

# The Ternary System $\text{H}_3\text{PO}_4$ - $\text{Ca}(\text{OH})_2$ - $\text{H}_2\text{O}$ Isotherms at 15 and 45 °C

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**Abstract:** The solid-liquid phase equilibria of the system  $\text{H}_3\text{PO}_4$ -  $\text{Ca}(\text{OH})_2$ - $\text{H}_2\text{O}$  were studied under air pressure using a synthetic method based on conductivity measurements. Two isotherms at 15 and 45 °C were completely defined. The stable solid phases which appear in this range of temperature are hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ), calcium hydrogen phosphate dihydrate ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ), calcium hydrogen phosphate anhydrous ( $\text{CaHPO}_4$ ) and calcium dihydrogen phosphate monohydrate ( $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ). These solid phases were characterized using X ray diffraction.

**Keywords:** Solid-liquid phase equilibria, ternary system  $\text{H}_3\text{PO}_4$ -  $\text{Ca}(\text{OH})_2$ - $\text{H}_2\text{O}$ , calcium phosphate, isotherm.

## 1. INTRODUCTION

The operation of purification is a major component in the process of extraction of the sugar from the beet or from the sugar cane. Phosphatation which consists of adding the phosphoric acid or a soluble phosphate to the raw juice of cane establishes a precious complement in the operation of clarification. Indeed, the precipitate of calcium phosphate formed by reaction of the phosphoric acid or a soluble phosphate with milk of lime, has the role to adsorb impurities, in particular the coloring impurities present in the raw juice and to agglomerate the floculat formed. However, the phases of calcium phosphates which precipitate remain little mastered.

With the aim of mastering the mechanisms of these reactions, and following the nature of calcium phosphates and of sugar-calcium compound, we began the study of the quaternary system: water - Phosphoric acid - lime - sugar.

To reach this objective, we approached, in the laboratory, the study of the phase equilibria of the various sub-systems of this quaternary. In a preceding work we established the isotherm 30 °C of the system  $\text{H}_3\text{PO}_4$ - $\text{Ca}(\text{OH})_2$ - $\text{H}_2\text{O}$  [1]. In the present work, we established isotherms 15 and 45 °C of this system, by basing us on the conductivity measurement. These two temperatures were chosen because they frame the ambient temperature in a sugar refinery which is 30 °C and which corresponds to the temperature of preliming. The characterization of the stable solid phases of these isotherms was driven by the method of the sets and the rests and by the X ray diffraction.

## 2. BIBLIOGRAPHIC STUDY

Because of the importance of calcium phosphates in diverse domains, several searches are made on the solubilization, the precipitation and the synthesis of these products for the temperature 25 °C. In this context, we can quote the works of K. Cameron and A. Seidl [2], Frank K. Cameron and Jannes M. Bell [3] and A. Jourani [4]. On the other hand, few works which handled the subject by the use of the phase diagrams, we quote the work of Bassett (1958), quoted by Roger I. Martin [5] who published a diagram of system  $\text{H}_3\text{PO}_4$ - $\text{Ca}(\text{OH})_2$ - $\text{H}_2\text{O}$  at the temperature 25°C, so Van Wazer who compiled this diagram in some temperature [6]. Another study concerns the establishment of the invariant points in the same system was more made recently (1977), by Roger I. Martin and Brown [5]. This study was dedicated to the establishment of the invariant metastable points containing combinations of solids  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CaHPO}_4$ .

## 3. EXPERIMENTAL METHODS

The curves of solubility are determined by the synthetic method based on conductivity measurements [7, 8]. It consists of adding step by step a solvent to a saline mixture of known composition. Conductivity of the solution is measured at thermodynamic equilibrium and the evolution, according to the quantity of the added liquid, is represented. The obtained curves present angular points and plateaux that correspond to phase transformations. The analysis of series of mixtures permits to identify the liquids curves and to determine the compositions of the isothermal invariant solutions and solid phases (anhydrous or hydrated). Calcium phosphates were identified by using the method of wet residues [9, 10].

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The starting materials are: concentrated phosphoric acid with 61.54 g%  $P_2O_5$  and calcium hydroxide having purity about 96 to 99.9%. The water used was two times distilled and its conductivity was of the order of 6  $\mu S$  at 18 °C.

#### 4. EXPERIMENTAL RESULTS

##### 4.1. 15 and 45 °C Isotherms of the System $H_3PO_4$ - $Ca(OH)_2$ - $H_2O$

The ternary system  $H_3PO_4$ - $Ca(OH)_2$ - $H_2O$  has been studied at 15 and 45 °C. The obtained results are described graphically in the classic representation in which the reference mark is an isosceles rectangle triangle whose right angle corresponds to pure water. The salts compositions are expressed in mass percentages.

