Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.8 No.8, 2016

Synthesis of Monocalcium Phosphate from the Syrian Phosphoric Acid and Calcium Carbonate

Lama Nour Aldeen * Lotfy Aothman Mouhammad Moudar Alkhuder
Department of Chemistry, Faculty of Science , Al-Baath University, Homs, Syria

Abstract
We have in this work the synthesis of monocalcium phosphate from the Syrian phosphoric acid and calcium carbonate ($CaCO_3$ / H_2O = 1/2 Weight). In this study it was to identify all of the time and temperature idealists for interaction , . Reduce the concentration of fluorine in wet phosphoric acid by deposition of fluorine in the form of salt Na_2SiF_6 by addition sodium carbonate , proving artificial composite identity by pulling the spectrums infrared.
Keywords: wet phosphoric acid , Monocalcium phosphate **(MCP)** , Calcium Carbonate , Titration with sodium hydroxide , the *yield* .

1. Introduction

Monocalcium phosphate is an inorganic compound with the chemical formula $Ca(H_2PO_4)_2$ ("ACMP" or "CMP-A" for anhydrous monocalcium phosphate). It is commonly found as the monohydrate (""MCP" or "MCP-M"), $Ca(H_2PO_4)_2 \cdot H_2O$. Both salts are colorless solids.[. 1] Monocalcium phosphate monohydrate, (MCPM) is an important calcium phosphate with a Ca/P ratio of 0.5 . [2] solubility in water 1.8 g/100 mL[3] , [4], It has been found that MCPM decomposes in water solution and evolves to monetite ($CaHPO_4$) and free phosphoric acid according to reaction:

$$Ca(H_2PO_4)_2 \cdot H_2O \rightarrow CaHPO_4 + H_3PO_4$$

They are used mainly as Super phosphate fertilizers and are also popular leavening agents **.**
Use in fertilizers:
Superphosphate fertilizers are produced by treatment of "phosphate rock" with acids. Using phosphoric acid, fluorapatite is converted to $Ca(H_2PO_4)_2$: $Ca_5(PO_4)_3F + 7\ H_3PO_4 \rightarrow 5\ Ca(H_2PO_4)_2 + HF$
This solid is called triple superphosphate. Several million tons are produced annually for use as fertilizers [1],When sulfuric acid is used, the product contains phosphogypsum ($CaSO_4 \cdot 2H_2O$) and is called single superphosphate. [5]

$$Ca_5F(PO_4)_3 + 5\ H_2SO_4 + 5n\ H_2O \rightarrow 3\ H_3PO_4 + 5\ CaSO_4.n\ H_2O + HF$$

Use as leavening agent:
Calcium dihydrogen phosphate is used in the food industry as a leavening agent, i.e., to cause baked goods to rise. Because it is acidic, when combined with an alkali ingredient, commonly sodium bicarbonate(baking soda) or potassium bicarbonate, it reacts to produce carbon dioxide and a salt. Outward pressure of the carbon dioxide gas causes the rising effect. When combined in a ready-made baking powder, the acid and alkali ingredients are included in the right proportions such that they will exactly neutralize each other and not significantly affect the overall pH of the product. AMCP and MCP are fast acting, releasing most carbon dioxide within minutes of mixing. It is popularly used in pancake mixes. In double acting baking powders, MCP is often combined with the slow acting acid sodium acid pyrophosphaten (SAPP) . [6]

2. Materials and methods

Wet phosphoric acid (the source: The General Company for fertilizers in Homs) , Sodium hydroxide 99% was purchased from Merck Laboratories . Calcium Carbonate 99% , Sodium Carbonate 99.5% , Methyl Orang 85% , Phenol phthalein were purchased from Sigma- Aldrich Laboratories..
Modified Syrian phosphoric acid (26%P_2O_5) by calcium carbonate ($CaCO_3$ / H_2O = 1/2 Weight) according to the reaction : $2\ H_3PO_4 + CaCO_3 \rightarrow Ca(H_2PO_4)_2 + CO_2 + H_2O$

