59
Methanol	31.86	6.30	55	0.25	30	78
				0.50	31	90
				1.00	26	75
				2.00	27	72
				4.00	19	50

Table 27. (Continued)

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent per Pound of Total P_2O_5 in Unreacted MCP	Reaction & Filtration Temp., °C	Reaction Time, Hours	Filtration Rate: Pounds of Filtrate P_2O_5 per Hour per Square Foot	Filtration Rate: Gallons of Filtrate per Hour per Square Foot
Methanol	31.86	12.62	55	0.25	21	107
				0.50	19	96
				2.00	24	120
				4.00	29	142
Methanol	31.86	24.63	55	0.25	14	154
				0.50	14	163
				1.00	16	170
				2.00	14	139
				4.00	17	152
Methanol	34.97	6.19	55	0.25	27	82
				1.00	29	90
				2.00	30	98
				4.00	30	89
Methanol	38.04	6.17	55	0.25	30	83
				0.50	27	82
				1.00	26	71
				2.00	27	79
				4.00	25	72
Methanol	41.17	6.19	55	0.25	25	89
				0.50	32	93
				1.00	33	105
				2.00	28	94
				4.00	30	94

Table 27. (Continued)

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction & Filtration Temp., °C	Reaction Time, Hours	Filtration Rate: Pounds of Filtrate P_2O_5 per Hour per Square Foot	Filtration Rate: Gallons of Filtrate per Hour per Square Foot
Methanol	43.97	6.17	55	0.50	24	69
				1.00	20	57
				2.00	22	62
				4.00	24	76
Methanol	47.00	3.11	55	0.50	23	40
				1.00	15	27
				4.00	8	17
Methanol	47.00	6.19	55	0.25	19	70
				0.50	18	58
				1.00	17	51
				2.00	16	52
				4.00	18	52
Methanol	49.97	6.19	55	0.25	12	42
				2.00	6	21
				4.00	4	16
Ethanol	31.86	6.15	55	0.25	36	124
				0.50	24	81
				1.00	28	94
				2.00	23	72
				7.00	22	68

Table 27. (Continued)

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction & Filtration Temp., °C	Reaction Time, Hours	Filtration Rate: Pounds of Filtrate P_2O_5 per Hour per Square Foot	Filtration Rate: Gallons of Filtrate per Hour per Square Foot
Ethanol	31.86	6.27	70	0.25	43	110
				0.50	41	137
				1.00	59	176
				2.00	47	155
				4.00	51	164
				8.00	51	168
Normal Propanol	31.86	6.29	25	0.25	50	138
				2.00	46	148
				8.00	44	143
Normal Propanol	31.86	6.31	70	0.33	114	388
				0.50	128	389
				2.00	38	115
				9.00	19	67
Normal Butanol	31.86	6.28	25	0.25	50	198
				0.50	53	200
				4.00	43	160
Normal Butanol	31.86	6.29	70	0.25	92	362
				0.50	100	337
				4.00	49	177

Table 27.(Continued)

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction & Filtration Temp., °C	Reaction Time, Hours	Filtration Rate: Pounds of Filtrate P_2O_5 per Hour per Square Foot	Filtration Rate: Gallons of Filtrate per Hour per Square Foot
Isoamyl Alcohol(85%)	31.86	6.29	40	0.25	80	500
				0.50	81	477
				4.00	46	280
Normal Hexanol	31.86	6.31	70	0.50	57	470
				1.00	53	368
				2.00	71	531
				4.00	64	417
				11.00	71	314
Normal Hexanol	47.00	6.17	70	0.25	10	78
				0.50	7	61
				1.00	3	24
				2.00	4	22
				4.00	3	23
Normal Octanol	47.00	6.19	70	0.25	13	67
				4.00	2	12
Acetone	31.86	6.30	25	0.25	282	1058
				0.50	300	1066
				2.00	279	1017
				4.00	152	573
				9.00	82	291

Table 27. (Continued)

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction & Filtration Temp., °C	Reaction Time, Hours	Filtration Rate: Pounds of Filtrate P_2O_5 per Hour per square Foot	Filtration Rate: Gallons of Filtrate per Hour per Square Foot
Acetone	31.86	6.42	50	0.25	250	898
				0.50	331	1078
				2.00	302	1030
				7.00	214	738
Acetone	47.17	1.57	55	0.25	423	596
				0.50	225	283
				1.00	53	79
				2.00	31	44
				4.00	22	31
Acetone	47.17	3.11	55	0.25	167	442
				1.00	55	133
				2.00	56	145
				4.00	32	85
Acetone	47.17	4.69	55	0.25	128	378
				0.50	73	202
				1.00	41	100
				2.00	34	87
				4.00	20	53
Acetone	47.17	6.22	55	0.25	74	256
				0.50	65	181
				1.00	60	182
				2.00	36	93
				4.00	24	64

