Effect of a Carboxylic Acid on Rheological Properties of a High Alumina Cement Mortar

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ABSTRACT: *In this work, we studied the effect of carboxylic acid on the rheological properties of a high-alumina cement mortar (CH45) produced by the Algerian firm REFRACTAL. The investigated properties are setting time, water consumption, electrical conductivity, pH, density and the compressive strength. The results show a setting time of about 200 min for the acid free, 180 min with 0.1 % of carboxylic acid and 18 hours with 2 % of this acid. A significant reduction in water consumption was noticed. The water/cement ratio of the acid free-mortar is reduced from 0.24 to 0.16 with 2% acid. The rheological investigations carried out on the mortar-water mixtures with and without carboxylic acid show a Newtonian behavior. The setting of hydrated mortar-water with acid mixtures shows an increase in the apparent density leading to an improvement of the compressive strength.*

KEY WORDS: *C: CaO, S: SiO$_2$, H: H$_2$O, A: Al$_2$O$_3$, CAC: Calcium Aluminate Cement.*

INTRODUCTION

Calcium Aluminate Cements (CAC) are considered as the most widely used refractory hydraulic binders [1]. Among cementious materials, calcium aluminates cements are the most resistant to chemical and thermal aggressive environments, abrasion and impact [2]. They consist of aluminate phases, mostly monocalcium aluminate CaAl$_2$O$_4$ and dodecacalcium heptaaluminate Ca$_{12}$Al$_7$O$_{33}$ respectively noted CA and C$_{12}$A$_7$ in cement chemistry nomenclature. These phases are present in most calcium aluminate cements.

In many applications of alumina cement (grout / concrete anchors and fast repairs), it is essential to have mixtures of high workability while maintaining its fast curing properties by using appropriate accelerators, retarders and plasticizers. These admixtures are used to modify the basic properties of CAC based mortars and concretes. They act by affecting the dissolution rate of anhydrous cement phases and/or the precipitation rate of hydrates [3,4].
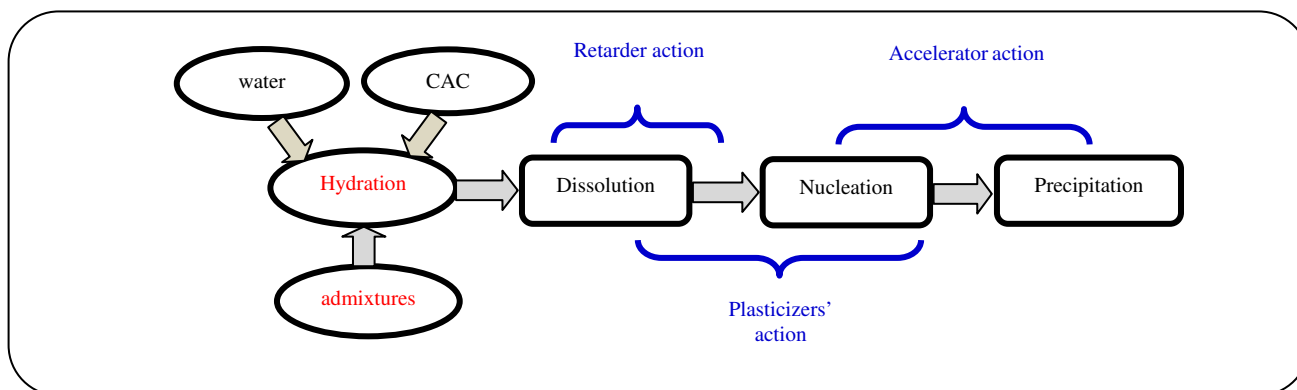

Fig. 1: Flow chart showing the different stages in cement hydration, and admixtures action.

Usually, admixtures interact with the cement during the hydration phase. They generally influence cement properties such as setting time and mechanical strength. The diagram, presented in Fig. 1, shows how the hydration process is influenced by the kind of admixtures.

