A STUDY FOR SYNTHESIS OF DICALCIUM PHOSPHATE FROM VARIOUS GRADES OF PHOSPHATIC MATERIALS

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ABSTRACT

Anhydrous dicalcium phosphate with monetite structure plays a significant biological importance for the mineralization of bones and teeth. This compound can reconstruct the hard tissues due to its high solubility in the body than other calcium phosphate compounds. Di calcium phosphate is being used as a food - additive supplying calcium and phosphate for humans and animals. Due to the high effective P_2O_5 content, this compound is also used efficiently as a slowly soluble fertilizer in agriculture for all soil and crop types. This paper presents results of synthesis of di calcium phosphate monetite from $Ca(OH)_2$ and phosphoric acid and di calcium phosphate brushite from the resulting solution after enriching of type II - Lao Cai apatite ore by phosphoric acid. The samples were examined by volumetric titration methods, XRD, SEM and EDS.

Keywords: synthesis dicalcium phosphate, monetite, brushite.

1. INTRODUCTION

Anhydrous dicalcium phosphate $CaHPO_4$ with monetite structure plays an important role for the biomineralization in bones and teeth. Using this material, the hard tissues can be reconstructed more efficiently than other calcium phosphates due to its high solubility in the body thus one can find practical applications of $CaHPO_4$ in dental cements and restorative materials [1 - 3], and in the food additive calcium and phosphate supplements for humans and animals as well [4]. Also due to the high effective P_2O_5 content, dicalcium phosphate is a slowly soluble form of fertilizer which is often used in agriculture for all types of soil and crops [5, 6]. There are many studies of preparation of dicalcium phosphate (DCP) recently [1, 2, 7 - 8]. The authors [1] prepared anhydrous dicalcium phosphate from $Ca(NO_3)_2{\cdot}4H_2O$ and H_3PO_4 by the sol gel method. Gel obtained after 24 h of aging was heated at 300^oC to create products. The authors [2] have produced of anhydrous calcium phosphate material with monetite structure from dihydrate calcium phosphate with brushite structure under hydrothermal method. The authors [4] have manufactured brushite dihidrat calcium phosphate from $Ca(OH)_2$ suspension and phosphoric acid with concentration of 50 to 400 mmol/dm^{-3}. This work presents the results of monetite synthesis from Ca $(OH)_2$ and phosphoric acid and brushite from the solution obtained after enriching type II - Lao Cai apatite ore with phosphoric acid [9]. The samples were

examined by volumetric titration methods, XRD, SEM and EDS for the estimation of the synthesis performance.

2. EXPERIMENTAL

2.1. Equipments and chemicals

Raw materials: solution obtained after enriching type II - Lao Cai apatite ore (AP2) by phosphoric acid, H_3PO_4, $Ca(OH)_2$ and other chemicals.

Some of main devices: X-ray diffraction was measured at the Faculty of Chemistry, Hanoi National University. The SEM and EDS were measured at the Hungyen University of Technical Education.

2.2. Experimental

DCP was synthesized from H_3PO_4 and $Ca(OH)_2$ or from the solution after enriching type II - Lao Cai apatite ore by phosphoric acid. In the former case, to examine the effect of phosphoric acid concentration, for 5 ml 85 % H_3PO_4 in 250 ml beaker, add various amounts of distilled water and heat to a temperature of 80 ^{0}C. The solution was stirred at a speed of 200 rev / min together with gradual addition of the required amount of $Ca(OH)_2$ in 30 minutes and then stirred in 10 minutes more. The precipitation after filtering and washing was dried at 105 ^{0}C for 1 h. The synthesized performance was evaluated on the basis of the mass of obtained precipitation.

3. RESULTS AND DISCUSSION

3.1. Synthesis of dicalcium phosphate from $Ca(OH)_2$ and phosphoric acid

3.1.1. The influence of the concentration of phosphoric acid

To investigate the influence of the concentration of phosphoric acid, for 5 ml 85 % H_3PO_4 in 250 ml beaker, change the volume of distilled water added and heat to a temperature of 80 ^{0}C. Stir and add gradually the amount of $Ca(OH)_2$ needed for 30 minutes, then stir 10 minutes further. After the reaction, pH of the solution was about 7 and this indicates that the acid is reacted completely. The precipitation was filtered, washed and dried at 105^{0}C for 1 h. The synthesized yield was determined on the basis of the mass of obtained precipitation. The results are shown in Table 1.

