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Effect of a carboxylic acid on the rheological behavior of an aluminous cement paste and consequences on the properties of the hardened material

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Abstract

Aluminous cement pastes (Secar 71 from Lafarge) containing increasing quantities of acetic acid, HOAc, are prepared (($w_{\mathrm{HOAc}}/w_{\mathrm{cement}}$) × 100 ranges from 0 to 10%). Pastes containing HOAc present a Newtonian behavior. The best dispersion is obtained when the mass content of acid with respect to the cement is equal to 0.5%. Microstructural characterizations of samples aged for 4 days at 20 °C and 95% relative humidity reveal a significant increase in density, a reduction in porosity as well as a displacement of pore diameter towards low sizes. The open porous volume decreases with time from 25 to 9 vol.% when samples are 4 days and 6 months old, respectively. The addition of HOAc also has a beneficial effect on the flexural strength of set samples.

Keywords: Cements; Rheology; Dispersion; Acetic acid; Strength

1. Introduction

Aluminous cements are a variety of cementitous materials, primarily made up of alumina and calcium oxide. They resist aggressive environments—high acidity, bacterial attacks, high temperatures, abrasive media—because of their alkalinity related to their high alumina content.[1] Progress still needs to be made to augment the density of these materials once hardened. One way is to use organic additives. This step, which has been largely developed in the case of cements for civil engineering applications by using water reducing additives that act as dispersants,[2] has been less developed in the case of aluminous cements. Some additives that have been tested for these cements are the alkaline or alkaline-earth salts. The aim of our study is to propose an organic additive, which is able to increase to a significant extent the density of an aluminous cement. Rheological measurements on the paste have been carried out. Microstructural and mechanical characterizations of the corresponding set materials are also presented.

2. Material and methods

The starting cement is a calcium aluminate cement from Lafarge (Secar 71). Its main constituents are Al_2O_3 (69.8–72.2 wt.%) and CaO (26.8–29.2 wt.%). The initial material has a particle size that ranges between 1 and 100 μm with an average of 10 μm. For preparing the pastes, we have used a food processor (Kenwood).[3] One hundred grams of cement were mixed with distilled water containing increasing quantities of HOAc, i.e. from 0 to 10 mass% with respect to cement ($0 \leq (w_{\mathrm{HOAc}}/w_{\mathrm{cement}}) \times 100 \leq 10\%$ where w_{HOAc} and w_{cement} represent the mass of acetic acid and cement,

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respectively). 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 mould or a cell for rheological characterization. For rheological measurements, the liquids (water + acetic acid) over cement mass ratio, L/C, is constant for each tested percentage of HOAc and equal to 0.4. For the other characterizations, we used a water over cement mass ratio, W/C, equal to 0.6.[4]

Rheological measurements were carried out on the pastes using a rheometer with rotary cylinders in steady state configuration (HAAKE—Viscotester VT550 with the device of measurement MV II). This type of rheometer is most frequently used for characterizing cement pastes.[5] The fluid to be analyzed is placed between two coaxial cylinders. The experiment consists in shearing the fluid, in the annulus, between the outer cylinder, which is fixed, and the internal cylinder which has a uniform rotative movement with an angular velocity ω_0. The fluid itself breaks into cylindrical coaxial layers; each layer has an angular velocity, which varies continuously from 0 (for the layer in contact with the fixed outside cylinder) to ω_0 (for the layer in contact with the mobile interior cylinder). Due to the relative movement of the layers with respect to each other, there is a shear strain, γ, and a shear stress, τ, at every point in the paste. The protocol which has been used to characterize our cement pastes is the following:[4]

- a linear rise of $\dot{\gamma}$ from 0.1 up to 100 s^{-1}, during 30 s;
- a waiting time at the maximum value of $\dot{\gamma}$ (i.e. 100 s^{-1}) that lasts the duration of the rise to this maximum (i.e. 30 s);
- a decrease of $\dot{\gamma}$ down to 0.1 s^{-1} for the same duration as the rise (i.e. 30 s).

The microstructure of hard cement was characterized by mercury porosimetry.[6,7] The pore radius, r_p (which is assumed to be cylindrical) is given by Washburn's Eq. (1):

$$r_p = \frac{-4\nu\cos\theta}{P_{Hg}} \tag{1}$$

where P_{Hg} the mercury pressure; ν, surface tension of mercury and θ (equal to 140°), contact angle between mercury and solid phase.

The apparatus used in the present work (Autopore II Micromeritics 9200) allows the analysis of pores ranging from 0.003 to 630 μm. It is then possible to calculate the percentage of open porous volume, P, and density, ρ.