The hydration process of cements starts when water comes into contact with their surfaces [1,2]. The hydration process can be described by three main phases [3]. The first phase is the dissolution of the anhydrous cement grains at contact with water. Ca^{2+} and $AlOH^{4-}$ ions will pass into solution, until saturation. This phase is followed by the nucleation after an incubation period, during which the kernels of CAH_{10} and C_2AH_8 are formed. After nucleation, a massive precipitation phase starts. Macroscopically, the precipitation of the calcium aluminate hydrates corresponds to the setting and hardening of the cement.

At the onset of the dissolution phase, heterogeneity of cement particles occurs on the surface due to the nucleation of the formed hydrates. This leads to the formation of a surface layer of hydrated phases. This hydrated layer must be considered in order to predict the interaction of cement particles with admixtures and with other neighboring particles.

The setting time of cement is usually characterized either by the measurement of electrical conductivity or by the Vicat test (penetration of a metal needle in the cement paste). Studies on the mechanisms governing the cement setting were performed on dilute solutions (generally, a liquid/cement mass ratio of 10). *Novinson et al* [4] found that the increase in setting rate of cement paste are partly influenced by the pH and the concentration of the admixture used in the suspension. In other works [5],

it was shown that the role of cation-anion pair of the additive is the most important factor. The behavior of aluminous cement pastes may be significantly influenced by the addition of very small amounts of chemical compounds. It is shown that the cation-anion pair has an important effect on the chemical mechanisms that cause the hardening of the aluminous cement paste. The influence of cations and anions on the setting time is ranked as follows [5]:

- For the cations: $Na < Li < K < Ca < Mg < Sr < NH_4$
- For the anions: $OH < Cl < NO_3 < Br < Acetate$

The anions, with the exception of hydroxide ion, cause setting retardation. This effect is due to the replacement of OH groups linked to Aluminum $(Al(OH)^{-4})$, by preventing the formation of oxobridges. The delay in setting will be governed by the rate of replacement of OH by other anions.

The retarders influence the kinetics of hydration by slowing the dissolution of the particles of anhydrous cement. The mechanism of adsorption takes place at the surface of the cement grains and/or in combination with calcium ions, which blocks the dissolution. The plasticizers (water reducers) are adsorbed on the surface of cement grains, leading to an increased zeta potential. This causes good dispersion by repulsion between positively charged grains. The accelerators act towards the end of hydration. They affect the incubation period by forming nuclei of inorganic chemical compounds (such as lithium aluminates) which reduces the time required for the formation of homogeneous nuclei [3].

Many efforts have been devoted in the past to the development and selection of deflocculating, plasticizing, or stabilizing agents. They assured the required fluidity of

Table 1: Chemical composition of the mortar CH45.

Oxides	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	ZrO_2	Na_2O	Cr_2O_3	Cal. Loss
Weight (%)	43.05	42.37	6.40	4.11	0.42	0.78	0.35	0.20	0.17	2.15

concrete mixtures at a minimum content of the dispersion medium (water) under controlled setting and hardening conditions [6]. The traditional additives contain chemicals in small amounts such phosphates (hexametaphosphate, tripolyphosphate), citric acid, sodium citrate, and organic additives [6]. They can either have a retarding or an accelerating effect on cement setting [2]. The nature and amount of the used additive are an important factor in improving the flow ability of the mix. The choice of proper mass ratio of deflocculant such as alkaline, alkaline-earth salts or organic additives is an important factor in improving the flow ability of the mix [7,8].

In this work, we studied the effect of adding various amounts (from 0 to 10%) of an organic admixture (carboxylic acid CH_3COOH) having small molecular size and complete solubility in water, on the properties of high alumina cement mortar. The used admixtures for cements are usually of inorganic nature. Rheological measurements on mortar pastes were carried out. Their effect on the density, the pH, the conductivity and the setting time of the mortar are evaluated and discussed.

