

## Role of a Small Addition of Acetic Acid on the Setting Behavior and on the Microstructure of a Calcium Aluminate Cement

## A. Smith,<sup>†</sup> Y. El Hafiane, and J. P. Bonnet

Groupe d'Etude des Matériaux Hétérogènes (EA 3178), Ecole Nationale Supérieure de Céramique Industrielle, 87065 Limoges cedex, France

## P. Quintard

Science des Procédés Céramiques et Traitements de Surface (UMR CNRS 6638), Faculté des Sciences, 87065 Limoges cedex, France

#### B. Tanouti

Laboratoire de Chimie du Solide Minéral, Faculté des Sciences Semlalia, 40000 Marrakech, Morocco

In order to be able to monitor dispersion and setting of cements, admixtures can be added, which usually can consist of large organic molecules. Here, the choice is different since small organic molecules have been used as in ceramic processing. This work concerns the preparation of calcium aluminate cement paste in the presence of acetic acid; the water to cement mass ratio is equal to 0.6 and the acid to cement mass ratio,  $m_{\rm HOAc}/m_{\rm cement}$ , ranges between 0 and 0.05. This admixture can have either a retarding or an accelerating effect on cement setting. The retarding effect is because of adsorption of acetate complexes,  $CaCH_3CO_2^+$  positively charged, at the surface of CA particles, negatively charged, which leads to the delay (slowing down) of dissolution; it can reach 52 h (case of  $m_{\text{HOAc}}/m_{\text{cement}} = 0.005$ ). When  $m_{\rm HOAc}/m_{\rm cement} \ge 0.01$ , there is a remarkable accelerating effect. The setting starts 2 h after mixing the cement with the liquid and is fairly constant for higher acetic acid contents. This rapid setting in acid conditions is because of the formation of hydrated calcium acetate in very low quantities and possibly gibbsite; the setting mechanism is quite different since there is no formation of conventional calcium and aluminum hydrates. As an example, with the highest amount of HOAc  $(m_{HOAc}/m_{HOAc})$  $m_{\text{cement}} = 0.05$ ), no C<sub>x</sub>A<sub>y</sub>H<sub>z</sub> type of calcium aluminum hydrate is formed after aging for 4 days at 20°C and 95% relative humidity. There is also a densifying effect of acetic acid; the open porosity of set samples left to age for 4 days at 20°C and 95% relative humidity decreases from 35 to 25 vol% when  $m_{\rm HOAc}/m_{\rm cement}$  goes from 0 to 0.005 and remains relatively constant afterwards. Lastly, this decrease in the porosity continues with aging time; at 6 months, we obtain values as low as 9 vol% in samples where  $m_{\text{HOAc}}/m_{\text{cement}} \ge 0.005$ .

### I. Introduction

CALCIUM aluminate cements (CACs) are a variety of hydraulic binders that find applications where their resistance to chemical attack, to abrasion, or impact is needed. They have also been essential in the successful development of refractory castables or monolithics.<sup>1</sup> These cements consist of aluminate phases, mostly monocalcium aluminate CaAl<sub>2</sub>O<sub>4</sub> (CA<sup>‡</sup>). CACs are believed to hydrate through a dissolution followed by a precipitation process as shown by several studies.<sup>2–5</sup> Admixtures are used to modify the properties of CAC-based mortars and concretes. These typically modify the rate of dissolution of the anhydrous cement phases and/or the rate of precipitation of the hydrates. They can also lead to the precipitation of new phases. Additives can either have a retarding or an accelerating effect on cement setting. The setting time is usually studied either by calorimetric measurements or by a Vicat needle. Fundamental studies on the mechanisms were carried out on diluted solutions (typically, a water to cement weight ratio of 10). Several authors considered that the pH of admixture is the most important factor controlling the kinetics of setting time.<sup>6</sup> Others think that it is the role of the cation-anion couple of the additive that is most important.<sup>7</sup> According to the chemical nature and the concentration of these ions, the effect can be an acceleration or a retardation of setting time. Indeed, if the effects of the cation and the anion are similar (both accelerators or both retarders), this amplifies the trend: stronger acceleration or greater retardation. In contrast, if the effects are opposed, the evolution depends on which has the greatest influence. Furthermore, the intensity of the ion effects can change with the admixture concentration.<sup>8</sup> Lastly, for the same cation, its behavior can change according to the anion considered. For example, Currell et al.<sup>7</sup> show that the setting time follows a different order for potassium and lithium salts: (i) lithium salts: NO<sub>3</sub><sup>-</sup><OH<sup>-</sup><Cl<sup>-</sup>; (ii) potassium salts:  $Cl^- < OH^- < NO_3^-$ . Admixtures reported in the literature are usually inorganic compounds.<sup>3-10</sup> This paper concerns the specific and remarkable effect of an organic additive, namely acetic acid, on the setting time of the paste and on the microstructure of the set product. The results presented here concern the characterization of the paste and data collected on set samples.