Three branches of solubility were defined (ME), (EF) and (FS), in this system at 15 and 45°C, correspond respectively to products:  $CaHPO_4 \cdot 2H_2O$ ,  $CaHPO_4$  and  $Ca(H_2PO_4)_2 \cdot H_2O$ .

The compositions of the invariant points E and F are obtained by extrapolation of the branches of solubility.

However, the branches of solubility of the hydroxyapatite and the calcium hydroxide did not mate on the diagram. The same observation was made by Bassett (1958) quoted by Martin and al. [5]. Now, the stability domain of hydroxyapatite was experimentally defined by determining the limit rights by conductimetric method.

The experimental values of solubility of both isotherms 15 and 45°C, are respectively gathered in Tables 1 and 2 and are represented on Figures 1 and 2.

##### 4.2. Characterization

With the aim of identifying the nature of the solid phases of these isotherms, the mixtures of compositions appropriately chosen were prepared. These mixtures denoted  $N_1$ ,  $N_2$ ,  $N_3$  and  $N_4$  (Figure 2), were maintained separately at  $45 \pm 0.1$  °C and slowly

Table 1: Composition of the Saturated Solutions of the System  $H_3PO_4$ - $Ca(OH)_2$ - $H_2O$  at 15°C

Liquid Phase Composition (Mass Percentages)				Solid Phases in Equilibrium with the Saturated Solution
System $H_3PO_4$ - $Ca(OH)_2$ - $H_2O$		System $CaO$ - $P_2O_5$ - $H_2O$		
$H_3PO_4$	$Ca(OH)_2$	$P_2O_5$	$CaO$	
3.30	1.50	2.39	1.14	$S_2$
4.86	2.25	3.52	1.70	$E^*(S_2 - S_3)$
6.50	2.42	4.71	1.83	$S_3$
10.00	3.00	7.24	2.27	-
13.20	3.70	9.56	2.80	-
16.00	4.20	11.58	3.18	-
20.70	5.00	14.99	3.79	-
23.50	5.41	17.01	4.10	-
27.00	6.00	19.55	4.54	-
32.00	7.00	23.17	5.30	-
33.50	7.20	24.25	5.45	-
34.80	7.92	25.20	6.00	$F^*(S_3 - S_4)$
36.00	7.50	26.06	5.68	$S_4$
41.50	6.00	30.05	4.54	-
52.48	3.4	38.00	2.57	-
62.00	1.50	44.89	1.14	-
69.50	1.00	50.32	0.76	-
80.00	0.50	57.92	0.38	-

\*Points obtained by manual extrapolation of the liquids curves.  
 $S_2$ :  $CaHPO_4 \cdot 2H_2O$ ;  $S_3$ :  $CaHPO_4$ ;  $S_4$ :  $Ca(H_2PO_4)_2 \cdot H_2O$ .

Table 2: Composition of the Saturated Solutions of the System  $\text{H}_3\text{PO}_4\text{-Ca(OH)}_2\text{-H}_2\text{O}$  at 45°C

Liquid Phase Composition (Mass Percentages)				Solid Phases in Equilibrium with the Saturated Solution
System $\text{H}_3\text{PO}_4\text{-Ca(OH)}_2\text{-H}_2\text{O}$		System $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$		
$\text{H}_3\text{PO}_4$	$\text{Ca(OH)}_2$	$\text{P}_2\text{O}_5$	$\text{CaO}$	
3.50	1.20	2.53	0.91	$\text{S}_2$
5.00	1.50	3.62	1.14	-
6.00	2.15	4.37	1.63	$\text{E}^+(S_2 - S_3)$
7.00	2.00	5.07	1.51	$\text{S}_3$
10.00	2.52	7.24	1.91	-
13.00	3.00	9.41	2.27	-
20.00	4.00	14.48	3.03	-
24.50	4.80	17.74	3.63	-
28.00	5.50	20.27	4.16	-
30.00	5.80	21.72	4.39	-
32.50	6.00	23.53	4.54	-
35.00	6.80	25.34	5.15	-
36.50	6.80	26.43	5.15	-
37.30	7.26	27.01	5.50	$\text{F}^+(S_3 - S_4)$
41.50	6.87	30.05	5.20	$\text{S}_4$
42.86	6.50	31.03	4.92	-
50.21	5.16	36.35	3.91	-
55.40	4.00	40.11	3.03	-
62.00	2.80	44.89	2.12	-
71.38	1.20	51.68	0.91	-
80.00	0.57	57.92	0.43	-

\*Points obtained by manual extrapolation of the liquids curves.