[1] Klaus Schrödter, Gerhard Bettermann, Thomas Staffel, Friedrich Wahl, Thomas Klein, Thomas Hofmann "Phosphoric Acid and Phosphates" in *Ullmann's Encyclopedia of* Industrial *Chemistry* 2008, Wiley-VCH, Weinheim.
[2] Bohner, M.; Tadier, S.; van Garderen, N.; de Gasparo, A.;Döbelin, N.; Baroud, G. Synthesis of spherical calcium phosphate particles for dental and orthopedic applications. Biomatter 2013, 3, e25103.1−15.
[3] Budavari, S (ed.) The Merck Index Encyclopedia of Chemicals, Drugs and Biologicals; Merck and Co., Inc.: Rahway, NJ, 1989; p 256.
[4] Lide D. R. Handbook of Chemistry and Physics, 73rd ed; CRC:1992; pp 4−49.
[5] Gunnar Kongshaug et al. "Phosphate Fertilizers" in Ullmann's Encyclopedia of Industrial Chemistry, 2002, Wiley- VCH, Weinheim.
[6] John Brodie, John Godber "Bakery Processes, Chemical Leavening Agents" in *Kirk-Othmer Encyclopedia of Chemical Technology* 2001, John Wiley & Sons.

3. Experimental Procedure:

we take 25 grams of wet phosphoric acid(6.5 gr P_2O_5) and placed this amount in Beaker 150 ml and placed beaker in a water bath and heating to different temperatures and running magnetic motor and then we added calcium carbonate ($CaCO_3$ / H_2O = 1/2 Weight) on batches during different times. After the end of the interaction , dried the resulting at 90C° until the moisture content of 1-3% .

Calculate the amount of calcium oxide interaction: $P_2O_5 + CaO + 2H_2O \rightarrow Ca(H_2PO_4)_2$

For 25 gr H_3PO_4(26% P_2O_5) be the amount of CaO equal to: (6.5×56) /142=2.563gr

Calculate the amount of calcium carbonate interaction : $CaCO_3 \rightarrow CaO + CO_2$ (2.563×100) /56 =4.577 gr

- Study the effect of time on the interaction yield:

This experiment was conducted during different times at constant temperature at 85C°, after which been the product drying at 90 C° and then we take 2 grams in volumetric flask 250 ml and we complete with distilled water until the volumetric reference and then we filtration and take 25 ml of the Leachate and add 2-3 drops of methyl orange indicator and titration by sodium hydroxide (0.085N) until the advent of the color yellow (We note V_1) then add 2-3 drops of phenol phthalein indicator and follow titration until the appearance of the color pink (We note V_2) **.**

-Study the effect of temperature on the interaction yield:

conducted the same Previous experiment at different temperatures and during the time of 60min and after the end of the reaction the product was dried at 90C° and was taking 2 grams for analysis by titration with sodium hydroxide (0.085N).

Results and discussion

3.1. Study the effect of time on the interaction yield:

Interactions occurring :[1]

$$H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O$$

$$Ca(H_2PO_4)_2 + 2NaOH \rightarrow CaHPO_4 + Na_2HPO_4 + 2H_2O$$

$V_1 < V_2$, Calculates the free phosphoric acid content and mono calcium phosphate formed in the final product from following relationships:

% H_3PO_4 = (0.049×0.085×2V1×250×100) / (m..25)

%$Ca(H_2PO_4)_2$ = (0.117×0.085×(V2-V1)×250×100) /(m..25)

Calculates phosphorus pent oxide mass in the free phosphoric acid of the following reaction :

$$2H_3PO_4 \rightarrow P_2O_5 + 3H_2O$$

Calculates phosphorus pent oxide mass in the mono calcium phosphate of the following reaction *:*

$$Ca(H_2PO_4)_2 \rightarrow P_2O_5 + CaO + 2H_2O$$

The yield % = (mass P_2O_5 in mono calcium phosphate)/(mass P_2O_5 in phosphoric acid a user) × 100

observation that commercial MCPM will always contain a proportion of monetite derived from hydrolysis according to reaction :

$$Ca(H_2PO_4)_2 + H_2O \rightarrow CaHPO_4 + H_3PO_4 + H_2O$$

Thus, the released phosphoric acid will remain between the MCPM crystals and form an amorphous-like phase as the water evaporates. Similar images were found by Boonchom[2] and Desai et al.[3]

Mass P_2O_5 in dicalcium phosphate = Mass P_2O_5 in Phosphoric acid inside the interaction Minus the mass sum P_2O_5 for each of the free phosphoric acid and monocalcium phosphate..

record the results in the following tables: Table 1,2,3 show effect of time on the interaction yield.

[1] Yamazoe F , Determination of free phosphoric acid in superphosphate, Soil Science and Plant Nutrition ,1960 , 5:4, 161-166 p.

[2] Boonchom, B. Parallelogram-like microparticles of calcium dihydrogen phosphate monohydrate (Ca(H2PO4)2, H2O) obtained by a rapid precipitation route in aqueous and acetone media. J. Alloy Compds. 2009, 482, 199−202.