### **II. Experimental Procedure**

#### (1) Starting Materials

The anhydrous cement is a CAC (Secar 71 from Lafarge, Paris, France). 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. Particles larger than 40 µm have been eliminated by sieving in this study. This material is kept at 20°C in a dry atmosphere before being used. The acetic acid is from PROLABO (Paris, France, 90 vol%).

### (2) Preparation of Pastes and Suspensions

The pastes were prepared with a water to cement ratio,  $m_{\text{water}}/m_{\text{cement}}$ , equal to 0.6;  $m_{\text{water}}$  and  $m_{\text{cement}}$  correspond to the mass of water and cement, respectively. Increasing quantities

H. Jennings-contributing editor

Manuscript No. 20263. Received May 16, 2003; approved March 4, 2005. <sup>†</sup>Author to whom correspondence should be addressed. e-mail: a\_smith@ensci.fr <sup>‡</sup>Cement chemistry nomenclature.

of HOAc (noted  $m_{\text{HOAc}}$ ) were introduced in water; the  $m_{\text{HOAc}}/m_{\text{cement}}$  ratio was varied from 0 to 0.05. Liquid was extracted by centrifugation from these slurries 1 h after mixing the constituents (apparatus: HERMELE, model Z 383, Wehingen, Germany). The conditions for centrifugation were the following: 8000 rotations per minute (rpm) for 10 min. The pH of these extracted solutions was measured, and their aluminum and calcium contents were analyzed by the inductive coupled plasma technique (IRIS, Thermo Jarrell Ash Corporation, Franklin, MA).

For electrokinetic sonic amplitude (ESA) measurements, the standard procedure for preparing suspensions was applied; it involved mixing  $m_{\text{cement}} = 20$  g with  $m_{\text{water}} = 200$  g of deionized water at 20°C. This water contained increasing quantities of acetic acid.

#### (3) Characterizations

The Vicat test was used to assess the beginning of hardening for the different pastes.<sup>11</sup> In the following, this time will be referred as the "setting time." X-ray diffraction (XRD) was carried out with an INEL CPS 120-Curved Position Sensitive diffractometer apparatus (Artenay, France). For each sample, the acquisition time was 45 min. Density values were deduced from helium pyconometry measurements (Micromeritics, Multivolume Pycnometer 1305, Norcross, GA). Thermal analysis was carried out with a DTA-TG-coupled Rigaku thermoflex (Tokyo, Japan); each experiment was conducted on 50 mg of the product under dry nitrogen with a heating ramp of 10°C/min. The reference material was a calcined alumina from PROLABO. Scanning electron microscopy (SEM) was used to determine the microstructure of hardened material (Scanning electron microscope: reference Hitachi SC 2500 Elex-Science, Verrieres-le-Buisson, France). Raman characterization on set samples was carried out with a spectrometer from Spectra-Physics (model 2017, Lille, France). Electrokinetic measurements provide information on the particle charges. This technique is based upon an electroacoustic effect that occurs when an alternative electric field of high frequency (1 MHz) is applied between two electrodes immersed in a suspension of charged particles. The application of the electric field leads to a periodic deformation of the distribution of the mobile charges of the electric double layer of each particle and creates a sonic wave of the same frequency as the applied electric field. The amplitude of this sonic wave is called the ESA. The signal ESA is detected with a piezoelectric sensor that delivers an electric signal proportional to the amplitude of the measured sonic wave. It is a function of the moved charges and can be connected to the  $\zeta$  potential,  $\xi^{12}$ :

$$\xi = \frac{\eta \text{ESA}(\omega)}{c\epsilon\phi\Delta\rho G(\alpha)} \tag{1}$$

where  $\omega$  is the angular frequency of the applied field,  $\eta$  the viscosity of the liquid, *c* the velocity of sound in the suspension,  $\varepsilon$  the dielectric permittivity of the suspension,  $\phi$  the volume fraction of the particles,  $\Delta \rho$  the difference of density between the particles and the liquid, and  $G(\alpha)$  is a term that corrects for the inertia of the particle in the alternating field that acts to reduce the velocity amplitude of the particle motion for a given  $\zeta$  potential.  $G(\alpha)$  is dependent on  $\omega$ , the particle radius, and the kinematic viscosity of the liquid.

The suspensions were characterized using an ESA measurement apparatus (Model ESA8000, Matec, Northborough, MA).