$\text{S}_2$ :  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{S}_3$ :  $\text{CaHPO}_4$ ;  $\text{S}_4$ :  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ .

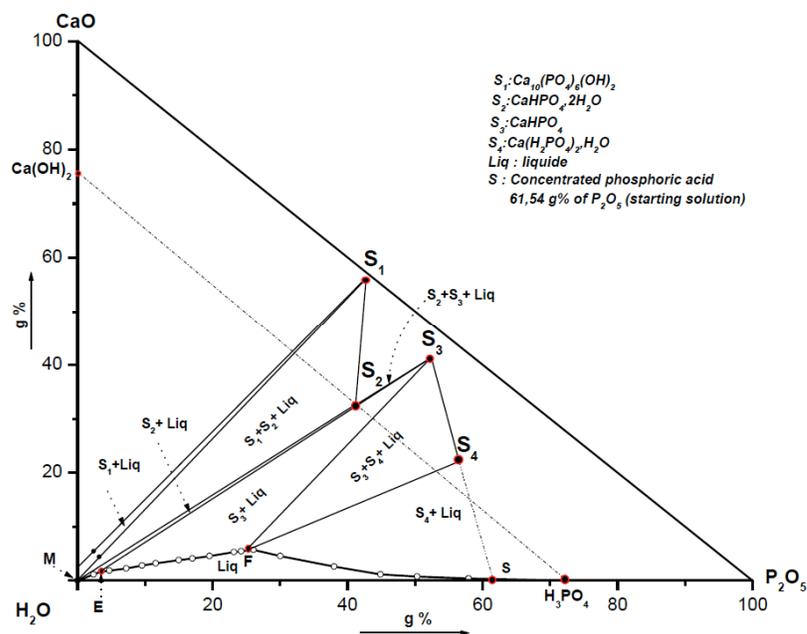


Figure 1: System  $\text{H}_3\text{PO}_4\text{-Ca(OH)}_2\text{-H}_2\text{O}$ , Isotherm 15°C.

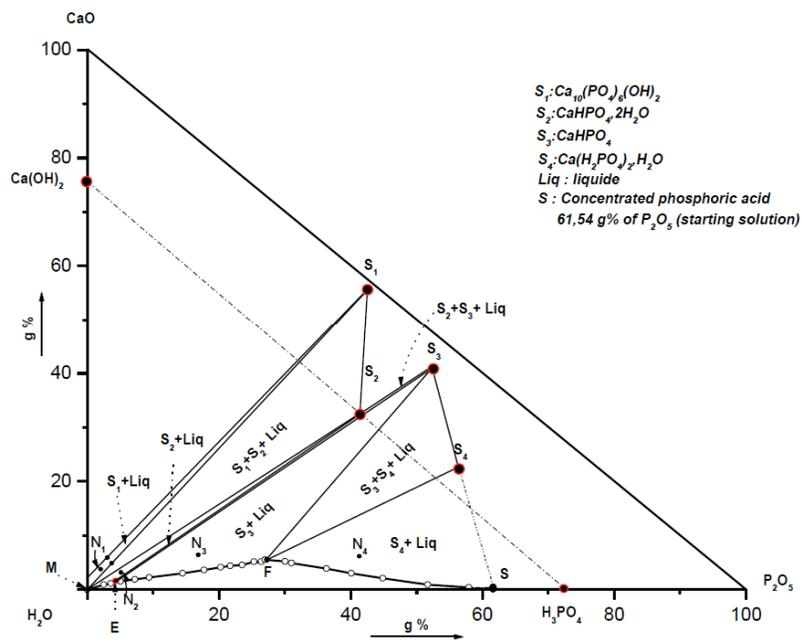


Figure 2: System  $H_3PO_4$ - $Ca(OH)_2$ - $H_2O$ , Isotherm  $45^\circ C$ .

