



Effect of curing conditions on the dimensional and thermal stability of calcium phosphate cement for elevated temperature applications



Johan Blom^a, Hubert Rahier^b, Jan Wastiels^{a,*}

^a Vrije Universiteit Brussel, Department of Mechanics of Materials and Constructions, Pleinlaan 2, Brussels 1050, Belgium

^b Vrije Universiteit Brussel, Research Group of Physical Chemistry and Polymer Sciences, Pleinlaan 2, Brussels 1050, Belgium

ARTICLE INFO

Article history:

Received 4 April 2014

Accepted 28 July 2014

Available online 16 August 2014

Keywords:

Curing (A)

Temperature (A)

Microstructure (B)

Shrinkage (C)

Mechanical properties (C)

ABSTRACT

Calcium phosphate cements (CPCs) are attractive materials for elevated temperature applications, like moulds to process thermoplastics up to 300 °C. The CPC resulting from the reaction of wollastonite with phosphoric acid cured at room temperature however contains hydrated phases like brushite, and is thus not stable when exposed to temperatures above 200 °C. A non-contact method based on digital image correlation demonstrated that isothermal curing at 60 °C reduces the thermal shrinkage up to 300 °C by 25%. This curing method results in the direct formation of the more stable monetite in a shorter curing time. The correlated results of TGA, pH of the filtration water, and DSC analysis on partially cured material indicate this. XRD diffractograms and SEM images in combination with EDX show the evolution of the transformation of wollastonite into monetite, and the structure and morphology of the formed material.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The discovery of calcium phosphate cements (CPCs) is ascribed to Brown and Chow [1] and was published in 1983. CPCs generally consist of a concentrated mixture of one or several calcium phosphate powders and an aqueous solution. A drawback for some applications of calcium phosphate cements can be their exothermal reaction and high reactivity. The calcium phosphate cement used in this study was developed at the Department of Mechanics of Materials and Constructions, Vrije Universiteit Brussel (VUB) [2]. The development of a phosphoric acid solution containing metals and a retarder, which will react with the calcium from wollastonite, makes it possible to formulate a cement paste which will harden relatively slowly at room temperature (RT), leaving enough time for industrial processing. In general the reaction between calcium and phosphoric acid is a dissolution followed by a precipitation and crystallization process. The crystallization of amorphous calcium phosphate (ACP) will result in dicalcium phosphate dihydrate (DCPD) or brushite [3,4]. At completion of the reaction, the initially acidic pH (value around 1) is increased to a neutral 7. Brushite however is thermodynamically unstable at pH values above 6–7 [6] and undergoes a slow transformation into more stable calcium phosphates [7]. Calcium phosphates (CaPs) belong to the family of apatites [8]. Several CaP phases exist and the phase which is formed depends on the Ca/P ratio, the reaction conditions (like pH and temperature) and the storage temperature [5,6].

If the molar ratio $\text{Ca/P} = r$ is between 0.39 and 1, only one type of calcium phosphate namely brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) is formed according to Eq. (1) [7].



For $1 \leq r \leq 1.66$ two additional calcium phosphates (monetite and calcium dihydrogenphosphate monohydrate) can be formed. The reactions leading to monetite (CaHPO_4) and calcium dihydrogenphosphate monohydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) are given in Eqs.(2) and (3), respectively.



When monetite is heated (390–515 °C) dehydration will result in the formation of pyrophosphate according to Eq.(4)[9,16]:



An interesting property, apart from being pH neutral after hardening, is that the CPC can resist elevated temperatures (up to 800 °C), without releasing toxic gases. However, when brushite is heated, mass loss will occur in combination with dimensional and phase changes. Previous studies confirmed that the studied CPC is not stable, due to transformations of the material when it is exposed to elevated temperatures [9]. Researchers have demonstrated that meta-stable brushite may even convert at relatively low temperatures (RT–80 °C) to octacalcium phosphate (OCP) or to calcium

* Corresponding author. Tel.: +32 2 629 29 24; fax: +32 2 629 29 28.
E-mail address: Jan.Wastiels@vub.ac.be (J. Wastiels).

hydroxyapatite (HAp) [10,11]. On the other hand, while brushite transforms into monetite at temperatures above 80 °C, the presence of foreign atoms could push this temperature up to 105 °C [12]. A hydrothermal post curing method was presented to stabilize the material, based on thermally induced transformations of the unstable phases into more stable phases with reduction of the bulk shrinkage [13]. A different approach to obtain a stable material is developed in this paper by optimizing the curing process itself, since it seems to be rational to obtain a more stable phase immediately during setting. The main goal of this study is to examine the effect of curing conditions on the mass loss, shrinkage and phase changes in order to optimize the stability of the material when exposed to elevated temperatures.