Table 27. (Concluded)

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction & Filtration Temp., °C	Reaction Time, Hours	Filtration Rate: Pounds of Filtrate P_2O_5 per Hour per Square Foot	Filtration Rate: Gallons of Filtrate per Hour per Square Foot
Tetrahydrofuran	31.86	6.30	55	0.25	306	899
				0.50	217	729
				4.00	202	675

*MCP containing 32 and 35 percent P_2O_5 was a slurry while MCP containing 38 and 41 percent MCP was a pasty material. MCP containing 44 percent P_2O_5 or more was a solid material.

presented in Table 28. Both Table 27 and Table 28 show the dissociation solvent, reactant monocalcium phosphate P_2O_5 concentration and solvent/monocalcium phosphate P_2O_5 ratio along with the reaction temperature and reaction time.

It may be seen that the filtration rate was relatively constant for monocalcium phosphate dissociated at a certain set of conditions up to at least one hour of dissociation time for most solvents with the exception of acetone and tetrahydrofuran. Consequently, the dissociation slurry filtration rates were averaged for those experimental runs made using a certain set of reaction conditions and not more than one hour of dissociation reaction time. These time-averaged filtration rates were presented in Tables 5, 6, 7, 8, 9 and 10. However, the dissociation filtration rates when using acetone which were presented in Table 11 represent the filtration rates occurring after dissociating for fifteen minutes. The dissociation slurry filtration rate when dissociating in the presence of acetone decreases as the dissociation reaction time increases.

Table 28. Variation of Filtration Rate with Dissociation Reaction Time for Phosphoric Acid from the Dissociation of Crude Monocalcium Phosphate Prepared from North Carolina Phosphate Rock.

Solvent	Percent Total P_2O_5 in Unreacted MCP*	Pounds of Solvent per Pound of Total P_2O_5 in Unreacted MCP	Reaction & Filtration Temperature, °C	Reaction Time, Hours	Filtration Rate: Pounds of Filtrate P_2O_5 per Hr./Square Foot	Filtration Rate: Gallons of Filtrate per hr./square foot
Methanol	46.60	1.59	55	1.00	<1	<2
Methanol	46.60	3.16	55	0.25	8	18
				0.50	8	16
				1.00	4	8
				2.00	4	7
				4.00	3	5
Methanol	46.60	6.30	55	0.25	7	24
				0.50	5	18
				1.00	5	16
				2.00	5	14
				4.00	4	11
Acetone	46.60	1.60	55	0.25	40	64
				0.50	23	35
				1.00	9	13
				2.00	6	9
				4.00	2	3

* The MCP containing 46.60 percent P_2O_5 was a solid material.

APPENDIX D

EXPERIMENTAL RESULTS CONCERNED WITH COMBINATION OF THE CRUDE MONOCALCIUM PHOSPHATE PREPARATION AND DISSOCIATION STEPS

The feasibility of combining the crude monocalcium phosphate preparation and dissociation steps was experimentally investigated as a variation of operating the phosphoric acid-dicalcium phosphate process. In this alternative, the reaction of phosphate rock and crude phosphoric acid and the dissociation of crude monocalcium phosphate (Steps C and E in Figure 1) are combined into one reaction step so that crude phosphoric acid, phosphate rock and solvent all react to form dicalcium phosphate, undissociated monocalcium phosphate and purified phosphoric acid. The crude monocalcium phosphate drying Step D is omitted and water removal from the system occurs either during a crude phosphoric acid concentration step which takes place immediately after gypsum filtration or during a purified phosphoric acid concentration step which takes place after separation of solvent and dissociation phosphoric acid. The experimental procedure outlined in Chapter II was used to investigate this process variation.

A number of experiments simulating the process variation described above were performed during which five organic solvents were used as dissociation media, i.e., methanol, normal propanol, normal butanol, isoamyl alcohol and acetone. Results of the experiments during which Florida phosphate rock and crude phosphoric acid containing approximately 30 percent P_2O_5 were treated with either normal propanol, normal butanol,

isoamyl alcohol or acetone are presented in Table 29. The filtrate P_2O_5 yields and the impurity concentrations of the resulting product acids are shown as well as the reaction conditions at which the experiments were performed.