[3] Desai, T. R.; Bhaduri, S. B.; Taş, A. C. A self-setting monetite (CaHPO4) cement for skeletal repair. In Advances in Bioceramics and Biocomposites II; The American Ceramic Society: Westerville, OH, 2007; pp 61−69.

Table1

Time(min)	m(g) Mass the product after drying	Mass taken for analysis (g)	V_1 ml	V_2 ml	H_3PO_4 %	$Ca(H_2PO_4)_2$ %	yield %
15	13.784	2	3.3	13.6	13.744	51.216	65.907
30	13.702		2.95	15.05	12.286	60.167	76.969
45	13.635		2.8	15.5	11.662	63.150	80.384
60	12.795		1.8	16	7.497	70.6095	84.338
75	12.747		1.7	16.1	7.080	71.604	85.2
120	12.745		1.6	16.2	6.664	72.598	86.369

Table2

time (min)	$\%P_2O_5$ in H_3PO_4 free	in $\%P_2O_5$ $Ca(H_2PO_4)_2$	$\%P_2O_5$ in $CaHPO_4$	$\%P_2O_5$ total
15	9.953	31.079	6.123	47.155
30	8.896	36.511	2.028	47.435
45	8.448	38.318	0.902	47.668
60	5.431	42.848	2.525	50.804
75	5.1227	43.445	2.424	50.9917
120	4.825	44.0417	2.126	50.993

Table3

Time(min)	m H_3PO_4 (g)	m P_2O_5 (g) in H_3PO_4	m $Ca(H_2PO_4)_2$ (g)	m P_2O_5(g) in $Ca(H_2PO_4)_2$	m P_2O_5(g) in $CaHPO_4$
15	1.8945	1.372	7.0597	4.284	0.844
30	1.683	1.219	8.244	5.003	0.278
45	1.590	1.152	8.611	5.225	0.123
60	0.9592	0.695	9.034	5.482	0.323
75	0.9025	0.653	9.127	5.538	0.309
120	0.853	0.615	9.252	5.614	0.271

Draw the a graph line between the reaction time and the interaction yield:

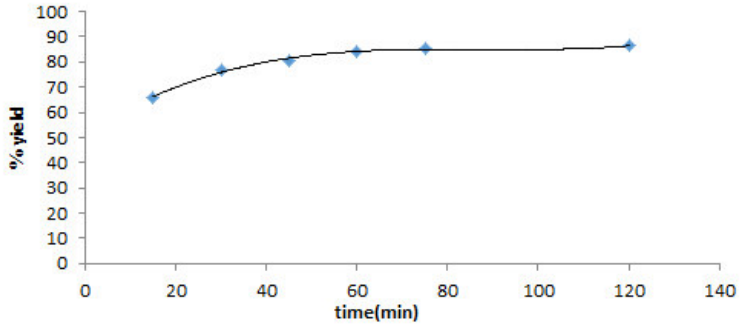

Figure 1 the relationship between the time and the interaction yield

From the experimental results in the table and figure shows that the yield increases dramatically when increasing the time from 15min to 60min and any increase for a time above 60 min lead to a relative increase in yield.

3.2 . Study the effect of temperature on the interaction yield:

conducted the same Previous experiment at different temperatures and during the time of 60min and after the end of the reaction the product was dried at 90C° and was taking 2 grams for analysis by titration with sodium hydroxide (0.085N).

record the results in the following tables: Table 1,2,3 show effect of temperature on the interaction yield.

Table1

t (c°)	Mass the product after drying (g)	Mass taken for analysis g	V_1 ml	V_2 ml	H_3PO_4%	$Ca(H_2PO_4)_2$%	yield %
35	14.280	2	3.7	14.8	15.410	55.194	73.584
45	12.924		3.2	15.5	13.328	61.126	73.752
55	12.918		2.9	15.6	12.078	63.1507	76.16
65	12.901		2.5	15.9	10.412	66.631	80.246
85	12.795		1.8	16	7.497	70.6095	84.338
95	12.783		1.7	16	7.080	71.1067	84.861

Table2

t (c°)	m H_3PO_4 (g)	m P_2O_5 (g) in H_3PO_4	m $Ca(H_2PO_4)_2$ (g)	m P_2O_5(g) in $Ca(H_2PO_4)_2$	m P_2O_5(g) in $CaHPO_4$
35	2.200	1.594	7.881	4.783	0.123
45	1.722	1.248	7.899	4.7939	0.458
55	1.560	1.1290	8.157	4.9504	0.426
65	1.343	0.9732	8.661	5.216	0.3104
85	0.959	0.695	9.034	5.482	0.323
95	0.905	0.6557	9.089	5.516	0.328