EXPERIMENTAL SECTION
Starting Materials

The studied anhydrous mortar (CH45) is produced by an Algerian company (REFRACTAL, Annaba). It is prepared by mixing 1:4 (mass) of fused cement called "Ciment Fondu" from Kernos (France) with andalusite waste fillers. The main chemical compositions of this batch based on XRF analyses are indicated in Table 1.

The mineralogical analyses were carried out with X-ray diffraction using a BRUCKER D8 Advance diffractometer [Ni-filtered CuKα radiation, with a scanning speed of 2θ = 2°/min and step of 0.02°]. The main mineralogical constituents of the batch, estimated by quantitative X-ray diffraction as shown in Fig. 2, are (in weight%): mullite ($2Al_2O_3.3SiO_2 \sim 32$), andalusite ($Al_2O_3.SiO_2 \sim 12.44$), cristobalite ($SiO_2 \sim 6.52$), silica-rich amorphous phase (~ 23) and other constituents coming from the cement phase, which are mainly ($CaO.Al_2O_3 \sim 8.98$) and $Ca_{12}Al_{14}O_{33}$.
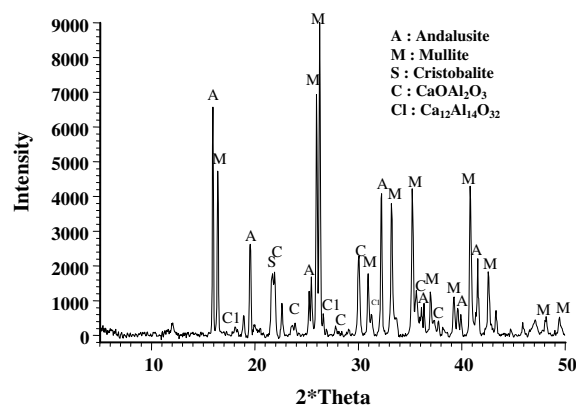

Fig.2: XRD patterns of CH 45 mortar.

The particle size distribution of the CH45 mortar was investigated using a laser granulometer (Malvern Mastersizer 2000). Ethanol was used as a solvent (Riedel-de Haën 96%). The obtained distribution is presented in Fig. 3. It appears that the mortar has a monomodal and a homogeneous distribution with an average size (d_{50}) of about 7.3 µm. It appears that the mortar powder is mainly composed of grains with sizes ranging from 0.557 to 60 µm. Fig. 4 shows a sample of the used powder. We see that there is a good dispersion of particles. We note that the grains are of irregular shape and size, as a result of the andalusite fire bricks grinding, which offers a relatively high specific area of about 6.9m²/g as determined by BET (Brunauer–Emmitt–Teller).

Before use, the batch was kept for 24 hours at 20°C in a dry atmosphere. The carboxylic acid was obtained from BIOCHEM in the form of one liter bottles at a 99-100% concentration.

Hydrated mortar characterization

The rheological behavior was studied on pastes prepared by adding a liquid mix (water + acid) to the mortar. The weight ratio ((water + acid)/mortar) was chosen on a base of preliminary tests and is maintained constant equal to 0.6. The concentration in the mixture was varied from 0 to 10% of the dry mortar weight. The preparation of each paste was performed according to the ASTM C305-99 standard [9] at 20°C for a total duration of 200 s.
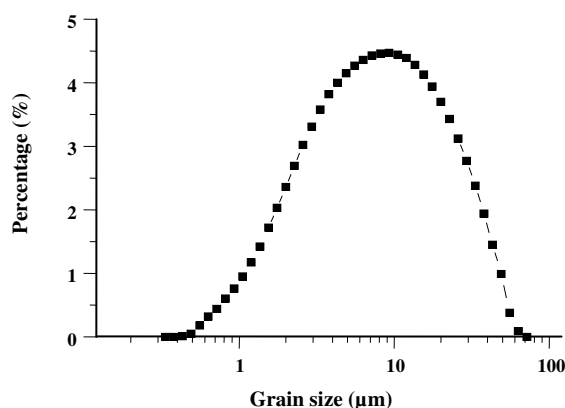
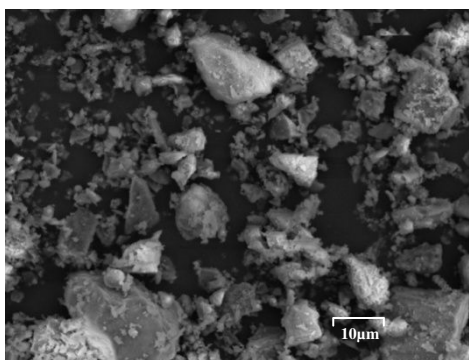**Fig. 3: Particle size distribution of CH 45 mortar.**

