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Thermokinetic Investigation of the Drying Conditions on Amorphous Calcium Phosphate

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Abstract. The present work investigated dried calcium phosphate powders which still retain an amorphous or poorly crystalline structure under a variety of conditions. In previous studies, freeze-drying was found to be the optimum drying condition. However, several publications, as well as our previous studies, have shown that calcium phosphate amorphous, or a poorly crystalline structure, can retain their structure even if the samples are dried immediately after synthesis up to 200^{o}C. In our study, we used the thermokinetic studies FTIR and XRD and showed that the samples are amorphous, or poorly crystalline, but were unable to answer the questions: Is there a difference between the differently dried amorphous calcium phosphates? What are the optimum drying conditions under which the amorphous calcium phosphate (ACP) structure loses the physically bounded water, but still retains the chemically bounded water?

Introduction

In manufacturing, the synthesis process and synthesis conditions have the same level of importance as drying due to the importance of maintaining an amorphous or micro-crystalline structure. The most frequently offered drying conditions are freeze-drying at < -50^{o}C and in a vacuum for 48h – 72h [1,2] or air-drying the collected precipitate at room temperature [3], at 70 – 90 ^{o}C for 15 - 24h [4-9], at 100 – 150 ^{o}C for 24 – 48h [10,11]. Other drying conditions have also been used, for example: washing the precipitate with alcohol and acetone followed by drying at >100 ^{o}C. [12-14].

The disadvantage of drying wet amorphous calcium phosphate is that it is thermodynamically unstable, and the calcium phosphate structure appears to be altered: amorphous to crystalline. Therefore, it is important to understand the change of the chemisorbed and physically bounded water in amorphous and poorly crystalline calcium phosphate.

In this study, we set the following tasks: 1. Produce a calcium phosphate powder with an amorphous structure, and dry it to keep the amorphous structure. 2. Study physically and chemically bound water changes in the drying process using FTIR PAS and TG/DTA analysis. 3. Analyze the loss of mass during the drying process using TG and MS.

Materials and Methods

Sample preparation

In this study we used carbonated calcium phosphate in order to decrease crystallinity and increase phase stability at room temperature [15]. Amorphous calcium phosphate was synthesized by the wet

chemical method at room temperature in a basic environment (reactants $Ca(NO_3)_2{\cdot}4H_2O$, $(NH_4)_2HPO_4$ and $(NH_4)_2CO_3$; molar ratio Ca/P is 2.5:1). The suspension was stirred, filtered, and washed several times with deionized water containing ammonia. Wet ACP was dried at room temperature (25+/-3°C), 50°C, 80°C, 120°C, 130°C, or freeze-dried, or washed with acetone and ethanol and dried at room temperature (25+/-3°C).

Characterization of powder

X-ray powder diffraction (XRD). Diffraction patterns were recorded with Bruker D8 ADVANCE diffractometer, from 5° to 60° using Cu Kα radiation (λ = 1.54 Å generated at 40 mA and 40 kV) at a step size of 0.2°. The crystallinity and crystallite size was evaluated using Profex 3.7.0 software [16] (Fig.1.).

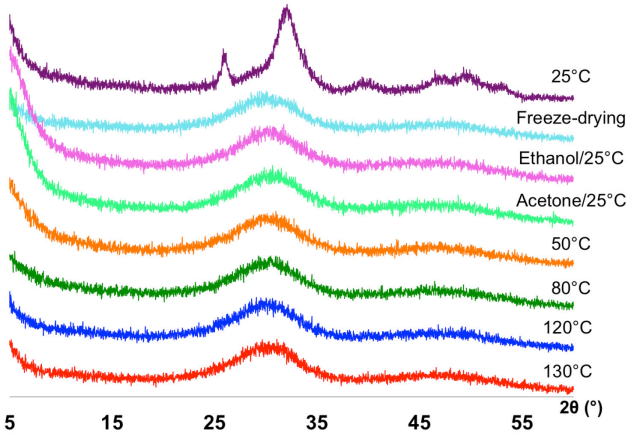

Fig.1. XRD patterns of dried ACP

Cantilever-enhanced photoacoustic spectroscopy (FTIR-PAS). PAS spectra were taken at 450 – 4000 cm^{-1} at a resolution of 4 cm^{-1}, with the average found from 10 scans with a Gasera PA301, and the cell filled with helium gas (flow 0.5 l/min). A special preparation method was not required; 0.01 g of powder was placed in the PAS cell.

Thermogravimetric and differential thermal analyses (TG/DTA) (Seiko EXSTAR 6000 TG/DTA 6300) were conducted to determine the moisture content in the dried samples. Powdered samples were heated to 500°C in the air at a heating rate of 1, 2, 5, 10, 20, 40°C/min.