Table 1. Effect of concentration of phosphoric acid for DCP synthesis.

Samples	M1.1	M1.2	M1.3	M1.4	M1.5
Distilled water (ml)	10	20	35	45	70
Precipitate mass (g)	8,854	8,860	9,044	9,455	8,875
$CaHPO_4$ yield (%)	89,00	89,06	90,91	95,04	89,21

As indicated by Figure 1, the precipitated product after drying is $CaHPO_4$, so the reaction occurs during the synthesis:

$$H_3PO_4 + Ca(OH)_2 \rightarrow CaHPO_4\downarrow + 2H_2O$$

and from the above equation, mass of obtained $CaHPO_4$ can be calculated based on the material balance as follows:

$$m_{CaHPO4\ theoretically} = 5\ ml * 1{,}4341 \frac{g\ H_3PO_4}{ml} * \frac{1\ mol}{98\ g\ H_3PO_4} * \frac{136\ g\ CaHPO_4}{1\ mol} = 9{,}95\ g.$$

- Phosphoric acid is a weak acid, its interaction is determined by two factors: the acid dissociation and concentration. It is two opposing factors: the more concentration decreases, the more dissociation increases and this favor the reaction between phosphoric acid and $Ca(OH)_2$. Therefore, precipitating performance is increased from M1.1 to M1.4 samples. However, when the concentration decreases, the rate of collisions between reactant molecules decreases and this determines reduced performance from M1.4 to M1.5. As given in Table 1, the reaction between $Ca(OH)_2$ and H_3PO_4 most effective at temperature of 80 ^{0}C for 40 minutes with 5 ml of 85% H_3PO_4 and 45 ml of distilled water.

3.1.2. Influence of the synthesis temperature

Experiments were conducted similarly as M1.4 sample at various synthesis temperature. The results in Table 2 show that the reaction rate increases with temperature. The synthetic product yield of M2.5 samples reaches 97.43 %.

Table 2. Influence of temperature for CaHPO4 synthesis from H_3PO_4 and $Ca(OH)_2$.

Samples	M2.1	M2.2	M2.3	M2.4	M2.5
Temperature (^{o}C)	50	60	70	80	90
Precipitate mass (g)	7,910	9,077	8,995	9,455	9,693
$CaHPO_4$ yield (%)	79,51	91,25	90,41	95,04	97,43

3.1.3 Product characterization

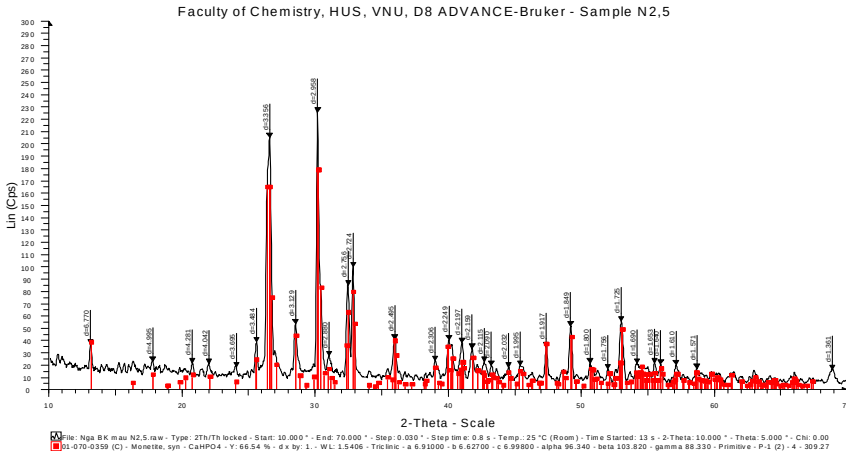

Figure 1. XRD diagram of M 2.5 sample.