Fig. 4: Sample of CH45 mortar powder.

The viscosity of the pastes was measured 5 minutes after adding the liquid mix using a coaxial cylinder viscosimeter (HAAKE VT 501) equipped with a (MVII) device offering a wide range and high precision in measurements [10, 11]. The paste is placed between the two coaxial cylinders of the viscosimeter. The experiment consists in shearing the fluid in the annulus between the outer static cylinder and the inner cylinder by applying a uniform rotary motion with a given angular velocity (ω_0). The fluid itself breaks into cylindrical coaxial layers. The velocity of each layer varies from a null value, for the layers in contact with the fixed outside cylinder, to (ω_0) for those which are close to the rotating one. The relative displacement of the layers generates a shear strain rate ($\dot{\gamma}$) and a shear stress (τ) at every point in the fluid. In our experiments, we used the following experimental protocol:

- A linear increase in shear strain rate ($\dot{\gamma}$) from 0.1 to 100 s^{-1}, during 30 s.

- A dwell time of 30 s, at 100 s^{-1} shear strain rate.

- A linear decrease in ($\dot{\gamma}$) from 100 s^{-1} to 0.1 s^{-1}, during 30 s.

The pH values of the mortar suspensions before and after adding carboxylic acid were measured using a pH-meter (Orion Research). These measurements were carried out 5 min after the acid liquid addition.

Conductivity is a very good means for estimating the ion concentration in liquid. The conductivity of the mortar paste also provides information on the setting phenomenon by identifying the steps of dissolution / nucleation / precipitation of the hydration reaction of cement in water. The electrical conductivity of the mortar pastes was measured using a TACUSSEL conductivity meter. It was measured to monitor the changes in hydration state until paste setting.

The normal consistency tests were carried out according to the ASTM C187-98 standard in order to provide the amount of water required to prepare mortar pastes of normal consistency [12]. The pastes were prepared and inserted into the Vicat ring. They are centered in it and rested on a plate under the Vicat rod. The plunger end of the latter (10 ± 0.05 mm in diameter) is brought in contact with the surface of the paste and released immediately. The paste is considered to be of normal consistency if the rod settles to a point (10 ± 1 mm) below the original surface in 30 s after being released.

The setting time of the mortar pastes CH45 was measured using the Vicat needle test according to the ASTM C807-03a standard [13]. The determination of the setting time (St) is based on the following equation [14]:

$$St = \left(\left(\frac{(B-A)}{(C-D)} \right) \times (C-10) \right) + E \tag{1}$$

Where:

St : Setting time.

A: time in minute of last penetration greater than 10 mm.

B: time in minute of first penetration less than 10 mm.

C: penetration reading at time A.

D: penetration reading at time B.