Table 3

t (C°)	%P_2O_5 in H_3PO_4 free	P_2O_5 % in $Ca(H_2PO_4)_2$	P_2O_5 % in $CaHPO_4$	P_2O_5 % total
35	11.164	33.540	0.861	45.567
45	9.656	37.093	3.544	50.335
55	8.750	38.322	3.248	50.316
65	7.543	40.434	2.406	50.383
85	5.431	42.848	2.525	50.804
95	5.137	43.150	2.568	50.855

Draw the a graph line between the reaction temperature and the interaction yield**:**

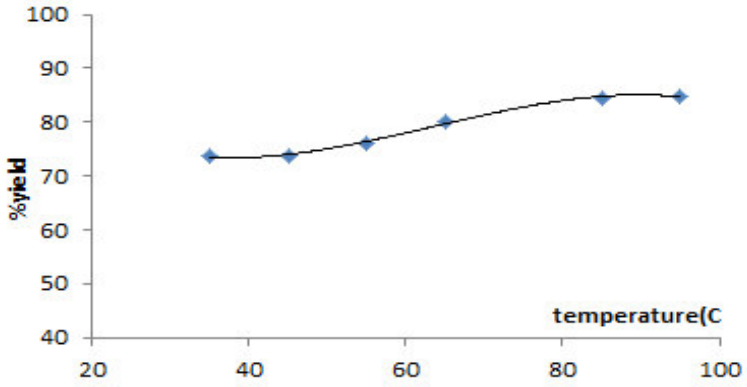

Figure 2 the relationship between the temperature and interaction yield

We find that the temperature a positive impact within the area (35-85C°) and the high temperature of 85 C° to 95C° lead to a slight increase in yield and thus the optimum temperature is 85C°..

3.3. Reduce the concentration of fluorine in wet phosphoric acid :

Phosphoric acid used contains a high content of fluorine(1.8%F), so the use of monocalcium phosphate as fertilizer resulting in air pollution and soil and ground water of fluorine compounds with a toxic effect on humans, animals and plants. So it should reduce the concentration of fluorine in the acid until a certain extent. Where possible, reduce the percentage of fluorine in the Syrian phosphoric acid by deposition of fluorine in the form of salt Na_2SiF_6 , it is achieved by using a sodium salts (NaCl , Na_2SO_4 , Na_2CO_3). By previous studies has been reached optimal conditions for the process of deposition:

the salt used Na_2CO_3 , optimal quantity for salt 160% , reaction time 40 min , reaction temperature 40c°.[1]

The method of work :

Weighed 100 gr of phosphoric acid (26% P_2O_5) and placed this amount in beaker capacity of 400 ml and then the beaker placed in a water bath in temperature of40-50 C ° and then added sodium carbonate According to the calculated value it on batches and mix beaker content using a magnetic stirrer for 40 min, after that separates the liquid phase from the solid phase by filtration, Phosphoric acid output is used to produce monocalcium phosphate as already when class 85 C ° during 60 min..

- Calculate the amount of sodium carbonate needed to experience:

The fluorine content in the phosphoric acid is user 1.8% by weight , the amount H_2SiF_6 in phosphoric acid in equal

$$\frac{144 \times 1.8}{6 \times 19} = 2.273\ gr$$

Of the following reaction calculated the amount of Na_2CO_3 for 100 gr phosphorus acid:

$$Na_2CO_3 + H_2SiF_6 \rightarrow Na_2SiF_6 + CO_2 + H_2O$$

$$\frac{106 \times 2.273}{144} = 1.673\ gr$$

As the separation process of fluorine are the existence of an excessive amount of salt of 60% of that amount Na_2CO_3 the necessary become equal to 2.6768 gr..

[1] Abdulbaki M A , Removal of fluoride from commercial Syrian wet phosphoric acid by precipitation , Atomic Energy Commission, Hydrometallurgy Office, P.O Box 6091 Damascus, Syria .

3.4. The method used to determine the percentage of fluorine in the General Company for Fertilizers in Homs :
Principle: distillation fluorine gases by water vapor and absorbed by the sodium hydroxide solution (0.5 N) , then titration by thorium nitrate solution (0.1N) , after adding a little of the detector methyl thymol blue.[1]
It calculates the percentage of fluorine found in the sample of the following relationship:

$$\%F = \frac{1.9 \times V/v \times a \times 100}{G \times 1000}$$

G : Weight Sample taken for analysis (gr).
V: The size of titration flask 250ml
v : The sample size (100 ml).
a : The size of thorium nitrate consumed in the titration process (ml).