Results of the experiments during which Florida phosphate rock and crude phosphoric acid were treated with methanol are presented in Table 30 and Table 31. Table 30 shows the results of experiments during which the crude phosphoric acid reactant contained approximately 30 percent P_2O_5 while Table 31 shows the results of experiments involving the use of crude phosphoric acid which had been concentrated to 52 percent P_2O_5 by vacuum evaporation. The filtrate P_2O_5 yields and the impurity concentrations of the resulting product acids are shown along with the reaction conditions at which the experiments were performed.

The filtrate P_2O_5 yields and product acid impurity concentrations appearing in Tables 29, 30 and 31 are relatively constant as a function of reaction time with all other processing variables held constant. In order to facilitate analysis of the data resulting from this experimentation, the filtrate P_2O_5 yields and the product acid impurity concentrations were time-averaged over all dissociation reaction periods investigated using a certain set of conditions. These summarized data were presented in Table 15.

Table 29. Variation of P_2O_5 and Impurity Concentration with Reaction Time for Phosphoric Acid from the Combination of Crude Monocalcium Phosphate Formation and Dissociation Steps Using Various Organic Solvents. (Florida Phosphate Rock and Acid Containing 34.28 percent P_2O_5 Prepared from Florida Phosphate Rock were used as Reactants).

Solvent	Pounds Solvent per lb. P_2O_5 in Reactants	Pounds Reactant Acid P_2O_5 per lb. P_2O_5 in Reactants	Reaction Temperature, °C	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5		
						CaO	Fe_2O_3	Al_2O_3
Normal Propanol	6.28	0.726	70	0.25	78.9	0.08	1.46	0.21
				4.00	75.9	0.10	0.96	0.08
				24.00	71.5	0.27	0.20	0.04
Normal Butanol	6.28	0.725	70	2.00	64.8	0.60	0.61	0.20
Isoamyl Alcohol (85%)	6.28	0.725	70	2.00	62.6	4.39	2.21	1.81
Acetone	6.28	0.726	51	0.25	75.4	0.12	1.67	0.28
				0.50	73.9	0.15	1.82	0.42
				2.00	76.9	0.12	0.99	0.80
				8.00	76.5	0.16	0.63	0.33

Table 30. Variation of P_2O_5 Yield and Impurity Concentration with Reaction Time for Phosphoric Acid from the Combination of Crude Monocalcium Phosphate Formation and Dissociation Steps Using Methanol at 55°C. (Florida Phosphate Rock and Acid Containing 34.28 Percent P_2O_5 Prepared from Florida Phosphate Rock were used as Reactants).

Pounds Solvent per Pound P_2O_5 in Reactants	Pounds Reactant Acid P_2O_5 per lb. P_2O_5 in Reactants	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54% P_2O_5		
				CaO	Fe_2O_3	Al_2O_3
1.57	0.726	0.25	76.3	0.42	2.44	1.11
		1.00	80.5	0.35	2.23	0.27
		8.00	75.4	0.35	2.16	1.12
3.14	0.726	0.25	81.3	0.21	2.80	2.11
		0.50	82.3	0.18	2.16	1.79
		1.00	78.7	0.28	2.31	3.57
		4.00	79.4	0.23	2.51	1.64
		8.00	80.2	0.26	2.33	1.62
6.28	0.726	0.25	75.3	0.37	2.86	1.86
		0.50	73.5	0.36	2.20	1.43
		1.00	73.0	0.08	2.77	2.91
		2.00	73.3	0.11	2.86	1.68
		4.00	74.4	0.10	2.45	1.34
		8.00	76.7	0.03	2.65	1.01
12.57	0.726	0.25	80.0	0.41	1.97	1.50
		1.00	74.4	0.68	2.04	1.30
		24.00	80.3	0.99	2.10	1.07

Table 31. Variation of P_2O_5 Yield and Impurity Concentration with Reaction Time for Phosphoric Acid from the Combination of Crude Monocalcium Phosphate Formation and Dissociation Steps Using Methanol at 55°C.
(Florida phosphate rock and acid containing 52.11 percent P_2O_5 prepared from Florida phosphate rock were used as reactants.)