The initial Vicat setting time is the elapsed time between the initial contact of mortar with the liquid (water + acid) coupled with a penetration of 10 mm. The final Vicat setting time is the elapsed time between the time of initial contact of mortar with the liquid
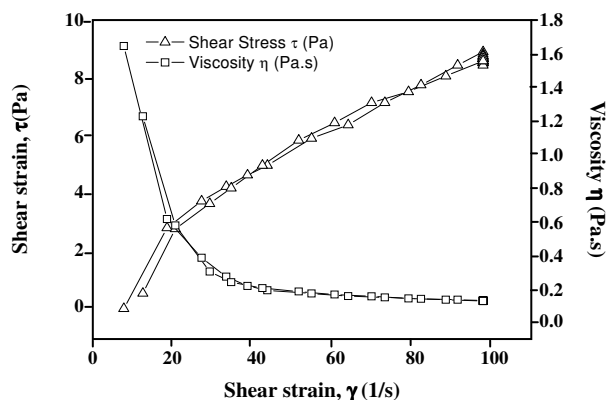
Fig. 5: Shear stress, (τ) and viscosity (η), versus shear strain rate, ($\dot{\gamma}$) for a mortar paste prepared with 2% (w_{acid}/w_{mortar}) ratio.

Fig. 6: Effect of acid content on paste viscosity.

(water + acid) and the time when the needle does not sink into the paste.

Set Mortar characterization

The structure of the mortar samples after setting was characterized using a Micromeritics 9300 porosimeter, enabling simultaneous obtention of apparent density and porosity. We used high pressure measurements with a wetting angle of 130°. The change in these two characteristics was deduced from the change in the amount of the carboxylic acid [15,16].

The compressive strength tests were performed on cylindrical samples of 50 mm diameter and 60 mm height. The samples were made by molding the pastes into plastic moulds, immediately after mixing. After setting, the obtained samples were stored at 20 °C in 98 % relative humidity during 3 days. Finally, they were subjected to mechanical compressive tests using a Zwick/Roell Z100 universal testing machine.

RESULTS AND DISCUSSION

The variation of shear stress (τ) and viscosity (η) versus shear strain rate ($\dot{\gamma}$) for pastes containing carboxylic acid is shown in Fig. 5. It can be seen that shear stress curves are fairly linear and do not show any hysteresis effects. This linear variation is typical of a Newtonian rheological behavior. It was noticed by some authors [17,18] that mortar pastes without additives exhibit a thixotropic rheological behavior. No hysteresis was noticed.

For shear strain rates $\dot{\gamma} \geq 39s^{-1}$, the shear stress ($\tau$)

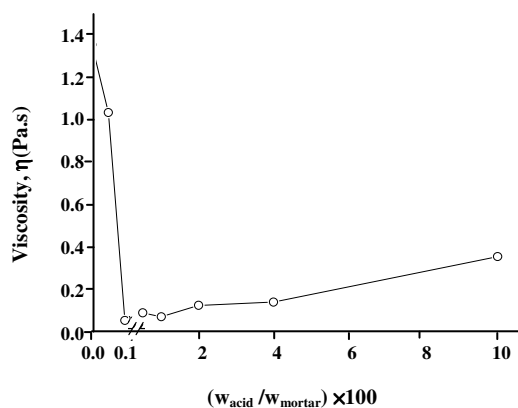varies linearly with ($\dot{\gamma}$) and the viscosity becomes nearly constant. In order to understand the rheological behavior of the pastes, we use the OSTWAL model [19] expressed as:

$$\tau = K \times \dot{\gamma}^n \qquad (2)$$

Where K is the index of consistency and n is a coefficient characterizing the pastes behavior. If n = 1, the behavior will be Newtonian. If n is higher or lower than 1, the pastes will have respectively a rheothickening or rheofluidizing behavior [20]. When we applied this equation to our experimental data, we found a value close to 1 for all samples containing carboxylic acid, thus suggesting a Newtonian behavior.

Fig. 6 shows the variation of viscosity η of the cement samples paste with increasing acid content. The values of viscosity coefficient were deduced from the (τ-$\dot{\gamma}$) curves of different compositions, for $\dot{\gamma} = 39s^{-1}$

The highest value of viscosity is observed for the paste without addition (η=1.35Pa.s). We can observe that small increases of the carboxylic acid reduce significantly the η values until reaching a minimum of 0.1%.

Beyond this value, the viscosity increases slightly up to a value of 0.4 Pa.s. The additive content related to the best particles dispersion usually corresponds to the lowest viscosity value [21].