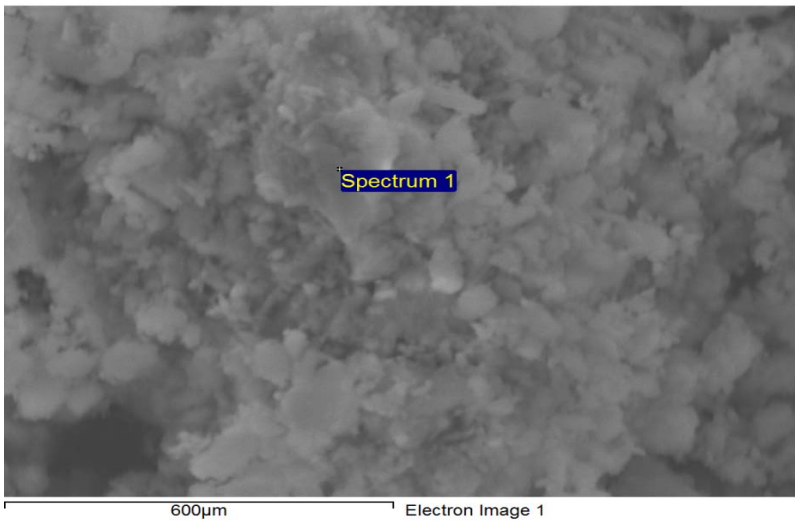

Figure 2. SEM image of M 2.5 sample.

According to obtained SEM images, the product consists of spherical particles with fairly uniform and the majority of particles have a size of about 50 µm.

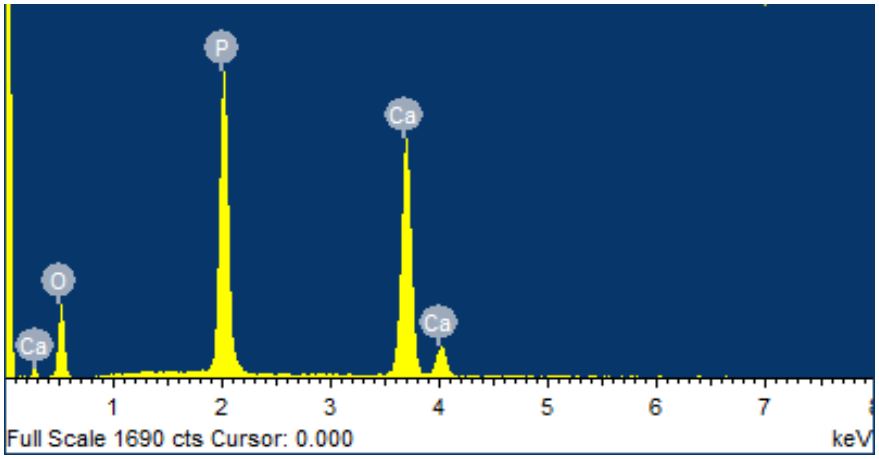

Figure 3. EDS spectrum of M2.5 sample.

The phase forms, morphology and composition of the product sample M2.5 are examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy scattering spectroscopy (EDS). Results are shown in Figure 1 – 3, respectively.

XRD results show that the obtained product is of single phase anhydrous dicalcium phosphate with monetite triclinic structure. Unlike what shown in reference [4], the creation of monetite here is due to higher reaction temperatures. Compared to the works [1 - 2], the synthesis of anhydrous dicalcium phosphate with monetite structure presented in this paper is energy saving and simpler technology.

According to the EDS results (depicted in Figure 3), the product contains the elements such as calcium, phosphorous, oxygen. Thus, the product contains fully elements specific to DCP.