Pounds Solvent Per Pound P_2O_5 in Reactants	Pounds Reactant Acid P_2O_5 Per Pound P_2O_5 in Reactants	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5		
				CaO	Fe_2O_3	Al_2O_3
3.16	0.498	0.25	55.5	0.16	2.22	1.55
		1.00	54.6	0.09	2.27	1.34
3.15	0.666	0.25	69.8	0.57	1.89	2.26
		1.00	75.2	<0.01	1.07	3.27
		4.00	74.3	<0.01	1.70	2.49
3.15	0.726	0.25	68.0	<0.01	1.71	1.99
		1.00	71.9	0.10	2.11	1.77
		4.00	74.1	<0.01	2.10	1.91
3.13	0.749	0.25	76.5	0.22	2.01	1.99
		4.00	77.9	<0.01	2.09	1.98
3.13	0.799	0.25	82.2	<0.01	2.39	2.22
		1.00	81.7	<0.01	2.10	1.77
		4.00	83.6	<0.01	2.04	2.09
3.15	0.833	0.25	86.5	<0.01	2.33	1.37
		1.00	89.0	<0.01	2.19	1.67
		4.00	83.2	0.02	2.15	1.17

Table 31. (Continued)

Pounds Solvent Per Pound P_2O_5 in Reactants	Pounds Reactant Acid P_2O_5 Per Pound P_2O_5 in Reactants	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5		
				CaO	Fe_2O_3	Al_2O_3
6.39	0.500	0.25	50.3	<0.01	1.92	2.09
		1.00	51.5	<0.01	1.86	1.63
		4.00	48.3	<0.01	2.11	1.97
6.29	0.666	0.25	71.4	<0.01	2.21	0.74
		0.50	72.4	<0.01	2.01	0.98
		1.00	72.4	<0.01	2.00	0.96
		2.00	73.4	0.09	2.05	1.05
		4.00	76.8	0.15	2.37	2.48
6.64	0.726	0.25	76.7	0.08	2.31	3.09
		0.50	77.7	<0.01	2.09	1.12
		1.00	75.0	0.28	-	-
		2.00	74.5	<0.01	2.02	0.56
		4.00	73.2	<0.01	2.14	1.21
6.30	0.749	0.25	80.6	<0.01	2.49	0.97
		0.50	79.7	<0.01	1.55	1.62
		1.00	81.0	<0.01	1.79	1.49
		2.00	81.6	<0.01	2.40	1.53
		4.00	82.4	<0.01	1.89	1.56
6.29	0.799	0.25	86.0	<0.01	1.93	1.40
		0.50	87.1	<0.01	2.12	1.18
		1.00	85.7	<0.01	2.27	1.22
		2.00	84.3	<0.01	2.25	1.68
		4.00	85.6	<0.01	2.28	1.70

Table 31. (Concluded)

Pounds Solvent Per Pound P_2O_5 in Reactants	Pounds Reactant Acid P_2O_5 Per Pound P_2O_5 in Reactants	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5		
				CaO	Fe_2O_3	Al_2O_3
6.28	0.833	0.25	86.2	0.34	2.31	1.26
		0.50	86.8	0.03	2.24	1.60
		1.00	83.8	0.03	2.07	1.95
		2.00	85.6	0.34	2.14	1.92
		4.00	87.2	0.30	2.15	1.93
12.61	0.666	0.25	74.8	0.02	1.47	1.90
		1.00	73.9	0.08	3.47	2.98
		4.00	72.1	0.07	2.44	0.73
12.64	0.725	0.25	78.7	0.06	1.61	1.96
		1.00	81.1	0.01	1.52	1.77
		4.00	79.4	0.03	1.47	1.82

APPENDIX E

EXPERIMENTAL RESULTS CONCERNED WITH DISSOCIATION OF HIGHLY DRIED MONOCALCIUM PHOSPHATE WITH METHANOL AND WATER

Dissociation of highly dried crude monocalcium phosphate in the presence of methanol and small amounts of water was studied. The highly dried crude monocalcium phosphate was prepared from Florida phosphate rock and contained 57.41 percent total P_2O_5. This highly dried monocalcium phosphate was dissociated in the presence of methanol and an amount of distilled water which would dilute the monocalcium phosphate reactant to a P_2O_5 concentration in the range of 32 to 47 percent. The experimental procedure used in these experiments is outlined in Chapter II.

The filtrate P_2O_5 yields and product phosphoric acid impurity concentrations resulting from these experiments are presented in Table 32. The equivalent P_2O_5 concentration in the monocalcium phosphate reactant after water addition and the methanol/monocalcium phosphate P_2O_5 ratio are also shown along with the dissociation reaction time.