The variation of mortar paste pH and Vicat setting time as a function of the additive content is shown in Fig. 7. We can see that the addition of CH_3COOH decreases the pH of the paste to a value as low as 4.72

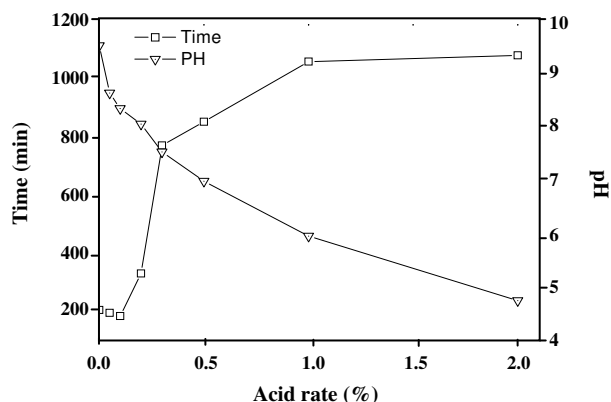*Fig. 7: Influence of carboxylic acid addition on setting time and pH.*

Fig. 8: Conductivity curves of mortar pastes with various amounts of carboxylic acid.

due to its acid nature. This value of pH is almost equal to the pKa of CH_3COOH (4.76). *Hidber et al.* [22] found that adsorption reaches its maximum when the pH value is equal the pKa of the dissociable molecule groups leading, to a significant retardation of the cement paste. The Vicat test reveals that the setting time (190.235 min) corresponding to the samples, prepared with no additives, remains nearly constant for w_{acid}/w_{mortar} ratios between 0.05 and 0.2% before it increases rapidly for higher rates due to the increase in adsorption.

Although calcium aluminate and calcium silicate cements are known to display distinct reaction rates and form different hydration products, similar interactions between the cementious phase and the chemical additives (admixtures) are expected to occur in aqueous suspensions.

According to *Jolicoeur & Simard* [23], the interactions that take place between dispersant molecules and cement particles in an aqueous medium may involve :

- The adsorption of dispersant molecules on the surface modifying the superficial features of particles through the electrostatic/electrosteric mechanism.

- The selective adsorption of molecules on reactive surface sites, locally blocking the dissolution of the anhydrous phase.

- The complexation of dissolving ions by the nonadsorbed dispersant molecules, which may either retard the precipitation of new hydrated phases or further aid the dissolution process.

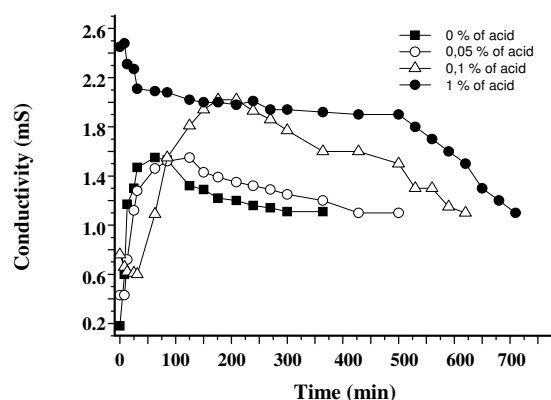*Smith et al.* [2] when studying the effect of such admixture on high alumina cement put forward the

hypothesis that it could be because of a delay (slowing down) of CA dissolution due to the adsorption of $CaCH_3CO^{2+}$ on the surface of negatively charged CA grains.

To observe the influence of carboxylic acid on setting time, we also measured the electrical conductivity. The corresponding curves are given in Fig. 8.

The variation with time of the electrical conductivity of the paste with no acid addition has the same basic shape of the hydration of any aluminous cement. By raising the acid rate we found, in the first moments of the mortar/liquid contact, that there is an initial increase followed by a slight decrease in conductivity inducing a small plateau. After that, the electrical conductivity increases with a hydration development over time to reach a maximum value.