- This experiment was performed on three samples where we got the following results:

1- 5.07gr phosphoric acid is subject to the process of deposition of chlorine from him , a = 0.8ml , **F = 0.0755%**
2- 2.179 gr Mono-calcium phosphate resulting from the modification of phosphoric acid content is (0.0755% F) by calcium carbonate when the temperature 85 C ° during 60 min, a = 0.15 ml , **F = 0.0326%**
3- 0.5444 gr Mono-calcium phosphate resulting from the modification of phosphoric acid content is (1.8% F) by calcium carbonate when the temperature 85 C ° during 60 min, a = 1.1 ml , **F = 0.959%**

- Show the FT-IR spectra of the As-prepared $Ca(H_2PO_4)_2 \bullet H_2O$ in Figure 3:

Of the spectrum Show The ν_{OH} stretching appear at 3466 cm^{-1} , bending vibrational mode of the interlayer water molecules (1638 cm^{-1}) , strong band at about 1240 cm^{-1} in FT-IR spectra is assigned to PO_2^- asymmetric stretching , while the other one at about 1124 cm-1 correspond to PO_2^- symmetric stretching , the FT-IR frequency of the $P(OH)_2$ asymmetric stretching shows the strong band at about 959 cm^{-1}, the weak band at about 888cm^{-1} is assigned to $P(OH)_2$ symmetric stretching , the medium band at about 568 cm-1 is corresponding to PO2 bending ,strong band appeared at about 500 cm^{-1} are attributed to PO2 rocking . A weak band occurs in the FT-IR spectra at approximately 671 cm^{-1} is assigned to rocking mode involving water molecules. [7] ,[8] ,[2] , [3] , [4]

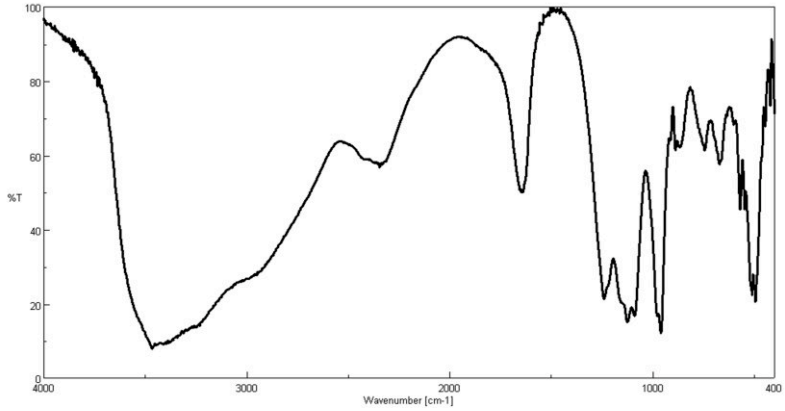

Figure3 FT-IR spectra of As-prepared Ca(H2PO4)2•H2O from phosphoric acid 26% P_2O_5 with calcium carbonate when the temperature 85 C ° during 60 min

4. Conclusions

- Optimal conditions for the synthesis of mono- calcium phosphate from the Syrian phosphoric acid and calcium carbonate($CaCO_3$ / H_2O = 1/2 Weight) is the temperature 85 C°, the time 60 min .
- The synthesis of mono-calcium phosphate within the Optimal conditions containing 42.848%P_2O_5 ..
- Reducing the concentration of fluorine in the Syrian phosphoric acid from 1.8% to 0.0755%.
- synthesis of mono-calcium phosphate containing 0.0326% F and the possibility of add it as fertilizer.

[1] Watson C. Official and Standardized Methods of Analysis. 3rd ed. Cambridge: The Royal Society of Chemistry, 1994:496-7.
[2] Ben-Dor, L.; Felner, I. An IR., T.G. and D.T.A. Study of some Hydrate Metal Phosphates. Inorg. Chim. Acta 1970, 4, 49−55.
[3] Nakamoto K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed; John Wiley and Sons: 1986; pp, 474−477.
[4] Fernandez, E.; Gil, F. J.; Ginebra, M. P.; Driessens, F. C. M; Planell, J. Calcium Phosphate Bone Cements for Clinical Applications, Part II: Precipitate Formation during Setting Reactions. J. Mater. Sci: Mater. Med. 1999, 10, 177−184.