The filtrate P_2O_5 yields and the product acid impurity concentrations appearing in Table 32 are relatively constant as a function of reaction time with all other processing variables held constant. In order to facilitate analysis of the data resulting from this experimentation, the filtrate P_2O_5 yields and the product acid impurity concentrations were time-averaged over all dissociation reaction periods investigated using a certain set of conditions. These summarized data were presented in Table 16.

Table 32. Variation of P_2O_5 Yield and Impurity Concentration for Phosphoric Acid from the Dissociation with Methanol at 55°C of Dried Crude Monocalcium Phosphate to which Water was Added to Aid Reaction.
(The crude solid MCP prepared from Florida phosphate rock was dried to contain 57.41 percent P_2O_5.)

Equivalent Percent Total P_2O_5 in MCP After Water Addition	Pounds of Methanol per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5		
				CaO	Fe_2O_3	Al_2O_3
32.0	6.16	0.25	1.9	<0.78	0.46	1.94
		0.50	2.2	<0.71	0.59	1.60
		1.00	2.9	<0.62	0.47	1.91
		2.00	3.7	<0.70	0.50	1.98
		4.00	2.7	<0.68	0.54	1.93
35.0	6.17	0.25	1.2	<1.60	2.04	5.36
		0.50	1.2	<1.40	2.00	4.90
		1.00	1.7	<1.21	2.36	5.29
		2.00	2.4	<1.01	1.37	5.61
		4.00	2.1	<1.12	1.64	6.58
38.0	6.20	0.25	0.9	<1.85	2.74	4.88
		0.50	0.8	<1.66	2.32	5.82
		1.00	1.0	<1.28	1.98	4.73
		2.00	1.2	<1.04	1.40	4.38
		4.00	2.1	<0.97	1.54	4.13
41.0	6.23	0.25	0.6	<3.73	4.77	4.62
		0.50	2.3	<1.07	2.01	2.48
		1.00	3.1	<0.85	1.63	6.59
		2.00	2.3	<1.25	1.65	5.20
		4.00	2.8	<1.10	2.06	6.65

Table 32. (Continued)

Equivalent Percent Total P_2O_5 in MCP After Water Addition	Pounds of Methanol Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5		
				CaO	Fe_2O_3	Al_2O_3
47.0	6.18	0.25	1.2	<2.42	2.80	2.80
		0.50	3.3	<1.26	1.31	3.72
		1.00	0.4	<3.44	-	-
		2.00	1.1	<1.58	-	-

APPENDIX F

SAMPLE CALCULATIONS

The following sample calculations are given in order to clarify the computational procedures used in this work.

Digestion of Ground Phosphate Rock or Dissociation Filter Cake Residue with Sulfuric Acid

Ground Phosphate Rock Digestion

Reactants used in the acidulation were ground Florida phosphate rock containing 34.28 percent P_2O_5 and 49.50 percent CaO, technical grade sulfuric acid containing 93.1 percent H_2SO_4, wet process phosphoric acid containing 25.0 percent P_2O_5 and water. For computational purposes, it was assumed that a crude wet process acid would be produced that contained 30.0 percent P_2O_5, 2.0 percent free sulfuric acid and 6.0 percent other contaminants such as calcium, iron, aluminum, magnesium, silica and fluorine. It was also assumed that 96.5 percent of the phosphate in the ground phosphate rock would be digested by the sulfuric acid leaving the remaining 3.5 percent of the P_2O_5 undigested in the by-product gypsum. An amount of the wet process acid containing 25 percent P_2O_5 was used as a slurry diluent which corresponded to 30 weight percent of the total reactor charge.

A basis of 100.0 grams of ground phosphate rock reactant is used in the following calculation.

$$(100.0 \text{ gm.rock})\left(0.3428 \frac{\text{gm.}P_2O_5}{\text{gm.rock}}\right)\left(0.965 \frac{\text{gm. } P_2O_5 \text{ digested}}{\text{gm } P_2O_5 \text{ in rock}}\right)=33.08 \text{ gm } P_2O_5 \text{ digested}$$

$$\frac{33.08 \text{ gm.} P_2O_5 \text{ digested}}{0.300 \text{ gm. } P_2O_5/\text{gm. phosphoric acid}} = 110.27 \text{ gm. phosphoric acid}$$

$$(110.27 \text{ gm. phosphoric acid})\left(0.02 \frac{\text{gm.sulfuric acid}}{\text{gm.phosphoric acid}}\right) = 2.21 \text{ gm. free sulfuric acid in phosphoric acid}$$

$$(110.0 \text{ gm.rock})\left(0.4950 \frac{\text{gm.CaO}}{\text{gm.rock}}\right) = 49.50 \text{ gm. CaO or } 0.8827 \text{ gm.mole CaO in phosphate rock}$$

$$(0.8827 \text{ gm.mole CaO in rock})\left(0.965 \frac{\text{gm. CaO digested}}{\text{gm. CaO in rock}}\right) = 0.8518 \text{ gm. mole CaO converted to gypsum}$$