3.2 DCP synthesis from the solution after enrichment

The volume of obtained solution after beneficiation of 100g type II- Lao Cai apatite with solid:liquid ratio of 1:3 and in the right conditions [9] is 310 ml - denoted L solution. Its major components are $Ca(H_2PO_4)_2$, $Mg(H_2PO_4)_2$ and residual H_3PO_4. Similar to the above observation, add gradually $Ca(OH)_2$ at 90 ^{0}C with stirring during 40 minutes, the received pH of the solution after the reaction was about 7. The precipitate was filtered, washed and dried at 10 ^{0}C - denoted as $DCP_{recovery}$. The precipitation yield was determined when analyzing the total magnesium and calcium content in the solution before and after the reaction. The results shown in Table 3 indicates that the performance of magnesium and calcium that enter precipitate reaches 95.5 %. The results are similar to solutions obtained when beneficiating with solid ratio: liquid of 1: 4 or 1: 5.

Table 3. Results of analysis of residual acid, calcium and magnesium and precipitate yield.

$C_{Ca, Mg}$, mol/l $^{(1)}$	1.11
$C_{Ca, Mg}$ $^{(2)}$	0.065
$CaHPO_4$ yield (%)	95.5

$^{(1)}$ *Prior to the reaction,* $^{(2)}$ *After the reaction*

The main reaction equations occur when adding $Ca(OH)_2$ into the solution L:

$$H_3PO_4 + Ca(OH)_2 \rightarrow CaHPO_4 + 2H_2O$$

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

$$Mg(H_2PO_4)_2 + 2Ca(OH)_2 \rightarrow 2CaHPO_4 + Mg(OH)_2 + 2H_2O$$

3.3. $DCP_{recovery}$ product features

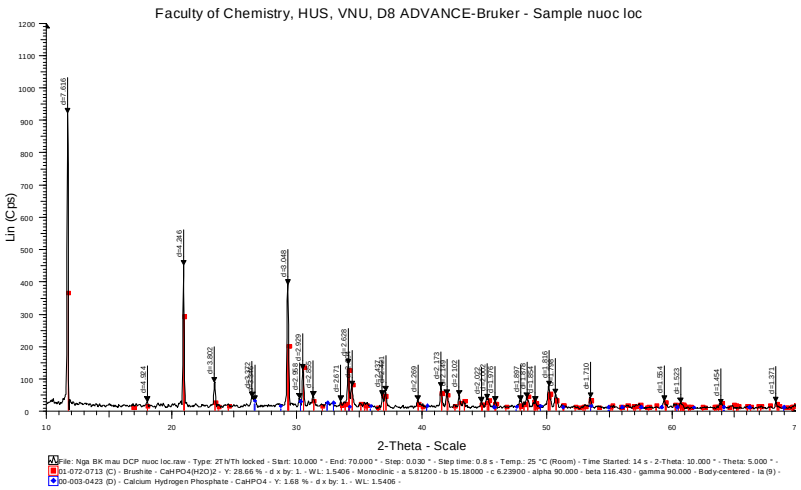

Figure 4. XRD diagram of $DCP_{recovery}$ sample.

The phase forms, morphology and composition of the product sample M2.5 were examined by X-ray diffraction, scanning electron microscopy and energy scattering spectroscopy (EDS). Results are shown in Figure 4-6, respectively.

According to Figure 4, the main component of product is dicalcium phosphate dihidrate $CaHPO_4.2H_2O$ with brushite monoclinic structure, that is mixed with a small amount of anhydrous dicalcium phosphate. This result is different from the one when synthesizing DCP from $Ca(OH)_2$ and phosphoric acid. This difference is probably due to the solution L contains magnesium and other trace impurities that affect the structure of formed crystal.

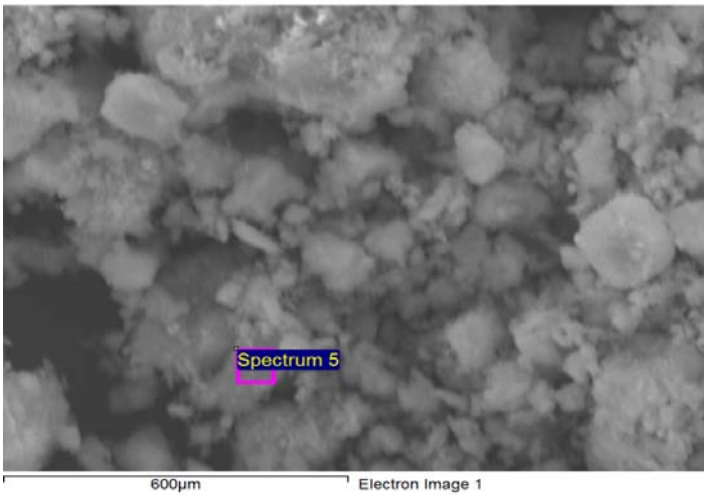

Figure 5. SEM image $DCP_{recovery}$ sample.