#### III. Results

The results of the Vicat test are presented in Fig. 1, together with the pH variations of the aqueous solution extracted by centrifugation. For the cement prepared with no HOAc, the setting time was 6 h. For  $m_{\text{HOAc}}/m_{\text{cement}} = 0.001, 0.005$ , and 0.008, the setting time was very long (43, 52, and 50 h, respectively). HOAc has a retarding effect on setting time when the pH is alkaline. Between  $m_{\text{HOAc}}/m_{\text{cement}} = 0.008$  and 0.01, the setting time drops



**Fig. 1.** Influence of HOAc addition  $(0 \le m_{\text{HOAc}}/m_{\text{cement}} \le 0.05)$  on setting time ( $\blacksquare$ ) and pH ( $\blacklozenge$ ). The reported values were measured on the extracted solution of paste where  $m_{\text{water}}/m_{\text{cement}} = 0.6$  ( $T = 20^{\circ}$ C; 95% relative humidity).

to 2 h, and the pH of the centrifuged solution decreases from 8.9 to 5.6. Lastly, for  $m_{\text{HOAc}}/m_{\text{cement}}$  ranging between 0.01 and 0.05, the setting time is stabilized between 2 and 3 h and the pH of the extracted solution remains acidic and goes from 5.6 to 4.8.

The molar concentrations of calcium and aluminum in the extracted liquid, measured by ICP, are given in Fig. 2. When  $m_{\rm HOAc}/m_{\rm cement} \leq 0.008$ , the Al content is very low compared with the reference sample (i.e. paste prepared with no addition of HOAc), and it increases as soon as  $m_{\rm HOAc}/m_{\rm cement} \geq 0.01$ . The concentration of Ca increases regularly from  $1.3 \times 10^{-3}$  to 0.25 mol/L as  $m_{\rm HOAc}/m_{\rm cement}$  goes from 0.001 to 0.05. The Al/Ca ratio is equal to 1.67 for the reference sample. This ratio has very low values as long as  $m_{\rm HOAc}/m_{\rm cement} \leq 0.008$ . When  $0.01 \leq m_{\rm HOAc}/m_{\rm cement} \leq 0.05$ , the Al/Ca ratio increases but is always lower than that in the reference sample. The pH of the extracted solution in this  $m_{\rm HOAc}/m_{\rm cement}$  range is acidic (Fig. 1).

Figure 3 shows the XRD results on hardened cements kept for 4 days (Fig. 3(a)) and 6 months (Fig. 3(b)) at 20°C in 95% relative humidity. For each  $m_{\text{HOAc}}/m_{\text{cement}}$  ratio, Tables I and II indicate the percentage of intensity of the most intense peak for the crystalline phases present in the hardened material. For each crystalline phase, there is a peak that corresponds to the highest intensity in the JCPDS cards; this peak is called "the most intense diffraction peak." Although no direct quantitative correlation can be made between the quantity of each crystalline phase and the data in Tables I and II, these numbers are indicators of the evolution of each phase with the addition of acetic acid. After aging for 4 days, the crystalline hydrated phases that have the most intense peaks are, in the case of the reference sample ( $m_{\text{HOAc}}/m_{\text{cement}} = 0$ ), CAH<sub>10</sub> (CaAl<sub>2</sub>O<sub>4</sub> · 10H<sub>2</sub>O) and C<sub>2</sub>AH<sub>8</sub> (Ca<sub>2</sub>Al<sub>2</sub>O<sub>5</sub> · 8H<sub>2</sub>O); AH<sub>3</sub> · (Al(OH)<sub>3</sub>) is also detected.



**Fig. 2.** Molar concentrations of aluminum ( $\blacktriangle$ ) and calcium ( $\blacksquare$ ) species as well as the aluminum over calcium ratio ( $\blacklozenge$ ) in the solutions extracted by centrifugation as a function of  $m_{\text{HOAc}}/m_{\text{cement}}$  ratio in the paste.



**Fig. 3.** X-ray diffraction spectra on set samples for different  $m_{\text{HOAc}}/m_{\text{cement}}$  ratios (0, 0.001, 0.005, 0.02, and 0.05). (a) Four-day-old samples; (b) 6-month-old samples (aging conditions: 20°C, 95% relative humidity).

Only small quantities of CA are left compared with the anhydrous cement. When HOAc is added,  $C_2AH_8$  forms preferentially to CAH<sub>10</sub> (case of  $m_{HOAc}/m_{cement} = 0.001$  and 0.005). For  $m_{HOAc}/m_{cement} = 0.02$ , the only crystalline calcium and aluminum hydrate that is detected is  $C_2AH_8$ . No crystalline hydrates are detected for the highest  $m_{HOAc}/m_{cement}$  ratio. We also notice that for increasing quantities of HOAc, the value of the intensity of the most intense peak for CA increases. It suggests that the amount of CA that dissolves diminishes when  $m_{HOAc}/m_{cement}$ rises. Lastly, for  $m_{HOAc}/m_{cement} = 0.05$ , a new phase appears; it is a crystalline hydrated calcium acetate,  $C_4H_6CaO_4.H_2O$  (noted

 

 Table I.
 Intensities of the Most Intensive Diffraction Peaks for the Crystalline Phases in the Slurries Prepared with Increasing Quantities of HOAc and also for the Starting Anhydrous Material