2. Experimental methods

2.1. Specimen preparation

Specimens were prepared by mixing wollastonite (CaSiO₃) powder (Nyad M200, supplied by Nyco) with a phosphoric acid based solution of metal oxides including a retarder (Vubonite liquid, supplied by Symbion), as described in [2]. The liquid to powder mass ratio was 1/0.8. The components were mixed using a Heidolph RZR 2102 overhead blade mixer. The mixing was performed in two stages starting at a speed of 500 rpm until homogenization and continuing for another minute at 2000 rpm. The mixture was left to rest for at least 30 s, in order to release the entrapped air. Square PVC moulds with sides of 50 mm and height of 5 mm were used to cast the test specimens. The reference specimens were cured in a conditioned room at 20 °C (RT) for 24 h (specimens labelled ‘Ref RT’). The specimens were covered with a plastic film during curing in order to avoid the evaporation of water. In this case the temperature variation (less than 5 °C) due to the exothermal curing reaction was uncontrolled. To prevent important temperature peaks when cured at a more elevated temperature (40–60 °C), specimens were cured between 15 mm thick preheated aluminium plates. In this case a nearly isothermal condition could be obtained. The temperature was monitored with a TESTO 830T4 IR temperature scanner, revealing a variation of less than 1 °C during the curing period. The effect of this isothermal curing method was examined at 40 °C and 60 °C heating for 24 h (specimens labelled as ‘40 °C i’ and ‘60 °C i’, respectively). Again the evaporation of water was prevented during the curing period. The samples for the thermogravimetric analysis (TGA) and the Scanning Electron Microscopy (SEM) were recovered from the plate specimens that did not undergo a prior drying process.

The evolution of the reaction was studied on partially cured specimens. They were produced in the square PVC moulds (50 × 50 × 5 mm) and cured according to three different methods. With intervals of 1 h, up to 5 h of curing time, a 2 g sample of the specimens was extracted. In order to stop the reaction of this sample, it was grinded and then washed in 200 ml of demineralised water. After washing, the samples were filtered using a Büchner funnel. Drying was performed by placing the samples in a vacuum oven at 60 °C for 72 h.

For the mechanical tests, beam specimens with dimensions of 160 mm (length), 15 mm (width) and 30 mm (height) were casted and cured in a similar way as described above.

2.2. Analytical techniques

2.2.1. Shrinkage measurement using digital image correlation (DIC)

Digital image correlation has major advantages. The method can be used on large specimens that are fabricated in realistic conditions. The non-contact method can measure the full-field deformation at the surface of objects under mechanical or thermal loading [14]. The

experimental setup (Fig. 1) was designed to measure real time in-plane thermal deformations under thermal loading.

The setup consists of an HERAEUS Type UT 6060 oven capable to heat the specimens up to 300 °C, and a DIC capturing system. An electronic temperature control unit with an accuracy of 0.1 °C for the interval 0–100 °C and 1 °C for the interval 100–300 °C was applied to the oven. In order to reduce errors due to the potential variation in thickness and refractive index a quartz glass window was placed in the oven door [15]. A QICAM 12-bit CCD camera was mounted on a sliding rail which is perpendicular to the specimen. A distance between camera lens and specimen of 300 mm was obtained. A Schneider compact VIS-NIR Xenoplan 1.4/23 lens was used. Before placing the specimens in the oven a heat resistant black paint speckle pattern was applied through a silk screen print process. Each measuring cycle started with taking a reference image at RT using the image capturing software VIC snap supplied by Correlated Solutions Inc. After taking the reference image the temperature of the oven was increased to 100 °C. Once this temperature was reached it was kept stable for 1 h. During this period every 5 min an image was captured. The procedure was repeated for 200 °C and 300 °C. After heating, the specimen was cooled to RT using the same steps. The images were imported in the VIC2D software in order to correlate the undistorted and distorted images. After correlation the linear deformation was computed at three different positions using a 20 mm virtual strain gauge. Finally the obtained strains were imported and processed in a spreadsheet.

2.2.2. Thermogravimetric analysis (TGA)

Thermogravimetric Analyser TGA Q5000 from TA Instruments purged with nitrogen was used. Crushed powders with an average mass of 5 mg were placed in platinum pans. The samples were heated from 50 to 500 °C at a heating rate of 10 °C/min under a flow rate of 25 ml/min nitrogen.

2.2.3. pH

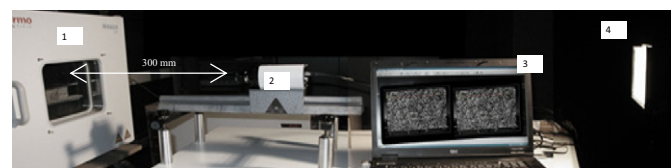
The pH of the filtration water was measured using a pHep 5 manufactured by Hanna instruments. This digital pH measuring device with an accuracy of 0.01 pH was cleaned with milli-Qwater and calibrated with a pH 7 reference liquid before each measurement.

2.2.4. Differential Scanning Calorimetry (DSC)

The isothermal DSC experiments were performed on a Mettler Toledo DSC822e, with mechanical cooling. The purged gas was N₂ (100 ml/min). Calibration was done with indium and zinc. Before placing the sample pans in the analyser, the furnace was preheated to the isothermal curing temperature.

2.2.5. Scanning Electron Microscopy (SEM)

A Phenom PRO-X desktop SEM was used. The microscope was equipped with a high-brightness CeB₆ electron source, set to an



1	oven	HERAEUS Type UT 6060
2	camera	QI cam CCD camera
3	Computer + data capturing software	VIC snap of correlated solutions
4	light	

Fig. 1. Schematic view of the DIC test setup.

Download English Version:

<https://daneshyari.com/en/article/1456278>

Download Persian Version:

<https://daneshyari.com/article/1456278>

[Daneshyari.com](https://daneshyari.com)