The mechanical resistance was measured by rupture under four point bending on parallepipedic samples (4 mm × 4 mm × 50 mm). Paste was cast into parallepipedic moulds immediately after mixing the components and the samples were stored at 20 °C in 95% relative humidity. For mechanical testing, we used an apparatus from J.J. Instruments S.A. (reference M30K) equipped with a cell of 100 N. The specimen is resting on two simple supports separated by a distance u. A load is applied at two points, distant of v, symmetrical with respect to the middle of the sample. Given the section, bh, of the specimen, the load, F_a, at which the sample breaks, gives the flexural strength, σ_R, as follows:

$$\sigma_R = \frac{3F_a(u-v)}{bh^2} \tag{2}$$

In the present study, u = 40 mm, v = 20 mm, b = 4 mm, and h = 4 mm. For each sample, at least five measurements are carried out; the data presented here correspond to average values.

3. Results and discussion

Fig. 1 presents typical curves for the variations of shear stress, τ, and viscosity, η, versus shear strain, $\dot{\gamma}$, in the case of pastes containing acetic acid. These measurements are done immediately after preparing the paste. It should be remembered that for cement paste without acid addition, the rheological behavior is thixotropic.[8,9] According to Fig. 1, the $\tau-\dot{\gamma}$ curves are linear and almost identical for the rising and the decreasing ramps. We did not notice any hysteresis. Lastly,

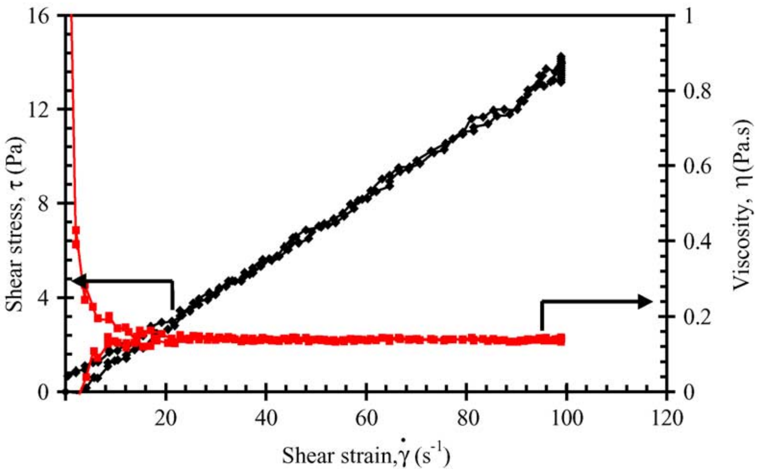

Fig. 1. Shear stress, τ, and viscosity, η, vs. shear strain, $\dot{\gamma}$. Case of a cement paste prepared with $(w_{HOAc}/w_{cement}) \times 100 = 2\%$.

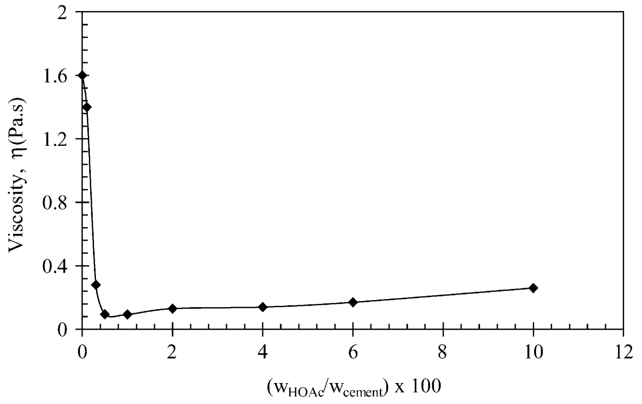

Fig. 2. Viscosity as a function of additive content ($\dot{\gamma} = 20\,\mathrm{s}^{-1}$ in each case).

when $\dot{\gamma} \geq 12\,\mathrm{s}^{-1}$, τ varies linearly as a function of $\dot{\gamma}$ and the viscosity has a constant value. In order to describe the paste behavior, we can apply Ostwald's model as described by (3):[10]

$$\tau = K\dot{\gamma}^n \tag{3}$$

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. By applying this equation to our experimental data, we find that for all the pastes containing HOAc, $n = 1$, which suggests a Newtonian behavior.