$m_{\rm HOAc}/m_{\rm cement}$	CAH <sub>10</sub>	C <sub>2</sub> AH <sub>8</sub>	C <sub>3</sub> AH <sub>6</sub>	AH <sub>3</sub>	CA	CA <sub>2</sub>	$\begin{array}{c} C_4H_6CaO_4 \cdot \\ H_2O \end{array}$
0	100	92		12	4	55	_
0.001	44	100		27	26	58	
0.005	19	100		17	70	92	
0.02		27		10	100	67	
0.05					100	69	5
Anhydrous					100	36	
cement							

Case of samples after 4 days of storage at 20°C and 95% relative humidity

 Table II.
 Intensities of the Most Intensive Diffraction Peaks

 for the Crystalline Phases in Slurries Prepared with Increasing
 Quantities of HOAc

$m_{ m HOAc}/m_{ m cement}$	CAH <sub>10</sub>	C <sub>2</sub> AH <sub>8</sub>	C <sub>3</sub> AH <sub>6</sub>	AH <sub>3</sub>	CA	CA <sub>2</sub>	$\begin{array}{c} C_4H_6CaO_4 \cdot \\ H_2O \end{array}$
0			68	100			
0.001	73	13	32	100		20	
0.005	72	20	26	38	88	100	
0.02		17	25	26	100	70	
0.05				8	100	70	3

Case of samples aged for 6 Months at 20°C and 95% relative humidity

Ca(OAc)<sub>2</sub>.H<sub>2</sub>O). When  $m_{\text{HOAc}}/m_{\text{cement}} > 0.001$ , it can also be pointed out that when the amount of HOAc increases, the intensity of the most intense peak for AH<sub>3</sub> progressively decreases when the amount of HOAc increases. This intensity is equal to 0 for  $m_{\text{HOAc}}/m_{\text{cement}} = 0.05$ , which suggests that very few crystals of AH<sub>3</sub> are formed or that AH<sub>3</sub> is amorphous.

For the 6-month-old sample, prepared with no addition of HOAc, CA and CA<sub>2</sub> disappeared and  $C_3AH_6 \cdot (Ca_3Al_2(OH)_{12})$ and AH3 were present; crystalline CAH10 and C2AH8 were not detected. For retarding percentages of HOAc ( $m_{\rm HOAc}/m_{\rm cement} = 0.001$  and 0.005), CAH<sub>10</sub> and C<sub>2</sub>AH<sub>8</sub> were present, together with C<sub>3</sub>AH<sub>6</sub> and AH<sub>3</sub>. When  $m_{\text{HOAc}}/m_{\text{cement}} = 0.02$ , there was no peak characteristic of CAH<sub>10</sub>, as already seen in 4day-old specimens. Compared with the 4-day-old samples, for these three percentages of HOAc, a decrease in the intensity of  $C_2AH_8$  peaks, a substantial increase of  $AH_3$  peaks, and the existence of C<sub>3</sub>AH<sub>6</sub> were noted. For  $m_{\rm HOAc}/m_{\rm cement} = 0.05$ , no crystallized calcium aluminate hydrate was present and the only crystallized hydrated phases were AH<sub>3</sub> and Ca(OAc)<sub>2</sub>  $\cdot$  H<sub>2</sub>O. Concerning the peak intensities for CA and CA<sub>2</sub> in samples that contained an accelerating percentage of HOAc (2% and 5%), there was no significant variation between 4-day and 6-month aging.

Figure 4 presents the density,  $\rho$ , and the percentage of open porous volume, P, in the samples left to age for 4 days (Fig. 4(a)) and 6 months (Fig. 4(b)) after mixing the constituents and increasing  $m_{\rm HOAc}/m_{\rm cement}$  ratios. For the 4-day-old samples, P decreased from 35 to 25 vol% and  $\rho$  increased from 2.27 to 2.46 g/ cm<sup>3</sup> when  $m_{\rm HOAc}/m_{\rm cement}$  changed from 0 to 0.005. Acetic acid acts as a good dispersant, and the consequence was a densifying effect accompanied by the closure of the porosity. Beyond this, P and  $\rho$  showed little variations. The SEM micrographs carried out on two fractured samples among those used for the study of the variations of the density and the porosity at 4 days of conservation, namely a reference sample  $(m_{\rm HOAc}/m_{\rm cement}=0)$  and another with  $m_{\rm HOAc}/m_{\rm cement}$  > 0.005 (Fig. 5), illustrate this densifying effect of HOAc. In Fig. 5(a), micrometer-size pores can be seen. In Fig. 5(b), these large pores are not present. After 6 months of aging, the following comments can be made: (i) for the reference sample, the open porous volume and the density had slightly decreased and increased, respectively; (ii) the density of the other samples were similar to those of 4-day-old specimens, but there was a drastic drop in the open porous volume since it was below 9 vol%.