Since each mole of CaO requires one mole of H_2SO_4 for gypsum precipitation:

$$(0.8514 \text{ gm.mole } H_2SO_4)\left(98.082 \frac{\text{gm.} H_2SO_4}{\text{gm.mole } H_2SO_4}\right) = 83.55 \text{ gm.} H_2SO_4 \text{ required for gypsum precipitation}$$

$$83.55 \text{ gm. } H_2SO_4 \text{ for gypsum} + 2.21 \text{ gm. } H_2SO_4 \text{ for phosphoric acid} = 85.76 \text{ gm. total } H_2SO_4 \text{ required}$$

$$\frac{85.76 \text{ gm. } H_2SO_4}{0.931 \frac{\text{gm. } H_2SO_4}{\text{gm. sulfuric acid}}} = 92.12 \text{ gm. sulfuric acid required}$$

$$92.12 \text{ gm.sulfuric acid} - 85.76 \text{ gm. } H_2SO_4 = 6.36 \text{ gm. free water in sulfuric acid}$$

Since each mole of gypsum contains two moles of water:

$$(0.8518 \text{ gm. mole gypsum})\left(36.032 \frac{\text{gm. water}}{\text{gm.mole gypsum}}\right) = 30.69 \text{ gm. water required for gypsum}$$

Since 30.0 percent P_2O_5 corresponds to 41.42 percent H_3PO_4 and since there are assumed to be 8.0 percent total contaminants including the free sulfuric acid in the resultant phosphoric acid, the remaining 50.58 percent of the phosphoric acid is assumed to be water.

$$(110.27 \text{ gm. phosphoric acid})\left(0.5058 \frac{\text{gm.water}}{\text{gm. phosphoric acid}}\right) = 55.77 \text{ gm. free water in phosphoric acid}$$

From a water balance, it may be determined that 86.46 grams of water are required and that 6.36 grams are supplied by the sulfuric acid leaving a remaining 80.10 grams of water to be added as a reactant.

Since an amount of the wet process phosphoric acid containing 25 percent P_2O_5 was used which corresponded to 30 weight percent of the total reactor charge, it may be determined that in this particular case 116.67 grams of the diluent wet process acid are required.

To summarize, the amounts of reactants required for this reaction are as follows:

100.00 grams ground phosphate rock

92.12 grams sulfuric acid

80.10 grams water

116.67 grams diluent wet process phosphoric acid

Dissociation Filter Cake Residue Digestion

The amounts of reactants required for the sulfuric acid digestion of dissociation filter cake residues were calculated in a manner analogous

to the calculation of the reactants required for the sulfuric acid digestion of ground phosphate rock. The P_2O_5 and CaO content of the residues were known from chemical analysis. It was assumed that 96.5 percent of the residue P_2O_5 was digested by technical grade sulfuric acid containing 93.1 percent H_2SO_4 leaving the remaining 3.5 percent of the P_2O_5 undigested in the by-product gypsum. It was assumed that the resultant phosphoric acid contained 2.0 percent free sulfuric acid and 6.0 percent other contaminants. An amount of wet process acid containing 25 percent P_2O_5 was used as a slurry diluent which corresponded to 25 weight percent of the total reactor charge.

Preparation of Monocalcium Phosphate from Phosphate Rock and Phosphoric Acid

Calculation of the amounts of the crude phosphoric acid and ground phosphate rock reactants used to prepare crude monocalcium phosphate will be illustrated. The reactants are calculated so that the P_2O_5/CaO mole ratio equals 1.0 (P_2O_5/CaO weight ratio equals 2.5312). For computational purposes it is assumed that the ground phosphate rock contains 34.28 percent P_2O_5 and 49.50 percent CaO while the reactant phosphoric acid contains 30.00 percent P_2O_5 and 0.50 percent CaO.

A basis of 100.0 grams of crude phosphoric acid is used in the following calculation.

$$(100.0 \text{ gm.acid})\left(0.30 \frac{\text{gm.}P_2O_5}{\text{gm.acid}}\right) = 30.0 \text{ gm. } P_2O_5 \text{ in acid}$$

$$(100.0 \text{ gm.acid})\left(0.005 \frac{\text{gm.CaO}}{\text{gm.acid}}\right) = 0.50 \text{ gm. CaO in acid}$$

If X is allowed to equal the weight of required ground phosphate rock reactant then the following calculations apply.