Mass spectrometry (MS). Hositrad MGT 6-300 Multi Gas Analyser with thermal desorption 6-300 amu, Quadrupole mass spectrometer with ±0.1 amu resolution, minimal detectible partial pressure $<10^{-10}$ mBar up to 1200°C sample heating temperature, maximum temperature increase – 10°C/s.

Analysis. The FTIR spectra were viewed and smoothed, and the baseline correction was performed with the freeware software SpectraGryph 1.0 and Grams/AI.987. The baseline correction and curve-fitting analysis was performed using *MagicPlotStudent* software Deconvolution involving both Lorentzian and Gaussian curve fittings.

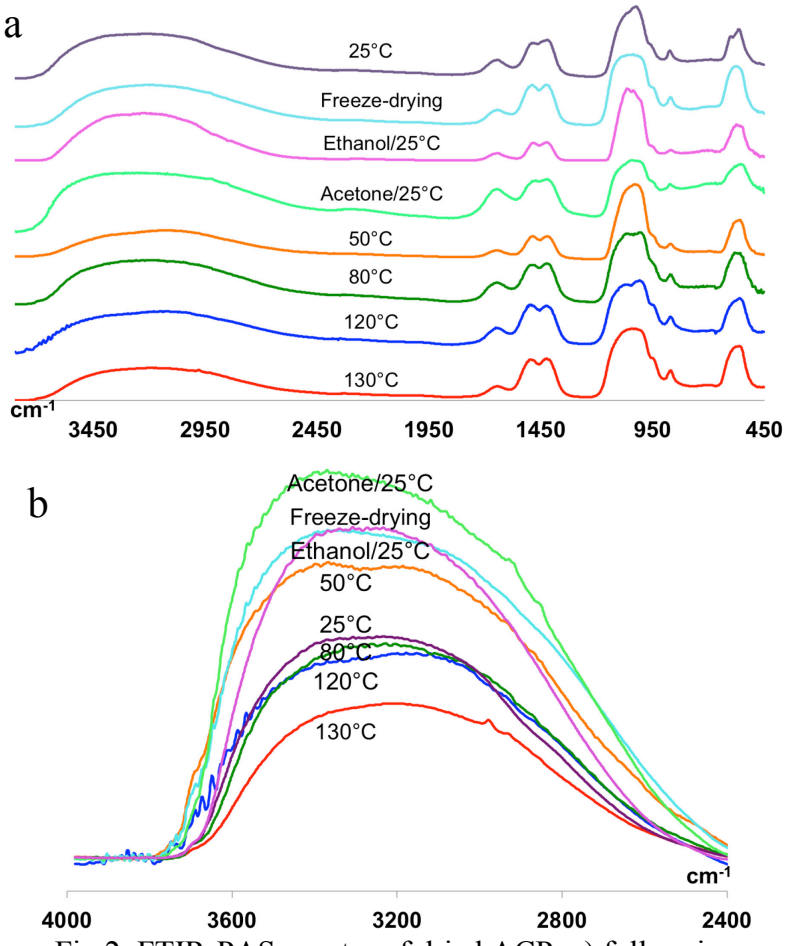

Fig.2. FTIR-PAS spectra of dried ACP: a) full region, b) 2400 -4000 cm^{-1} region

Results and Discussions

The recorded FTIR PAS spectra (Fig.2.) and XRD patterns (Fig.1.) showed that all powders have an amorphous structure after drying, except when air-dried at 25°C which are poorly crystalline. It was found that a precipitated ACP contains a large amount of water. The PAS spectra showed a decrease in the intensities of bands at 2400 – 4000 cm^{-1} in dried samples (Fig. 2b), which may be attributed to losses of the physically adsorbed water. When comparing the PAS spectra of samples dried at different temperatures, it can be observed that an increase of the drying temperature affects the intensities of the bands – the higher the temperature, the lower the intensity of the bands. Air–dried samples that were washed with the organic solvents ethanol and acetone showed higher band intensities than air–dried samples without organic solvents.