#### IV. Discussion

#### (1) Surface Charge of Aluminous Cement Particles

Since the surfaces of particles are involved in the hydration mechanisms of CACs,<sup>2</sup> the sign of the surface charge of starting cement particles can be estimated. Two approaches can be considered: the first one is based on a statistical representation of the charges on the surface of the grains and the second one considers the charges of crystalline planes likely to be present at the surfaces of the cement grains.



**Fig. 4.** Density,  $\rho$  (in g/cm<sup>3</sup>; symbol:  $\blacksquare$ ), and percentage of open porous volume, *P* (in %; symbol:  $\blacklozenge$ ), for different  $m_{\text{HOAc}}/m_{\text{cement}}$  ratios in samples prepared with  $m_{\text{water}}/m_{\text{cement}} = 0.6$ . (a) Four day-old samples; (b) 6-month-old samples (aging conditions: 20°C, 95% relative humidity).

For the first approach, Bombled<sup>13</sup> proposed an estimation of the electric state of the surface in the case of the major component of Portland cement, namely  $3CaO \cdot SiO_2$  (Fig. 6(a)). By denoting  $\sigma^+$  and  $\sigma^-$  as the surface charges of the positive and negative sites, for this component (2), it yields:

$$\frac{\sigma^{+}}{\sigma^{-}} = \frac{3(Ca^{2+})_{\text{surface projection}} + (Si^{4+})_{\text{surface projection}}}{5(O^{2-})_{\text{surface projection}}}$$
(2)



**Fig. 6.** Statistical representation of the distribution of the surface charges for an anhydrous grain of  $3\text{CaO} \cdot \text{SiO}_2^{13}$  (a) and  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  (b).

where  $(Ca^{2+})_{surface projection}$ ,  $(Si^{4+})_{surface projection}$ , and  $(O^{2-})_{surface projection}$  are equal to  $\pi r_{ion}^2$  and where  $r_{ion}$  is the ionic radius associated with each ion. Knowing the ionic radius of each element, namely 1.35 Å for oxygen, 1.05 Å for calcium, and 0.4 Å for silicon, it can be calculated that  $\sigma^+/\sigma^-$  is equal to 0.35. Bombled thus showed that there are three times fewer positive sites than negative sites. By applying this approach to CA (Fig. 6(b)), relation (2) becomes (3):

$$\frac{\sigma^{+}}{\sigma^{-}} = \frac{(Ca^{2+})_{\text{surface projection}} + 2(Al^{3+})_{\text{surface projection}}}{4(O^{2-})_{\text{surface projection}}}$$
(3)

Knowing the ionic radius of aluminum (0.5 Å),  $\sigma^+/\sigma^-$  is equal to 0.22. This means that the negative sites are dominant and that the surface of the anhydrous CA grains is consequently negatively charged. A similar calculation for CA<sub>2</sub>, a minor phase in aluminous cements, leads to  $\sigma^+/\sigma^- = 0.166$ . The surface of CA<sub>2</sub> would also be negatively charged.

Although this approach gives interesting results, it is somewhat too simplistic because it assumes that all surfaces have the same atomic arrangement and that the surface of the grains has the same chemical composition as the bulk. However, based on crystal growth consideration,<sup>14,15</sup> surfaces are regions that do not necessarily have the some composition as the bulk and are made of crystallographic planes of different natures. In order to predict which planes are most likely to be present at the surface, one can apply the Bravais, Friedel, Donnay, or Harker approach<sup>15</sup> to determine the equilibrium forms of crystals. One such approach was applied to predict the crystallization of



**Fig.5.** Scanning electron micrographs (a) of a reference sample  $(m_{\text{HOAc}}/m_{\text{cement}} = 0)$  and (b) of a sample prepared with a ratio  $m_{\text{HOAc}}/m_{\text{cement}} = 0.02$  (aging conditions: 4 days, 20°C, 95% relative humidity). The arrows in (a) indicate the micro-size pores.

Table III. Sign of the Electrical Charge of the Most Probable Surface Planes in CA

(hkl) plane	$d_{hkl}$ (Å)	Number of Ca	Number of Al	Number of O	Total charge	Surface area $(\text{\AA}^2)^{(*)}$	Charge per surface area $(\text{\AA}^{-2})$
(011)	7.170	4	0	9	-10	149.82	-0.066
(110)	5.926	0	0	10	-20	180.66	-0.110
(012)	5.540	2	2	11	-12	96.57	-0.124
$(11\overline{1})$	5.522	0	0	2	-4	96.98	-0.041

\*, area of plane in the unit cell

another hydraulic binder, namely gypsum, from a suspension of calcium sulfate hemihydrate.<sup>16</sup> In this approach, the most probable surface planes are those where inter-atomic spacing,  $d_{hkl}$ , is the greatest. In the case of CA particles, it has been assumed from crystallographic data<sup>17</sup> that the most probable surface planes are (011), (110), (012), and (111). From the reduced coordinates of each atom in the unit cell—which contains 12 CA motifs—and knowing the space group for CA ( $P2_1/n$ ),<sup>18</sup> it is possible to calculate the reduced coordinates for each element in the unit cell. The chemical composition of these four crystallographic planes, the total charge, and the charge per unit area can be estimated. These calculations assume that the chemical bond is mostly ionic and that each plane is stoichoimetric. The results are presented in Table III. The most interesting information from these data is the sign of the planes. It appears that the planes are all negatively charged. Therefore, CA particles are considered as having a strong affinity for positive species.

