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# Setting and hardening process of a wollastonite-based brushite cement

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## ABSTRACT

Wollastonite-based brushite cements are used for refractory material applications, but they may also offer prospects for the solidification/stabilization of hazardous waste. These binders are formed by the reaction of wollastonite with an orthophosphoric acid solution containing borax and metallic cations ($Al^{3+}$, $Zn^{2+}$). This work provides new insights into their setting and hardening process using a panel of characterization techniques (XRD, NMR, rheology…). A multi-step hydration process is evidenced by the formation of several products: amorphous silica, monocalcium phosphate monohydrate ($Ca(H_2PO_4)_2{\cdot}H_2O$ or MCPM), that precipitates transiently during the first stage of hydration, and brushite ($CaHPO_4{\cdot}2H_2O$) that crystallizes at higher pH (≥3). In addition, an amorphous phosphate phase containing aluminum, calcium and zinc massively precipitates at the beginning of hydration, and gets richer in calcium as hydration progresses. Setting of the cement paste occurs when brushite starts to form. The successive formation of MCPM and brushite is well predicted by thermodynamic modelling.

## 1. Introduction

Calcium phosphate cements are usually composed of one or several phases containing calcium and phosphates, to which other calcic compounds as calcium hydroxide or calcium carbonate can possibly be added as well as additives to control the setting and the properties of the hardened matrix [1–3]. Mixed with aqueous solutions, they can yield different end-products, such as stoichiometric or calcium-deficient hydroxyapatite, calcium octaphosphate ($Ca_8(H_2PO_4)_6{\cdot}5H_2O$) or brushite ($CaHPO_4{\cdot}2H_2O$), by an acid-base or hydrolysis reaction [4]. The main applications of phosphate cements are in the dentistry and medicine area since they form a product with a similar chemical composition to bones and teeth [5–11]. Regarding apatite cements ($Ca_5(PO_4)_2OH$), certain properties are also of interest for applications concerning radioactive wastes conditioning, such as their structural flexibility, high-temperature stability, very low solubility in slightly acidic, neutral, or alkaline aqueous media and irradiation stability [12]. However, a limitation of these binders for use on a large scale is the cost of some of the reactants prepared at high temperature (tetracalcium and tricalcium phosphates).

A less expensive calcium phosphate binder can be prepared from wollastonite ($CaSiO_3$), a natural calcium meta-silicate, and phosphoric acid ($H_3PO_4$), as firstly described by Semler [13,14]. The reaction starts in very acidic medium (pH ~1), but the pH increases rapidly to reach equilibrium at a value close to 6 [15]. For Ca/P molar ratios between 1 and 2.56, a calcium phosphate (brushite ($CaHPO_4{\cdot}2H_2O$)) and amorphous silica are formed according to equation (Eq. (1)) [15,16].

$$CaSiO_3 + H_3PO_4 + (1 + x)\, H_2O \rightarrow SiO_2{\cdot}xH_2O + CaHPO_4{\cdot}2H_2O \qquad (1)$$

However, wollastonite-based binders are highly reactive and can exhibit flash set as well as excessive heat output [15] and need to be strongly retarded, for instance by an addition of boron species, such as borax or boric acid [14].

Wollastonite-based brushite cements have found applications for refractory materials as they exhibit very good thermal resistance after hydrothermal post-curing [17]. Textile reinforced cementitious composites have been successfully designed for applications requiring high load-bearing capacity, good fire resistance and lightweight construction [18]. Due to very different cement chemistries, some retarders of Portland cement hydration such as heavy metals may be much less influent on the setting and hardening process of wollastonite-based binders. For instance, lead oxide can be incorporated up to 50% by weight of cement (wollastonite) without notable degradation of the mechanical and thermal properties [19]. The resulting composites have

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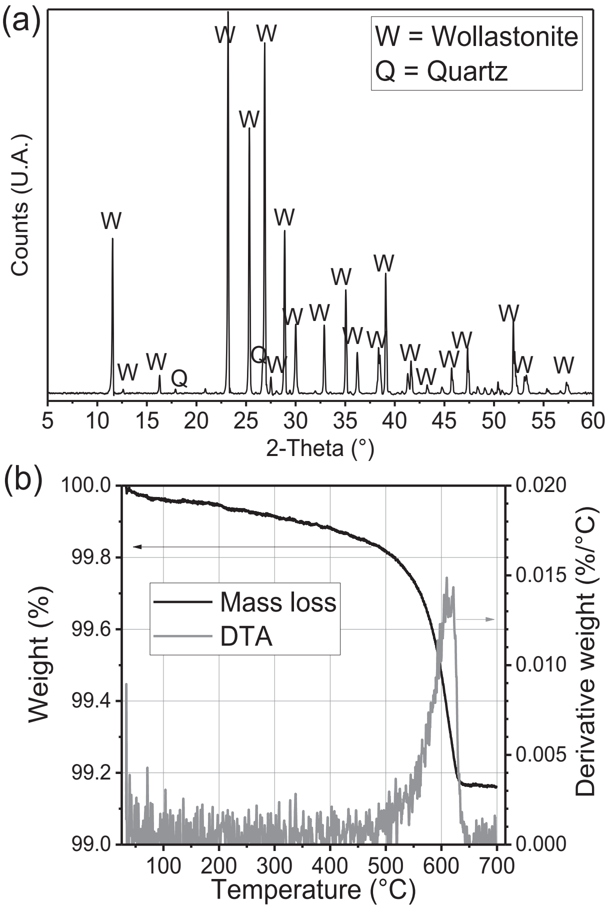

**Fig. 1.** Mineralogical characterization of the cement powder by X-ray diffraction (a) and thermogravimetry analysis (b).

potential for radiation shielding applications. Good adhesion properties with wood products, ceramics and concrete have also been recently reported, which opens up their spectrum of applications [20].