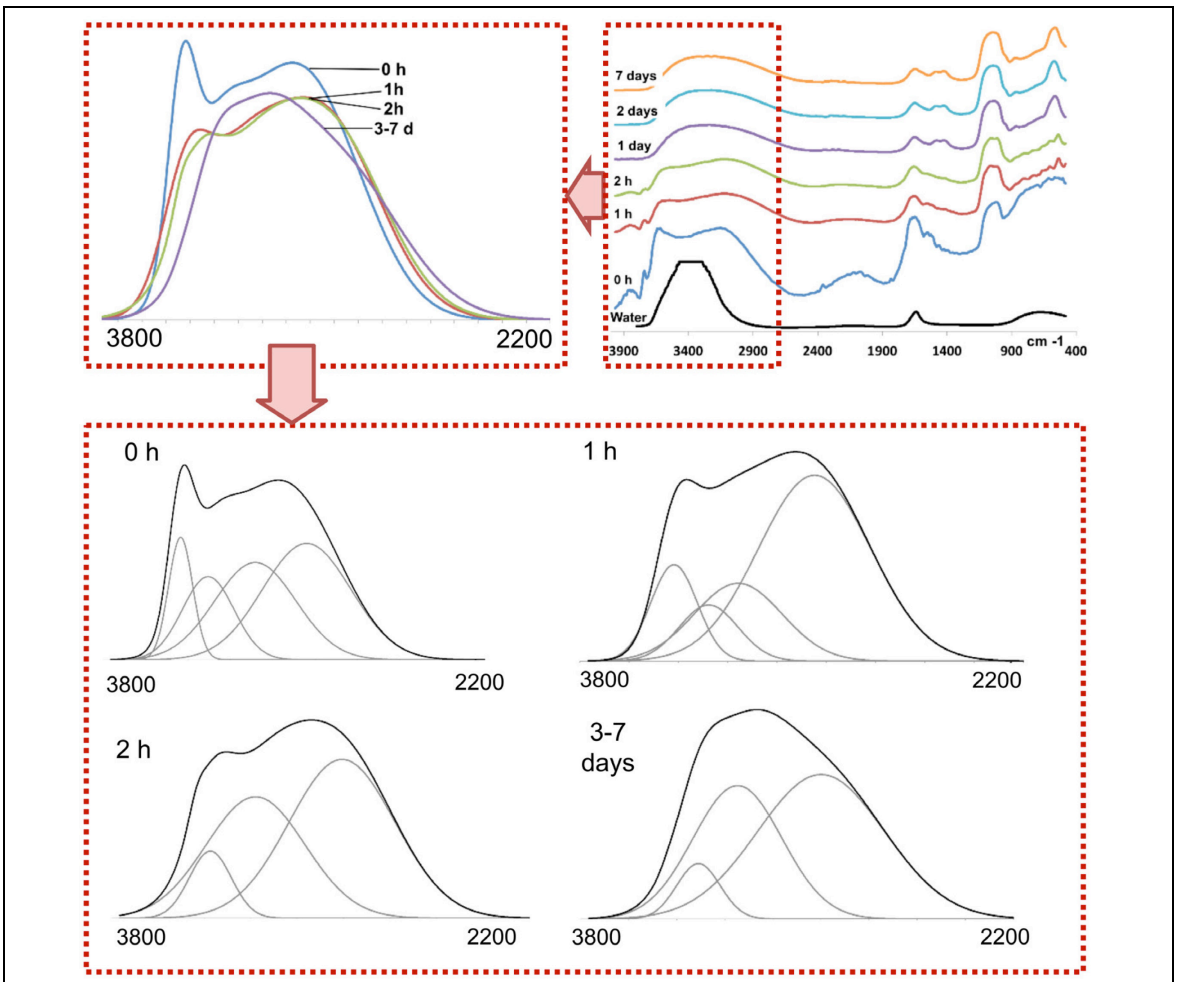

Fig.3. Drying process of ACP in air

However, the PAS measurement does not require any sample preparation [17] so the technique is non-invasive and measures the near-surface (~35 μm) [16], while FTIR-PAS spectra were taken during the drying process. The recorded spectra showed a fast desorption of water in the first two hours (Fig.3). The deconvolution of spectra in 2200 – 4000 cm^{-1} region showed a shift of bands that can be attributed to a change in the strength and length of the hydrogen bonds [18]. In the 2400 – 4000 cm^{-1} spectra region, 3-7-day dried powders showed very similar band intensities and maximum values as completely dried ACP.

A TG/DTA diagram showed one endothermic and one exothermic peak. It was observed that a large endothermic peak with an upper temperature of 76 – 125°C resulted from the dehydration of water molecules in dried ACP powders. Our work was focused on the endothermic peak; to obtain information about physically and chemically bounded water. A distinction between physically and chemically adsorbed water was possible from an Arrhenius plot relating the heating rate and the upper temperature of the endothermic peak to the thermal analysis.

The activation energy of physically and chemically adsorbed water, and the critical temperature for the dehydration of bound water, was calculated by both the Ozawa-Flynn-Wall and Kissinger methods (ASTM) [19].