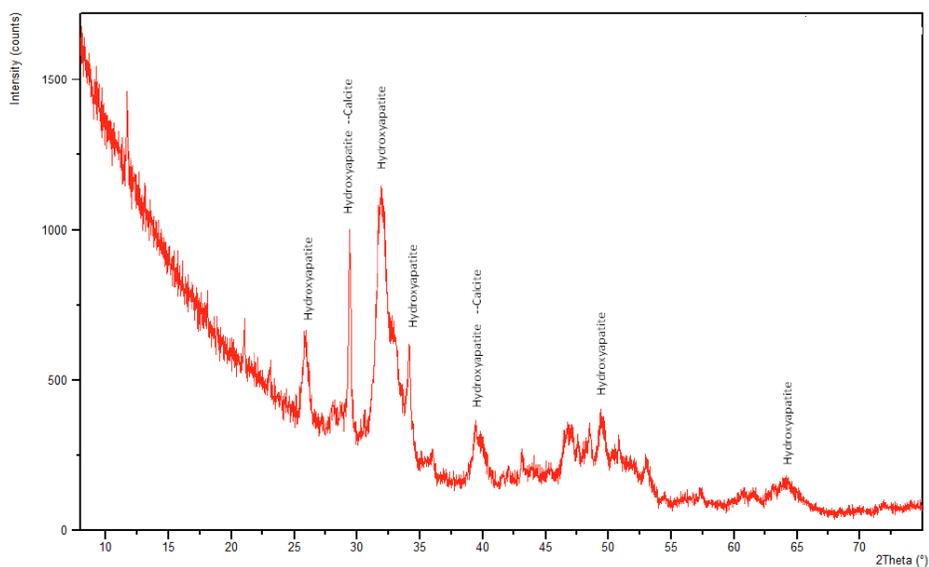


Figure 3: X-ray Diffraction of the solid resulting from the mixture  $N_1(Ca_{10}(PO_4)_6(OH)_2)$ .

stirred at least for one week, assuming that equilibrium was reached [11]. The obtained mixtures are composed each of a liquid phase in equilibrium with a solid phase.

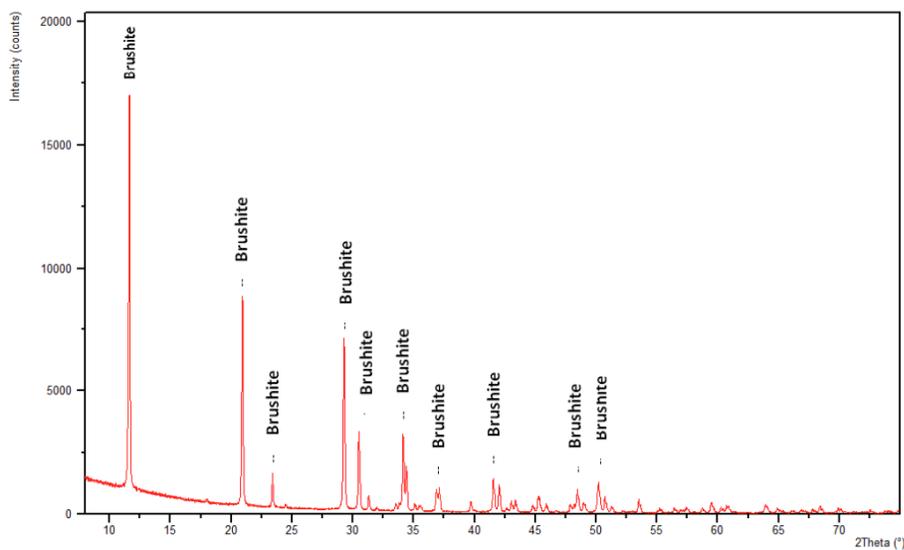
The characterization of the solids of these mixtures, by X-ray diffraction, allowed to define the nature of the solid phases in equilibrium with the various saturated solutions.

Indeed, on the Figure 3, we represented the X-ray diffraction diagram of the solid phase which derives from mixture  $N_1$ . This diagram shows that

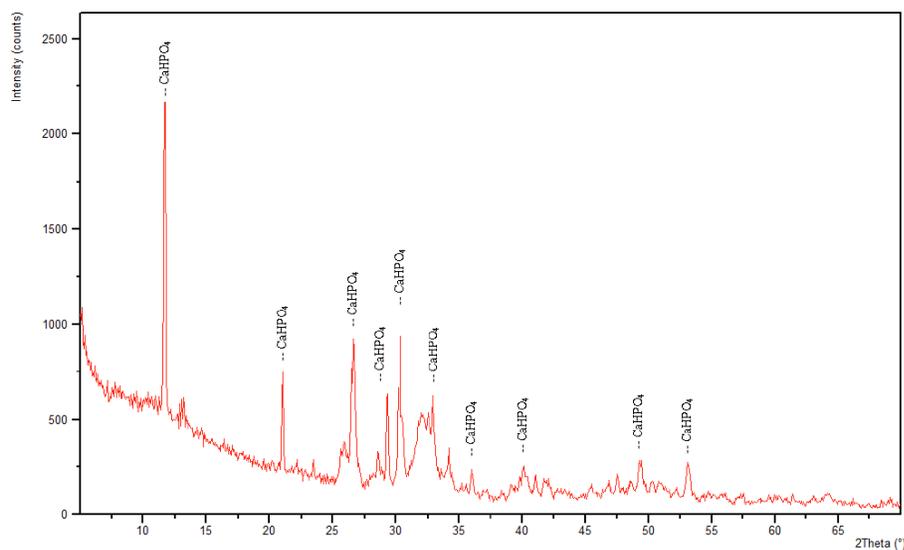
$Ca_{10}(PO_4)_6(OH)_2$  has formed [1], with the existence of calcium carbonate, likely originating from contamination by atmospheric  $CO_2$  trapped during separation.