According to SEM images, the sample consists of spherical particles with a majority of particles of about 50 µm size.

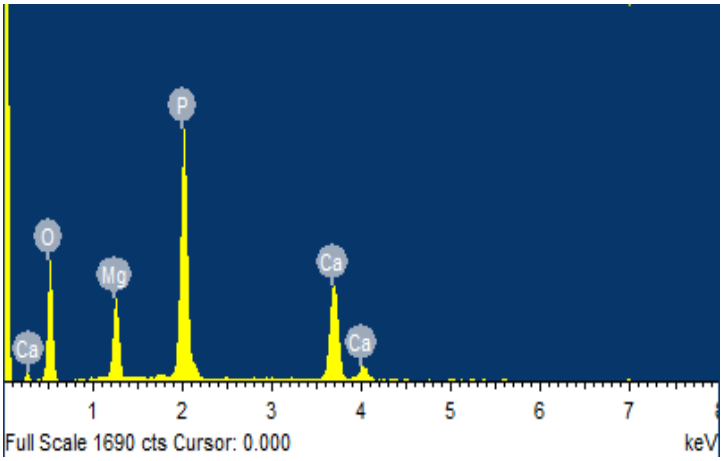

Figure 6. EDS spectrum of $DCP_{recovery}$ sample.

According to the results of EDS - Figure 6, the product contains elements such as calcium, magnesium, phosphorous and oxygen. Thus, the product fully contains elements specific to calcium magnesium phosphate.

4. CONCLUSION

The impact of solid-liquid ratio and the reaction temperature when synthesizing anhydrous dicalcium phosphate from phosphoric acid and $Ca(OH)_2$ was examined in detail. The results show that the performance reached 97.43 % when adding gradually required amount of $Ca(OH)_2$ into the mixture composed of 5ml 85 % phosphoric acid and 45 ml water with stirring at 90 ^oC during 40 minutes. Monetite product obtained is single phase, including spherical particles with the size of about 50 μm and can be used as additives for animal feed.

Magnesium hydroxide and calcium hydrophotphate was prepared successfully from the solution after enriching apatite ore by phosphoric acid. The performance of magnesium and calcium that enter precipitate reaches 95.5 %. The calcium hydrophotphate is $CaHPO_4.2H_2O$ with brushite structure including spherical particles with size of about 50 μm.The product can be used as slowly dissolved fertilizer.

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TÓM TẮT

NGHIÊN CỨU TỔNG HỢP DICANXI PHOTPHAT TỪ MỘT SỐ NGUỒN NGUYÊN LIỆU

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Dicanxi photphat khan cấu trúc monetit góp phần quan trọng trong việc hình thành cấu trúc của xương và răng. Hợp chất này có thể tái tạo những mô cứng do chúng có độ hòa tan cao, dễ được cơ thể hấp thụ hơn so với các hợp chất canxi photphat khác. Dicanxi photphat có thể được sử dụng làm thực phẩm chức năng cung cấp canxi và photphat cho con người và động vật. Cũng do hàm lượng P_2O_5 cao, hợp chất này cũng có thể sử dụng làm phân bón chậm tan trong nông nghiệp cho tất cả các loại cây trồng. Bài viết này trình bày kết quả tổng hợp dicanxi photphat có cấu trúc monetit từ $Ca(OH)_2$ và axit photphoric, đồng thời tổng hợp dicanxi photphat cấu trúc brush từ dung dịch sau làm giàu quặng apatit Lào Cai loại 2 bằng axít photphoric. Các mẫu được kiểm tra bằng phương pháp chuẩn độ thể tích, XRD, SEM và EDS.

Từ khóa: tổng hợp dicanxi photphat, monetit, brushit.