The curve plotted on Fig. 2 corresponds to η values deduced from $\tau-\dot{\gamma}$ curves of different compositions and at $\dot{\gamma} = 20\,\mathrm{s}^{-1}$, for pastes containing increasing quantities of HOAc. The highest value of viscosity (1.6 Pa s) is obtained without HOAc. Addition of admixture decreases the viscosity noticeably. η reaches a minimal value with a percentage equal to 0.5% and it increases slightly beyond this percentage. The additive content, which corresponds to the best dispersion, is the one, which gives the lowest viscosity value.[11]

Fig. 3 presents the variations of (i) the density, ρ, which takes into account the solid skeleton and the closed pores, and of (ii) the percentage of open porous volume, P, as function of additive content. After 4 days ageing, Fig. 3a indicates that P decreases from 35 to 25 vol.%, while ρ increases from 2.28 to 2.46 g cm^{-3} when the percentage of HOAc varies between 0 and 0.5%. Beyond, P and ρ show little variation. The addition of HOAc has a densifying effect on the cement. This effect is due to the dispersing character of the additive. In fact, when cement grains are mixed with water, they tend to agglomerate and form clusters as described by Aitcin.[2] This agglomeration induces a trapping of a certain volume of water inside clusters of grains ("flocs"). As soon as HOAc is added, dispersion occurs. The optimum of dispersion due to this additive (Fig. 2) and the resulting densification are obtained with 0.5% of HOAc. Densification and dispersion are linked phenomena. A good dispersion leads to a sedimentation of the cement grains in an organized way and consequently to a good densification. This results in a reduction in porosity and an increase in the density of hardened materials. For samples that are 6 months old (Fig. 3b), we notice the following phenomena: (i) for the reference sample (0% of HOAc), the porous volume has decreased and the density has increased compared to 4 days old specimens; (ii) the densities of samples containing 0.5% of HOAc or more are of the same order of magnitude as after 4 days ageing whereas the open porosity stays around 9 vol.%.

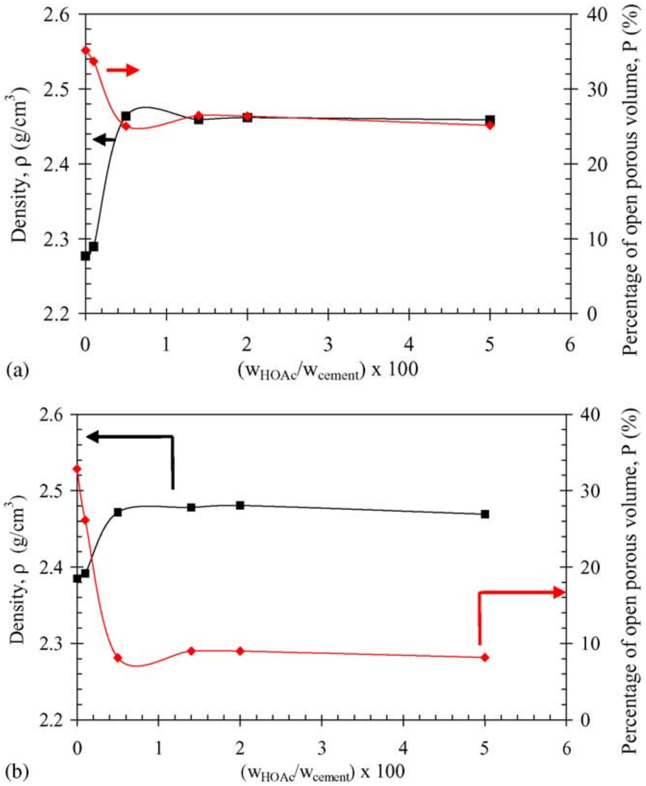

Fig. 3. Density and percentage of open porous volume for cements with increasing quantities of HOAc. The samples were kept at 20 °C and 95% relative humidity during 4 days (a) or 6 months (b).

The porous volume distribution as a function of pore size for the same samples are given on Fig. 4. After 4 days consolidation and in the absence of acetic acid, the porous volume curves present two peaks, one centered around 15 μm and the second in the vicinity of 0.03–0.04 μm. In the presence of acetic acid, the first peak moves towards lower values of pore size; we record a peak in the vicinity of 8 μm for percentages of acetic acid equal to 0.5 and 2%, then a dome around 1 μm with 5% of acid. Concerning the second peak, its position is identical whatever the percentage of acid. The existence of two populations corresponds to the presence of two kinds of pores. The largest ones are capillary pores or the vestiges of intergranular spaces in the cement paste.[12] The good dispersing effect of acetic acid has beneficial consequence on the pore size of the set material. The second pores, which have the smallest diameters, have a size, which is little affected by addition of acetic acid. They can be associated to porosity within crystallized or amorphous hydrates.[12] It is also interesting to notice that the quantity of