## (2) Retarding Action of HOAc: Case of $m_{\rm HOAc}/m_{\rm cement} \leq 0.008$

The action of organic retarders has been well studied in the case of Portland cement when mixed with glucose, carboxylic acids, or lignosulfonates.<sup>19,20</sup> The authors suggest that calcium is trapped in the form of complex molecules where  $Ca^{2+}$  is involved. In some cases, these complexes adsorb at the surface of cement particles and hinder the dissolution mechanism. In other cases, the retarders cause poisoning of the germs of hydrates and delay the precipitation reaction.

In the presence of acetic acid, calcium can form with acetates,  $OAc^-$ , calcium acetate complexes,  $CaCH_3CO_2^+$  (or  $CaOAc^+$ ), according to reaction:

$$Ca^{2+} + OAc^{-} \rightleftharpoons CaOAc^{+}$$
 (4)

An equilibrium constant associated to (4) has been defined for dilute solutions and is equal to:

$$K_{\rm c} = \frac{[{\rm CaOAc}^+]}{[{\rm Ca}^{2+}][{\rm OAc}^-]} = 10^{0.8}$$
(5)

Acetic acid is a weak acid with an acidity constant equal to  $K_{\rm A} = 10^{-4.8}$ .<sup>21</sup> In an alkaline solution, the concentration of CaCH<sub>3</sub>CO<sub>2</sub><sup>+</sup> must be significant.

Given the experimental results on cement pastes when HOAc is present, and also the prediction of affinity of anhydrous cement grains for positively charged species as well as the chemical nature of the ions that exist in the solution, an explanation for the very long setting time can be proposed. It could be because of a delay (slowing down) of CA dissolution because of the adsorption of CaCH<sub>3</sub>CO<sub>2</sub><sup>+</sup> at the surface of negatively charged CA crystal grains. ESA measurements on dilute cement suspensions justify this hypothesis (Fig. 7). These data permit the variations of surface charge to be followed. It should be kept in mind that the surface charge comes from the interaction between solid particles and the solution. Before the addition of HOAc, the ESA signal is equal to  $0.58 \text{ mPa} \cdot \text{m/V}$ , which corresponds to a positive surface charge, which may arise from the adsorption of protons on CA particles. When HOAc is added in the suspension, the calcium acetate complexes, which are positively charged, can adsorb at the surface of anhydrous grains. Ca- $OAc^+$  is a monovalent ion whose size is larger than that of  $H_3O^+$ . Because of this difference in size, less CaOAc<sup>+</sup> than  $H_3O^+$  can adsorb at the surface of CA grains, which may result in a lower capability to neutralize the negatively charged surface of these particles. This may explain the drop in the ESA value to  $m_{\rm HOAc}/m_{\rm cement} = 0.005$  (Fig. 7). This HOAc content is also the value where the setting time is the longest (Fig. 1). The consequence of this adsorption, which has been evidenced by ESA measurements, is a delay in setting of the paste.

Concerning the concentration of aluminum ions, it is observed that it is very low in the solution (Fig. 2) and that crystalline gibbsite is detected by XRD (Fig. 3). It suggests that when aluminum precipitates, it is in the form of AH<sub>3</sub>. The combination between delayed calcium dissolution and AH<sub>3</sub> precipitation means that the quantities of calcium and aluminum ions available for forming calcium and aluminum hydrates are probably very small, and thus the consequence is a very long setting time (Fig. 1). Lastly, it can be seen that when a retarding percentage of HOAc is present, the major hydrate that forms is  $C_2AH_8$ , probably because some aluminum is precipitated in the form of AH<sub>3</sub> and not available to precipitate CAH<sub>10</sub>.

# (3) Acceleration Action of HOAc: Case of $m_{HOAc}/m_{cement} \ge 0.01$

The products responsible for an acceleration in the setting time have been studied in the literature. For Portland cements, they are hydroxides, alkaline magnesium or zinc salts, carbonates, fluorides, and borides. These additives can accelerate the precipitation of hydrates or participate in the formation of new phases.<sup>22,23</sup> For a CAC, there is no information concerning the accelerating effect of acetic acid on the setting time.