$0.3428X$ = gm. P_2O_5 in rock

$0.4950X$ = gm. CaO in rock

$30.0 + 0.3428X$ = gm. P_2O_5 in monocalcium phosphate

$0.50 + 0.4950X$ = gm. CaO in monocalcium phosphate

$$\frac{30.0 + 0.3428X}{0.50 + 0.4950X} = 2.5312 = P_2O_5/CaO \text{ weight ratio}$$

Solving the above equation for X gives 31.57 grams as the value for the ground phosphate rock reactant. To summarize, the amounts of reactants required for this reaction are as follows:

31.57 grams ground phosphate rock

100.00 grams crude phosphoric acid

Dissociation Filtrate P_2O_5 Yield and Impurity Concentrations in Low Impurity Phosphoric Acid

Sample calculations for the determination of dissociation filtrate P_2O_5 yield and the impurity concentrations in the resulting low impurity phosphoric acid will be given.

For computation purposes, it will be assumed that the dried filter cake resulting from a dissociation experiment contains 1207.73 milligrams of P_2O_5 as determined by chemical analysis. The filtrate resulting from the experiment contains 449.53 milligrams P_2O_5, 1.25 milligrams CaO, 2.125 milligrams Fe_2O_3 and 3.275 milligrams of Al_2O_3 determined by chemical analysis.

449.53 mg. P_2O_5 in filtrate + 1207.73 mg. P_2O_5 in residue = 1657.26 mg. P_2O_5 in slurry sample

$$\left(\frac{449.53 \text{ mg. } P_2O_5 \text{ in filtrate}}{1657.26 \text{ mg. } P_2O_5 \text{ in slurry}}\right)(100) = 27.1 \text{ percent filtrate } P_2O_5 \text{ yield}$$

$$\left(\frac{1.25 \text{ mg.filtrate CaO}}{449.53 \text{ mg.filtrate } P_2O_5}\right)\left(0.54 \frac{\text{mg. filtrate } P_2O_5}{\text{mg.merchant acid}}\right)(100) =$$

0.15 percent CaO in merchant acid

$$\left(\frac{2.125 \text{ mg. filtrate } Fe_2O_3}{449.53 \text{ mg.filtrate } P_2O_5}\right)\left(0.54 \frac{\text{mg.filtrate } P_2O_5}{\text{mg. merchant acid}}\right)(100) =$$

0.26 percent Fe_2O_3 in merchant acid

$$\left(\frac{3.275 \text{ mg.filtrate } Al_2O_3}{449.53 \text{ mg. filtrate } P_2O_5}\right)\left(0.54 \frac{\text{mg.filtrate } P_2O_5}{\text{mg.merchant acid}}\right)(100) =$$

0.39 percent Al_2O_3 in merchant acid

Dissociation Slurry Filtration Rates

Sample calculations for the determination of the dissociation slurry filtration rates will be given.

For computational purposes, it will be assumed that filtration of a dissociation slurry sample occurs in a filtration crucible measuring 2.1 centimeters in diameter at 25°C. The dissociation solvent/P_2O_5 ratio used in the experiment was 6.2 pounds of methanol per pound of monocalcium phosphate P_2O_5. The time required for filtration was 65 seconds. Chemical analysis determined that 902.50 milligrams of P_2O_5 resulted in the filtrate.

$$(902.50 \text{ mg. } P_2O_5)\left(\frac{1\text{b. } P_2O_5}{453590 \text{ mg. } P_2O_5}\right) = 0.001990 \text{ lb. filtrate } P_2O_5$$

$$\frac{(\pi)(2.1 \text{ cm.})^2}{(4)}\left(\frac{\text{sq.ft.}}{929.03 \text{ sq. cm.}}\right) = 0.003728 \text{ sq. ft. filtration area}$$

$$(65 \text{ seconds})\left(\frac{\text{hr.}}{3600 \text{ seconds}}\right) = 0.01806 \text{ hr. filtration time}$$

$$\frac{(0.001990 \text{ lb. filtrate } P_2O_5)}{(0.1806 \text{ hr.})(0.003728 \text{ sq. ft. })} = 29.6 \text{ lb. filtrate } P_2O_5/\text{hr./sq.ft.}$$