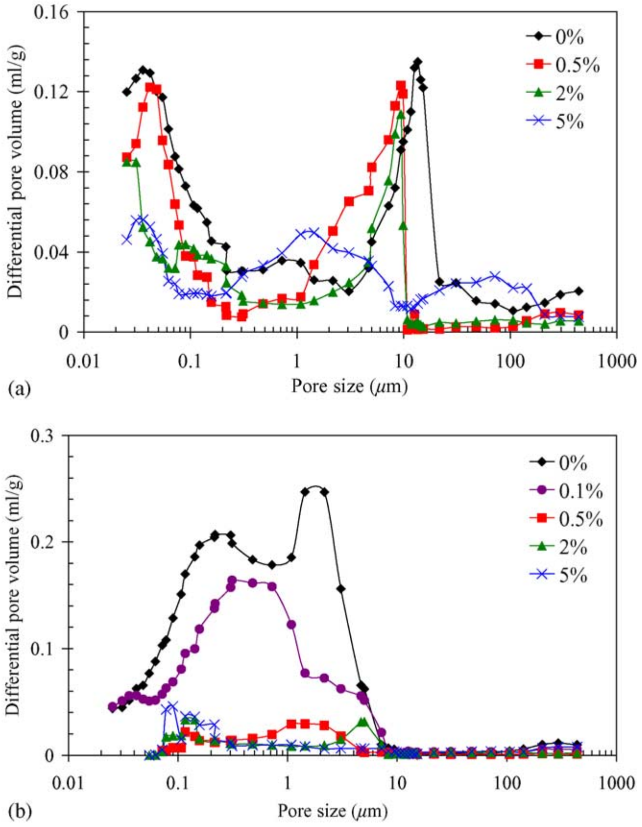

Fig. 4. Pore size distribution for cement pastes prepared with increasing mass percentages of acetic acid. The samples were kept at 20 °C and 95% relative humidity during 4 days (a) and 6 months (b).

porous volume corresponding to this second population of pores decreases appreciably when the percentage of acetic acid increases. XRD analysis on set samples prepared with increasing quantities of acetic acid have shown that less and less crystallized hydrates are formed,[3,13] which results in less porous volume. Lastly, acetic acid forms with calcium ions an hydrated calcium acetate compound that can probably fill up part of the open porous volume.[4]

After 6 months ageing the diameter of the first population of pores has moved towards lower dimensions (Fig. 4b). For percentages of HOAc larger than 0.5%, the total porous volume is about 9 vol.% whereas it is 25 vol.% for 4 days old specimens. Let us recall that the density for these samples remains quasi unchanged between 4 days and 6 months ageing. It suggests that the hydrated phases, that form with time, either calcium and aluminum hydrates or hydrated calcium acetate, fill part of the open porosity and that they have a density lower than the other components of material. The other possibility is that the hydrated phases include some pores. Whatever the valid hypothesis, the direct consequence is a decrease in the permeability of cement with time.

The last interesting set of data concerns the flexural strength for samples after 4 or 28 days ageing (Table 1). Compared to samples prepared with no addition of acetic acid, the presence of acetic acid leads to both an increase in the flexural strength and to a reduction in the standard deviation, which represents the dispersion of results between the tested specimens. In fact, in set aluminous cements, the flexural strength depends mainly on capillary porosity.[14] In the present case, the density of the samples increases with the percentage of HOAc and the porosity (size and volume of pores) decreases. This can contribute to an improvement of mechanical properties.

Table 1
Flexural strength (in MPa) at 4 days (a) and 28 days (b) for cements prepared with increasing mass percentages of HOAc and kept at 20 °C in 95% relative humidity

$(m_{\mathrm{HOAc}}/m_{\mathrm{cement}}) \times 100$ (%)	4 days	28 days
0	4.37 (± 0.47)	4.61 (± 0.5)
0.5	5.20 (± 0.22)	6.85 (± 0.33)
2	5.98 (± 0.25)	6.67 (± 0.21)
5	6.15 (± 0.33)	6.43 (± 0.16)

4. Conclusion

When acetic acid is added in an aluminous cement paste, the rheological behavior of the paste is Newtonian. Acetic acid is a good dispersant since it decreases drastically the viscosity of the suspension for very low contents. In 4 days old samples, the addition of acetic acid leads to a densification of the hardened material. In 6 months old specimens, the open porous volume has decreased to less than 9 vol.%; hydrated phases composed of calcium acetate compound have probably filled up this porosity. This has a beneficial effect on the mechanical characteristics.

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