When increasing amounts of acetic acid are added  $(m_{\text{HOAc}}/m_{\text{cement}}$  from 0.01 to 0.05), the quantities of calcium and aluminum in solution increase regularly (Fig. 2). XRD data on samples prepared with  $m_{\text{HOAc}}/m_{\text{cement}} = 0.05$  show that some calcium ions are also in the form of hydrated calcium acetate Ca(OAc)<sub>2</sub> · H<sub>2</sub>O. Raman spectra on the same samples show that there is a band at 1070 cm<sup>-1</sup>, which is characteristic of the interaction between surfaces of CAC particles and acetate groups (Fig. 8).<sup>24</sup> The interaction, probably via Ca(OAc)<sub>2</sub> · H<sub>2</sub>O particles, may ensure an efficient adhesion between the grains in a very short and fairly constant time, typically 2 h (Fig. 1).



2083

Fig. 7. Electrokinetic sonic amplitude values as a function of  $m_{\text{HOAc}}/m_{\text{cement}}$  ratio for cement suspensions ( $m_{\text{cement}} = 20 \text{ g}, m_{\text{water}} = 200 \text{ g}$ ).  $T = 20^{\circ}$ C.



Fig. 8. Raman spectra for the following cases: (a) cement prepared with  $m_{\rm HOAc}/m_{\rm cement} = 0.05$  and (b) calcium acetate (4-day-old sample stored at 20°C, 95% relative humidity).

With respect to alumina, it could still precipitate under the form of AH<sub>3</sub> in this pH range (pH 4.6–5.8, Fig. 1).<sup>25</sup> These particles, which are probably very small initially, can also participate in the adhesion of cement grains. They would grow with time to give crystalline AH<sub>3</sub> (Fig. 3). The last striking experimental fact is the absence of crystalline calcium and aluminum hydrate for the highest  $m_{\rm HOAc}/m_{\rm cement}$  content, in both the 4day- and 6-month-old specimens (Fig. 3 and Tables I and II). Together, these results indicate that the setting of the cement proceeds through a novel mechanism in which both hydrated calcium acetate and possibly gibbsite are involved, and where no calcium aluminate hydrates are formed. This has a beneficial effect on the microstructure. As observed in Fig. 4, the closure of the open porosity with time could be because of its filling up with these two compounds.<sup>2</sup>

#### V. Conclusion

This paper has presented results concerned with the effect of small additions of acetic acid on setting. This acid can either have a retarding or accelerating effect on the setting of a CAC. The hypothesis that can be made is that the retarding effect of HOAc could be because of the adsorption of cationic species, such as calcium acetate complex CaOAc<sup>+</sup>, at the surface of calcium aluminate particles; this delays the dissolution reaction. This proposed mechanism would be valid when the acetic acid over cement mass ratio is less than 0.01. The setting time can reach up to 52 h (case of  $m_{\rm HOAc}/m_{\rm cement} = 0.005$ ). The accelerating effect has been interpreted by the rapid consolidation of the cement particles with calcium acetates Ca(OAc)<sub>2</sub> · H<sub>2</sub>O and possibly AH<sub>3</sub>. In this case, the setting time is relatively constant and equal to 2 h. We have also noticed that the addition of HOAc has a densifying effect on the cement. For 4-day-old samples left to age at 20°C and 95% relative humidity, simultaneously, porosity decreases from 35 to 25 vol% and density rises from 2.27 to 2.46 g/cm<sup>3</sup> when  $0 \le m_{\text{HOAc}}/m_{\text{cement}} \le 0.005$ . Beyond this, porosity and density show little variations. After 6 months of aging in the same conditions, when  $m_{\rm HOAc}/m_{\rm cement} \ge 0.005$ , there is a spectacular decrease of porosity compared with 4-day-old samples since porosity is of the order of 9 vol%. It means that permeability has decreased with time.

#### Acknowledgment

The authors would like to thank Lafarge Aluminates for supplying the raw materials.

#### References

<sup>1</sup>K. L. Scrivener, "Historical and Present Day Applications of Calcium Aluminate Cements"; pp. 3-23 in Calcium Aluminate Cements 2001, Edited by R. J. Mangabhai and F. P. Glasser. The University Press, Cambridge, 2001.

<sup>2</sup>P. Barret, D. Ménétrier, and D. Bertrandie, "Contribution to the Study of the Kinetic Mechanism of Aluminous Cement Setting I: Latent Periods in Heterogeneous and Homogeneous Milieus and the Absence of Heterogeneous Nucleation,' Cement Concrete Res., 4, 545-56 (1974).

<sup>3</sup>P. Barret, D. Ménétrier, and D. Bertrandie, "Contribution to the Study of the Kinetic Mechanism of Aluminous Cement Setting II: Release of the Factor Responsible for Breaking the Latent Period by the Dissolution of a Fraction of the Initial Cement," Cement Concrete Res., 4, 723-33 (1974).