Most studies on wollastonite-based binders have been focused on the characterization of the final products [15,20], on the associated microstructure [15] and on the functional properties of the resulting materials [17,21,22]. This work aims at giving a new insight into the setting and hardening process of such binders, by characterizing the evolution of both the liquid and solid phases with ongoing hydration.

## 2. Experimental

### 2.1. Materials and specimen preparation

The wollastonite-based binder was provided by Sulitec. It was a two-component system, consisting of a calcium silicate powder and of a phosphoric acid-based solution. The powder mainly comprised wollastonite, and traces of calcite and quartz as shown by X-ray diffraction and thermogravimetric analysis (Fig. 1). Calcite resulted from carbonation of metastable wollastonite when exposed to air.

Based on the weight loss recorded at 654 °C (decarbonation of $CaCO_3$) by thermogravimetric analysis, the proportion of calcite was assessed to be 1.6 ± 0.1 wt%. The particle size distribution of the powder, determined by laser granulometry, ranged between 0.5 µm and 135 µm ($d_{10} = 2.8$ µm, $d_{50} = 15.2$ µm, $d_{90} = 48.3$ µm). During industrial crushing, wollastonite breaks into lath- or needle-shaped particles because of its cleavage properties. This tendency is measured by the ratio of the length-to-diameter of the particles. The average aspect ratio, measured on SEM images (characterization of 100 particles), was close to 4:1, which is rather small as compared to other commercial wollastonites.

The mixing solution was a phosphoric acid solution ([P] = 9.3 mol/L), containing metal cations ($[Al^{3+}] = 1.3$ mol/L, $[Zn^{2+}] = 1.3$ mol/L) and borax ($[Na_2B_4O_7] = 0.15$ mol/L) as a retarding agent. The weight ratio of the mixing solution to the cement powder was fixed to 1.25 in all samples, resulting in a Ca/P molar ratio of 1.2. Mixing was performed during 5 min using a laboratory mixer equipped with an anchor stirrer and rotating at 250 rpm. Paste samples were cast into airtight polypropylene boxes (20 mL of paste per box) and cured at 25 ± 1 °C for a period of time ranging from 30 min to 48 h, before being characterized to determine their mineralogy and microstructure (Section 2.2.2). The cement hydration process was also investigated using a panel of complementary techniques, as described in Section 2.2.1.

### 2.2. Characterization techniques

#### 2.2.1. Characterization of cement hydration

Hydration of the cement pastes was investigated using a TAM AIR conduction microcalorimeter under isothermal conditions at 25 °C. Calorific capacities of solution and cement were respectively taken equal to 3.76 and 0.75 J/°C/g. Mixing of the dry cement and solution was performed outside the calorimeter. About 2 g of cement paste was cast in a glass ampoule and introduced in the calorimeter. The heat flow was recorded versus time and compared to that of a sample maintained at 25 °C and consisting of water, the volume of which being adjusted to get the same calorific capacity as the paste sample.

The Vicat setting time was measured according to European standard EN 196-3. The needle was on a 300 g moveable rod and had a diameter of 1 mm ± 0.05 mm. A sample of fresh cement paste was cast in a frustum 40 mm in height. Initial setting time was considered as the time when the needle penetration was 39 mm ± 0.5 mm. The final setting time corresponded to < 0.5 mm penetration. To avoid any desiccation of the paste during setting, a layer of Vaseline oil was poured on the material before starting the experiment. Penetration was then measured every 30 min. Oil was used instead of water since it was observed that the presence of curing water retarded cement setting. This delay was likely due to the dilution of the acidic mixing solution and its pH increase. In the presence of oil, the samples exhibited the same setting time as the pastes cured in air tight polypropylene boxes at 25 °C.

In addition, the viscoelastic properties and electrical conductivity of the paste samples were simultaneously monitored with ongoing hydration using a specifically designed device [23]. It comprised a cylindrically shaped Plexiglas cell (inner radius of 15 mm, total volume of 70 mL) with two annular stainless steel electrodes, which was filled with the cement paste. The cell was thermostated at 25 °C by circulation of cooling water in a double envelope. It was connected to the EC channel of an electrochemistry meter (Consort C 861) with a BNC cable. A specific data acquisition software (Consort Dis Data) was used to collect conductivity measurements. The conductivity cell was calibrated using a 12.888 mS/cm standardized KCl solution at 25 °C. Evolution of the viscoelastic properties of the paste was followed by dynamic mode rheometry using a strain-driven controlled stress rheometer (AR-G2 TA Instrument, USA). A sinusoidal shear strain (γ) was applied to the cement paste at constant frequency (ω). The resulting stress (τ) was measured by the intermediary of the torque and was also sinusoidal with a δ phase lag with respect to the applied strain.

$$\gamma = \gamma_0 e^{i\omega t} \quad (2)$$

$$\tau = \tau_0 ei(\omega t + \delta) \quad (3)$$

The ratio between the stress and the shear strain is equal to the complex shear modulus (G*) and is defined by:

$$G^* = G' + iG'' \quad (4)$$