Substitution of aluminous cement by calcium carbonates in presence of carboxylic acid

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HIGHLIGHTS

- HOAc has a remarkable dispersive effect over paste mixture M1.
- The well-dispersed pastes lead to densification of the hardened material.
- The mechanical properties of the densified materials are improved.
- Materials based of mixtures: Secar 71 + $CaCO_3$ + HOAc favor the formation of $C_4A\bar{C}\_H_{11}$.

ARTICLE INFO

ABSTRACT

This paper presents results concerning the partial substitution of a calcium aluminate cement by calcium carbonate. The experimental parameters monitored in this study are the mechanical properties, the microstructure evolution through density measurements and the structure through analysis by X-ray diffraction.

The major results of this study are the following: (1) It is possible to substitute a portion (10 wt%) of an aluminous cement by calcium carbonate, while improving the mechanical properties of the hardened material. This is achieved with a mass percentage of the carboxylic acid between 1 and 5%, relative to the dry mass, which acts as a good dispersant and leads therefore to densification of the hardened material. (2) When the mix consists of 50 wt% of aluminous cement and 50 wt% of calcium carbonate, the mechanical properties of the cured material are low and this happens whatever the percentage of added dispersant is.

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1. Introduction

Secar 71 (Kerneos, France) is a calcium aluminate cement (∼70 wt% of Alumina) known for its good chemical resistance and its refractory character. These interesting characteristics offer possibilities for use in severe conditions such as acid or bacterial corrosion, abrasive environment, high temperatures, thermal cycling or a combination of these attacks. Recently, some works have been developed for use as a biomaterial [1,2]. These wide possibilities of uses are not only related to the nature of the phases developed during hydration, but also to the microstructure of the hardened material. The anhydrous cementitous phases in contact with water react to form hydrates, whose nature depends on the conditions of consolidation, particularly temperature and humidity [3–6]. CA ($CaO^*Al_2O_3$)[1], the main phase of an aluminous cement, gives rise mainly to the hydrated calcium aluminate hexagonal metastable phase, CAH_{10}, according to reaction (1):

$$CA + 10\,H \rightarrow CAH_{10} \qquad (1)$$

For medium temperatures (between 15 and 30 °C), the metastable hydrate that forms is C_2AH_8, according to the reaction (2):

$$2\,CA + 11\,H \rightarrow C_2AH_8 + AH_3 \qquad (2)$$

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[1] In the following, CaO, Al_2O_3, CO_2 and H_2O are noted according to cementitous terminology C, A, $\bar{C}$ and H.

Above 30 °C, the cubic stable hydrate, C_3AH_6, is formed according to reaction (3):

$$3\ CA + 12\ H \rightarrow C_3AH_6 + 2\ AH_3 \tag{3}$$

In addition, CAH_{10} and C_2AH_8 are thermodynamically metastable phases and transform into stable $C3AH_6$ hydrate [4–7].

In previous work, we studied and demonstrated the remarkable dispersive effect of acetic acid on aluminous cement pastes. This dispersive effect on the pastes led to a densification of the microstructure, and therefore influenced upon the properties of the hardened material. Indeed, the mechanical strength was improved [8–13].

However, the manufacturing process of a cement is energy consuming and any attempt to substitute part of the cement by a mineral addition without decreasing too much the mechanical characteristics of the final hardened product is worth to be explored. In this respect, studies were made on mixtures of aluminous cement and calcium carbonates. The studied parameters were the effect of $CaCO_3$ addition on hydration [14], the development of the mechanical strength [15,16] or the accelerating action on the hydration process [17] of the calcium aluminate cement.

The objective of this work is to prepare cement based materials by substituting some of the calcium aluminate cement by calcium carbonates. In particular, we examine the effect of acetic acid addition on the dispersion of the paste and the consequences on the physical characteristics of the hardened material.

2. Material and methods

2.1. Starting materials and preparation of pastes

The materials were mixtures of cement and calcium carbonate, $CaCO_3$. The anhydrous cement was a calcium aluminate cement (Secar 71 from Kerneos, France). The chemical and mineralogical compositions are given in Table 1. The main constituents are Al_2O_3 (69.8–72.2 wt%) and CaO (26.8–29.2 wt%). The cement had a particle size that ranged between 1 and 100 μm with an average value around 10 μm. This material was kept at 20 °C in a dry atmosphere before being used. The calcium carbonate (Ceradel, France) had of a purity of 99.2 wt% and a particle size characterized by $D40 = 2$ μm (40% of the particles had a size less than 2 μm).

Calcium aluminate cement and calcium carbonate were dry mixed in a porcelain jar containing porcelain beads of size ranging between 0.5 and 1.5 cm (volumic distribution: $\frac{1}{3}$ powders (cement and $CaCO_3$ mixture), $\frac{1}{3}$ beads, $\frac{1}{3}$ empty space), during 3 hours. The mixing carried out was rather for homogenization, since the starting powders were sufficiently fine. Two mixtures were prepared: the first, noted M1, consisted of 90 wt% of cement and 10 wt% of calcium carbonate and the second, noted M2, was composed of 50 wt% cement and 50 wt% calcium carbonate. The two mixtures were chosen because they correspond to the limits of significant variations in the characteristics of the pastes and of the hardened materials. Limits substitutions in Portland cement compositions are of the same order of magnitude [18].