4S. P. Jiang, J. C. Mutin, and A. Nonat, "Studies on Mechanisms and Physico-Chemical Parameters at the Origin of the Cement Setting I: The Fundamental Processes Involved During the Cement Setting," Cement Concrete Res., 25, 779-89 (1995).

<sup>5</sup>A. Smith, T. Chotard, N. Gimet-Bréard, and D. Fargeot, "Correlation Between Hydration Mechanism and Ultrasonic Measurements in an Aluminous Cement: Effect of Setting Time and Temperature on the Early Hydration," J. Eur. Ceram. Soc., 22, 1947–58 (2002).

<sup>6</sup>T. Novinson and J. Crahan, "Lithium Salts as Set Accelerators for Refractory Concretes: Correlation of Chemical Properties with Setting Times," ACI. Mater. J., 12–9 (1990).

<sup>7</sup>B. R. Currell, R. Grzeskowiak, H. G. Midgley, and J. R. Parsonage, "Acceleration and Retardation of Set High Alumina Cement by Additives," Cement Concrete Res., 17, 420-8 (1987).

<sup>8</sup>D. Damidot, A. Rettel, and A. Capmas, "Action of Admixtures on Fondu Cement: Part 1 Lithium and Sodium Salts Compared," Adv. Cement Res., 8 [31] 111-9 (1996).

<sup>9</sup>J. D. Cox and J. H. Sharp, "The Early Hydration of a Refractory Calcium Aluminate Cement in the Presence of Sodium Carbonate"; pp. 249-6 in Calcium Aluminate Cements 2001, Edited by R. J. Mangabhai and F. P. Glasser. The University Press, Cambridge, 2001.

<sup>10</sup>J. A. Stegemann and N. R. Buenfeld, "Neural Network Prediction of Setting of Calcium Aluminate"; pp. 267–79 in *Calcium Aluminate Cements 2001*, Edited by R. J. Mangabhai and F. P. Glasser. The University Press, Cambridge, 2001.

A. M. Neville, Properties of Concrete. Longman, London, pp. 49-51, 1995.

<sup>12</sup>C. Pagnoux, T. Chartier, M. F. Granja, F. Doreau, J. M. Ferreira, and J. F. Baumard, "Aqueous Suspensions for Tape-Casting Based on Acrylic Binders,"

 J. Eur. Ceram. Soc., 18, 241–7 (1998).
 <sup>13</sup>J. P. Bombled, "Rhéologie des mortiers et des bétons frais; Influence du facteur ciment," Proc. R.I.L.E.M. Leeds Sem., 1 [Sujet 3] 1–169 (1973). <sup>14</sup>K. Sangwal and R. Rodriguez-Clemente, "Review of Crystal Growth Proc-

esses"; pp. 11-38 in Surface Morphology of Crystalline Solids. Trans Tech Publications, Brookfield, VT, 1991. <sup>15</sup>P. Hartman (ed.), *Crystal Growth: An Introduction*; pp. 367–402. North Hol-

land Pub. Co., Amsterdam, 1973

<sup>16</sup>E. Badens, S. Veesler, and R. Boistelle, "Crystallization of Gypsum from Hemihydrate in Presence of Additives," J. Cryst. Growth, 198/199, 704-9 (1999).

<sup>17</sup>P. J. Baldock, A. Parker, and I. Sladdin, "X-Ray Powder Diffraction Data for Calcium Monoaluminate and Calcium Dialuminate," J. Appl. Crystallogr., 3, 188-91 (1970).

<sup>18</sup>W. Hörkner and H. K. Müller-Buschbaum, "Zür kristallstruktur Von CaAl<sub>2</sub>O<sub>4</sub>," J. Inorg. Nucl. Chem., 38, 983-4 (1976).

<sup>19</sup>N. B. Milestone, "Hydration of Tricalcium Silicate in the Presence of Lignosulfonates, Glucose and Sodium Gluconates," J. Am. Ceram. Soc., 62

 [7–8] 321–4 (1979).
 <sup>20</sup>J. F. Young, H. S. Tong, and R. L. Berger, "Compositions of Solutions in Contact with Hydrating Tricalcium Silicate Paste," J. Am. Ceram. Soc., 60 [5-6] 193-8 (1977).

<sup>21</sup>G. Charlot, Les réactions chimiques en solution aqueuse et caractérisation des ions; pp. 384. Masson, Paris, 1983. <sup>22</sup>H. F. W. Taylor, *Cement Chemistry*; pp. 345–61. Academic Press, London,

1990

<sup>23</sup>D. L. Kantro, "Tricalcium Silicate Hydration in the Presence of Various Salts," J. Test. Eval., 3 [4] 312-21 (1975).

<sup>24</sup>Y. El Hafiane, "Coulage en bande de ciment alumineux"; Thèse de Doctorat, Université de Limoges, France, 2002.

<sup>25</sup>G. Charlot, Les réactions chimiques en solution aqueuse et caractérisation des ions; pp. 190-1. Masson, Paris, 1983.