The filtration rate in units of gallons of filtrate per hour per square foot of filtration area may now be calculated assuming the density of the filtrate to be that of the pure dissociation solvent and assuming the volume of the resulting filtrate to be that of the solvent used in dissociation of the sample. Therefore, if it is assumed that the filtrate has a density equal to that of methanol, 0.80 grams per milliliter and that the filtrate volume equals the volume of the dissociation solvent, the following calculation is valid. It is also assumed that a 30 percent filtrate P_2O_5 yield resulted.

$$\left(0.80 \frac{\text{gm.solvent}}{\text{ml.solvent}}\right)\left(3785 \frac{\text{ml.solvent}}{\text{gal.solvent}}\right)\left(\frac{\text{lb.solvent}}{453.6 \text{ gm.solvent}}\right) =$$

$$6.675 \text{ lb.solvent/gallon}$$

$$\left(\frac{\text{gal.solvent}}{6.675 \text{ lb.solvent}}\right)\left(6.2 \frac{\text{lb.solvent}}{\text{lb.MCP } P_2O_5}\right)\left(\frac{\text{lb.MCP } P_2O_5}{0.30 \text{ lb.filtrate } P_2O_5}\right) =$$

$$3.096 \text{ gal.solvent/lb. filtrate } P_2O_5$$

Since the solvent volume is assumed to be equal to the filtrate volume, the volumetric filtration rate may now be calculated.

$$(29.6 \text{ lb.filtrate } P_2O_5/\text{hr./sq.ft})\left(3.096 \frac{\text{gal.filtrate}}{\text{lb.filtrate } P_2O_5}\right) =$$

$$92 \text{ gallons of filtrate/hr./sq.ft.}$$

Dissociation Residue Hydration State

A sample calculation showing the theoretical low impurity phosphoric acid product P_2O_5 concentration when certain assumptions are made concerning the hydration states of the product dicalcium phosphate and unreacted monocalcium phosphate will be given.

It will be assumed that the crude monocalcium phosphate monohydrate contains 47 percent total P_2O_5 and 0.5 percent free moisture prior to dissociation. After dissociation and subsequent separation of the solid residue and filtrate, it will be assumed that the anhydrous forms of product dicalcium phosphate and unreacted monocalcium phosphate exist in the residue and that all free water and water of crystallization in the original crude monocalcium phosphate monohydrate reactant exist with the product phosphoric acid. It will be further assumed that a 30 percent filtrate P_2O_5 yield results and that impurities in the product phosphoric acid are negligible.

A basis of 100.0 grams of crude monocalcium phosphate reactant is used in the following calculation.

$$\frac{(18.016 \text{ gm.water})}{(141.96 \text{ gm. } P_2O_5)} = 0.1269 \ \frac{\text{gm.water}}{\text{gm. } P_2O_5} \text{ in monocalcium phosphate monohydrate}$$

$$(100.0 \text{ gm. crude MCP})\left(0.47 \ \frac{\text{gm } P_2O_5}{\text{gm.crude MCP}}\right) = 47.0 \text{ gm. } P_2O_5 \text{ in crude MCP}$$

$$(47.0 \text{ gm. } P_2O_5 \text{ in crude MCP})\left(0.30 \ \frac{\text{gm.filtrate } P_2O_5}{\text{gm.}P_2O_5 \text{ in crude MCP}}\right) = 14.1 \text{ gm. filtrate } P_2O_5$$

$$(14.1 \text{ gm.filtrate } P_2O_5)\left(1.38075 \ \frac{\text{gm } H_3PO_4}{\text{gm. } P_2O_5}\right) = 19.47 \text{ gm. } H_3PO_4 \text{ in filtrate}$$

$$(47.0 \text{ gm. } P_2O_5 \text{ in crude MCP})\left(0.1269 \frac{\text{gm.water}}{\text{gm.}P_2O_5 \text{ in crude MCP}}\right) = 5.96 \text{ gm. water of crystallization in crude MCP}$$

$$(100.0 \text{ gm.crude MCP})\left(0.005 \frac{\text{gm. free water}}{\text{gm.crude MCP}}\right) = 0.50 \text{ gm.free water in crude MCP}$$

5.96 gm.water of crystallization + 0.50 gm. free water = 6.46 gm. free water in filtrate

19.47 gm. H_3PO_4 + 6.46 gm. free water = 25.93 gm. product acid

$$\left(\frac{14.1 \text{ gm. filtrate } P_2O_5}{25.93 \text{ gm. product acid}}\right)(100) = 54.4 \text{ percent } P_2O_5 \text{ in product acid}$$

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VITA

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