The Figure 4 represents the X-ray diffraction diagram of the solid phase resulting from mixture  $N_2$ , which corresponds to the calcium hydrogen phosphate dihydrate ( $CaHPO_4 \cdot 2H_2O$ ) [1].

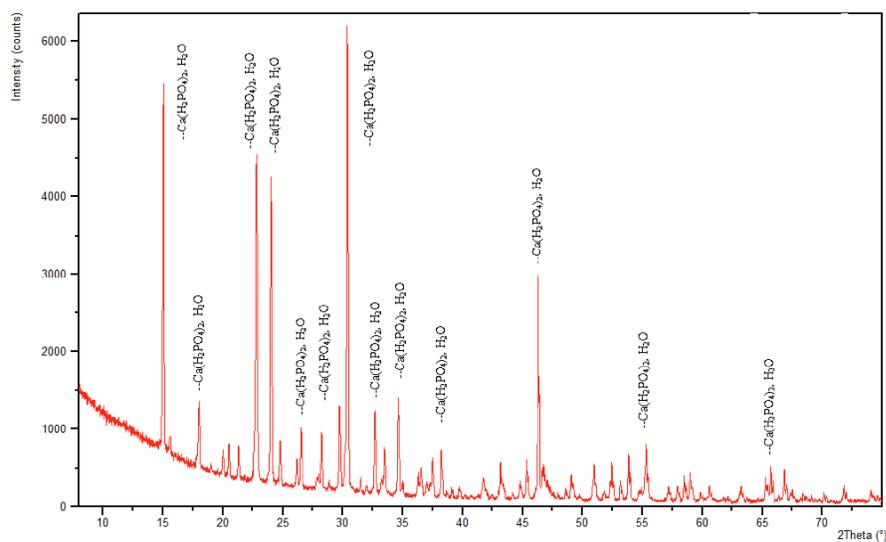
The X-ray diffraction diagram represented on the Figure 5, reveals that the solid phase of the mixture  $N_3$  corresponds to the calcium hydrogen phosphate anhydrous ( $CaHPO_4$ ) [1].



**Figure 4:** X-ray diffraction diagram of the solid resulting from the mixture  $N_2$  ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ).



**Figure 5:** X-ray diffraction diagram of the solid resulting from the mixture  $N_3$  ( $\text{CaHPO}_4$ ).



**Figure 6:** X-ray diffraction diagram of the solid resulting from mixture  $N_4$  ( $\text{Ca}(\text{H}_2\text{PO}_4)_2, \text{H}_2\text{O}$ ).

The X-ray diffraction diagram of the solid phase of the mixture  $N_4$  (Figure 6) shows that this phase corresponds to the product of calcium dihydrogen phosphate monohydrate ( $Ca(H_2PO_4)_2 \cdot H_2O$ ) [1].

## CONCLUSION

The present study allowed to establish the 15 and 45 °C isotherms of the system  $H_3PO_4$ - $Ca(OH)_2$ - $H_2O$ .

The stable solid phases which appear in this range of temperature are :  $Ca_{10}(PO_4)_6(OH)_2$ ,  $CaHPO_4 \cdot 2H_2O$ ,  $CaHPO_4$  and  $Ca(H_2PO_4)_2 \cdot H_2O$ .

Thus, this study show that the solubility of  $Ca_{10}(PO_4)_6(OH)_2$  is congruent, while that of  $CaHPO_4 \cdot 2H_2O$ ,  $CaHPO_4$  and  $Ca(H_2PO_4)_2 \cdot H_2O$  is incongruent.

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Received on 07-12-2015

Accepted on 21-01-2016

Published on 30-05-2016

DOI: <http://dx.doi.org/10.6000/1929-5030.2016.05.02.3>