Table 1. Activation energies and critical temperatures for dried ACP's

Parameters	**Air-drying 25°C**	**Freeze-drying**	**50°C**	**80°C**	**Ethanol/ 25°C**	**Acetone/ 25°C**
T_{crit}, °C	64±3	125±5	103±4	124±5	91±4	84±5
E_a (phys), kJ/mol	34±1	64±2	49±2	57±2	38±1	41±1
E_a(chem), kJ/mol	54±2	147±4	92±4	120±5	57±2	57±2

Samples showed various critical temperature T(crit) and activation energy (Ea) values. Significant differences between the activation energy of physically sorbed water Ea (phys) and chemically sorbed water Ea (chem) was detected in samples dried at higher temperatures, as well as for freeze-dried samples (Table 1).

Assignment of activation energy values are not inconsistent with the estimate before by J.M. Sedlak and Y. Kojima [20,21]. However, calcium phosphates without carbonate ions were studied in these studies.

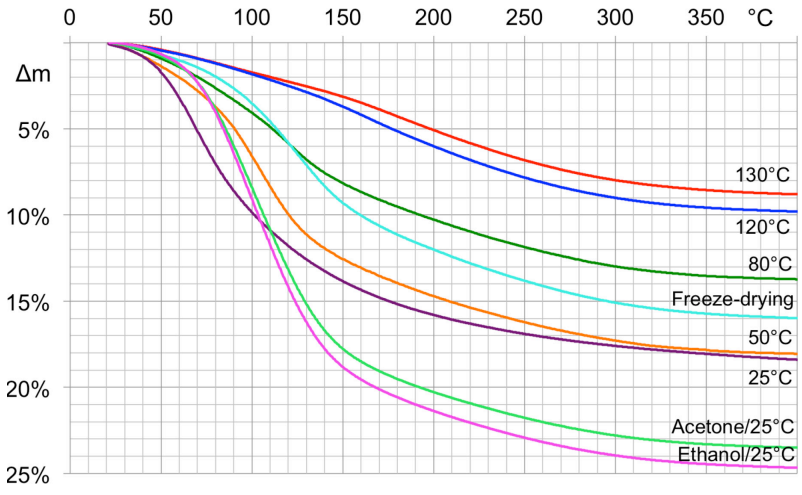

Fig.4. TG curves of dried ACP powders

TG curves showed a different weight loss at the end of the heating process (1200°C), and confirmed the information obtained with the PAS spectroscopy – the higher the drying temperature, the lower the weight loss, as more water was desorbed in the drying process (Fig.4. and Table 2).

Table 2. Weight loss in dried ACP's

Parameters	**Air-drying 25°C**	**Freeze-drying**	**50°C**	**80°C**	**Etanol/ 25°C**	**Acetone/ 25°C**	**120 °C**	**130 °C**
Δm %, T_{crit}	1,5±0,2	2,6±0,3	7,1±0,4	6,2±0,4	8,0±0,4	4,7±0,3	3,2±0,3	2,4±0,3
Δm %,$T_{crit-200}$	9,4±0,5	6,5±0,4	7,7±0,4	4,1±0,3	12,9±0,6	15,0±0,7	4,3±0,3	2,5±0,3
Δm %,$T_{200-600}$	3,7±0,3	4,2±0,3	4,3±0,3	4,2±0,3	4,5±0,3	4,3±0,3	5,0±0,3	4,8±0,3
Δm %,$T_{600-650}$	0,1±0,05	0,2±0,05	0,3±0,05	0,2±0,05	0,4±0,1	0,4±0,1	0,4±0,1	0,3±0,1
Δm %,$T_{650-1000}$	2,9±0,3	0,9±0,1	0,6±0,1	0,6±0,1	1,5±0,2	1,2±0,2	1,8±0,2	1,9±0,2
Δm %,$T_{20-1000}$	17,6±0,9	14,4±0,7	20,0±1,0	15,3±0,8	27,3±1,3	25,6±1,3	14,7±0,8	11,9±0,6

TG indicates the highest weight loss for samples dried with acetone and ethanol in air.

The most significant changes in the mass were detected before and after (up to 200°C) the critical temperature T(crit). With acetone and ethanol dried samples, weight loss up to 200°C is higher than for 80 – 130°C dried powders.

Mass spectrometry data showed that in the temperature range of 200°C – 600°C, ACP powder loses water and CO_2, over 600°C – CO_2. While ethanol and acetone dried samples in a temperature range up to 600°C lose traces of acetone and ethanol, and reach a maximum at 530°C.

Conclusions

TG and PAS data showed that by changing the drying conditions, it is possible to obtain poorly crystalline ACP with different water content. The calculation of the activation energy is an important tool when it comes to thermal and kinetic transformation occurring during the heat treatment. By correlating the activation energy calculations with other characterization tools (XRD, FTIR), the dehydration process of adsorbed and bound water on amorphous calcium phosphate can be explained, as well as information regarding the optimum temperature and conditions can be obtained. In conclusion, it was confirmed that the quantity of water and stability of sorbed and bound water depends on the thermal treatment process.

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