In order to prepare the paste, distilled water with increasing quantities of acetic acid (HOAc) was added. The acetic acid was from PROLABO, France (90 vol%). The pastes were prepared with liquid (water and acid) over solid (cement and $CaCO_3$) ratio, $\frac{m_l}{m_s}$, equal to 0.35 for the M1 mixture and 0.45 for the M2 mixture; m_l and m_s corresponded to the mass of liquid and solid, respectively. The $\frac{m_l}{m_s}$ ratio was chosen in order to obtain viscosities of paste within the measurement range of the rheometer. Increasing quantities of HOAc (noted m_H) were introduced in water; the $\frac{m_H}{m_s}$ ratio ranged from 0 to 0.05. To prepare the pastes, we used a food processor (Kenwood) [19]. The paste was prepared at 20 °C and the total duration for preparation was 3 min 15 s sequenced as follows: 90 s of mixing at low speed, resting period for 15 s and 90 s of mixing at high speed. Thereafter, the paste was poured into a mold or a cell for rheological characterization. Fig. 1 summarizes the protocol for sample preparation.

2.2. Characterizations

Rheological measurements were carried out on the pastes using a concentric cylinder rotational viscometer (Haake – Viscotester VT550). The concentric cylinders had a gap of 2.55 mm (device MV2). The rotor had smooth walls. Shear stress, τ, versus shear rate, $\dot{\gamma}$, curves were obtained at 20 °C just after the preparation of paste. In order to describe the paste behavior, we applied Ostwald's model as described by (4) [20]:

$$\tau = K\dot{\gamma}^n \tag{4}$$

Table 1
Chemical and mineralogical composition of the calcium aluminate cement, Secar 71.

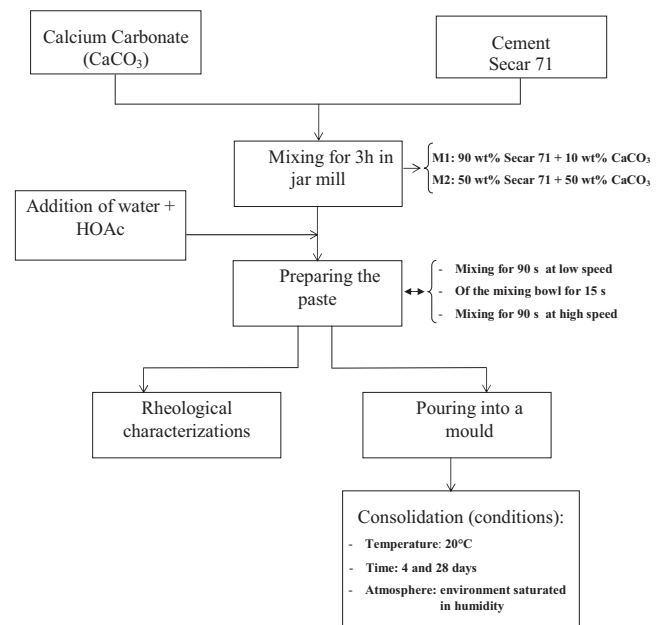| Constituent	Weight percentages%
Mineralogical phases:	
CA	56
CA_2	38
$C_{12}A_7$	<1
A	6
Oxide:	
C	28
A	72

Fig. 1. Sample preparation protocol.

where K represents the index of consistency and n is a coefficient. If n is equal to 1, lower than 1 or higher than 1, the paste behavior is Newtonian, rheofluidizing or rheothickening, respectively.

According to this model, the apparent viscosity, η, is calculated from the experimental data τ and $\dot{\gamma}$, at every point of the curve using Eq. (5):

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{K}{\dot{\gamma}^{(1-n)}} \tag{5}$$

The measurement cycle consisted of increasing $\dot{\gamma}$ from 0.1 up to 300 s^{-1} during 120 s and the slurry was left under the maximum shear rate for 60 s. $\dot{\gamma}$ was then decreased to 0.1 s^{-1} during the same duration as for the increase (120 s).

The determination of the samples density was achieved using a helium pycnometer (Micromeritics, Multivolume Pycnometer 1305 – Norcross the USA). The principle of the technique is based on the measurement of the P_1 pressure inside a gauged room and P_2 pressure in the cell containing the sample. The sample volume, V_s, is given by Mariotte's law (6):

$$V_s = V_{cell} - \frac{V_{exp}}{\frac{P_1}{P_2} - 1} \tag{6}$$

The volume of the cell, V_{cell}, and the expansion's volume, V_{exp}, are constant parameters given by the constructor. The determination of the sample's volume makes it possible to determine its density.

The identification of the hydrated phases and the detection of the crystallinity of these phases were carried out by X-rays diffraction, XRD. This technique is usually used to characterize the structural evolution of cementitious phases during the hydration [21,22]. The XRD spectra were obtained with an INEL CPS 120-Curved Position Sensitive diffractometer apparatus, using $K\alpha1$ radiation of Cu ($\lambda = 1.5406$ Å) and a curved quartz monochromator under a tension of 37.5 kV and an intensity of 28 mA. The samples were irradiated under a constant incidence angle and the diffracted beams were collected by the curved position sensitive detector [23]. The exposure time was fixed at 45 min for each sample. Crystalline