The conductogram curves, for 0.05 and 0.1% of acid, have a similar shape, with a plateau, which is caused by the dissolution of the acid in water and then an increase of the conductivity with some retardation (lower slopes of the curves). The increase in electrical conductivity is due to the increase in ionic concentration and mobility of Ca^{2+} and $Al(OH)^{4-}$. The gradual decrease in the electrical conductivity may be due either to the formation of thin layers, constituting an electric double layer of adsorbed calcium ions and counter ions, or to the hydrate formation causing cement setting. The period between the ascent and descent of the conductivity curve gives clear information about the total setting time.

For pastes containing 1% acid and more, the intensity of the conductivity is higher and is proportional to the acid rate. The induction period in these cases is longer
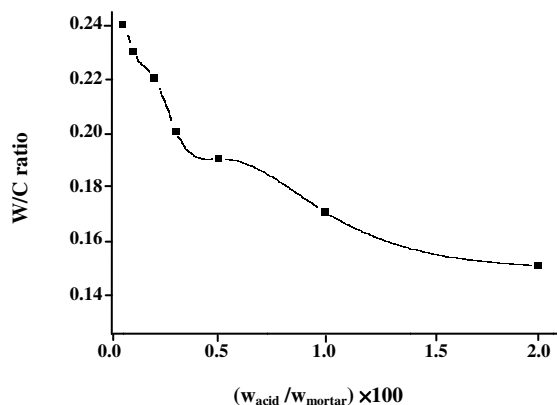
Fig. 9: Water/mortar ratio vs (W_{acid}/W_{mortar}) ratio.

Fig. 10: Density and percentage of open pore volume for mortar vs (w_{acid}/w_{mortar}) ratio.

because of complexations by metal ions of the cement with the acid carboxyl groups. The complexes formed lead to poisoning nuclei of hydrates which possess the power of delaying the precipitation reaction.

Fig. 9 shows the normal consistency versus the mass ratio (w_{acid}/w_{mortar}). We observe that the water consumption for 0.05 and 0.1% of acid additive is nearly the same as for the mortar without acid (0.24). On the other hand, we also notice from Fig. 5 that the variation of the viscosity in function of the additive shows the lowest viscosity for 0.1%.

For ratios greater than 0.1%, the water consumption decreases, but the setting time is much longer as observed in Fig. 7. It's therefore more interesting to choose the rate of 0.1% acid.

In Fig. 10, which shows the effect of acid content on density and porosity, we can see a densifying effect of the additive on the mortar. This effect is due to the dispersive character of the additive.

Densification and particles dispersion are linked phenomena. A good dispersion leads to a good organization of cement grains and consequently to a good densification. The density of the hardened samples increases with acid content, whereas the porosity volume decreases down to 23%.

The hardened samples were polished to observe the pore distribution with a JEOL 840 A Scanning Electron Microscope (SEM). Fig. 11 shows SEM micrographs taken from two mortar samples, with 0% and 0.1% acid content, used for studying the density and porosity variation. They illustrate the densifying effect of
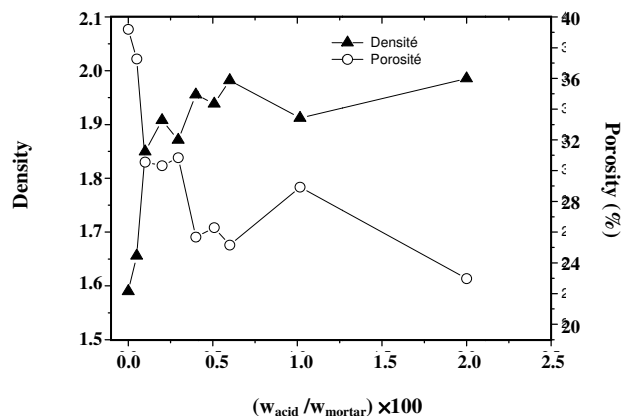
the additive and the pores distribution change in number and size. We notice that the open porous volume decreases and, consequently, the density slightly increases for 0.1 % acid content.
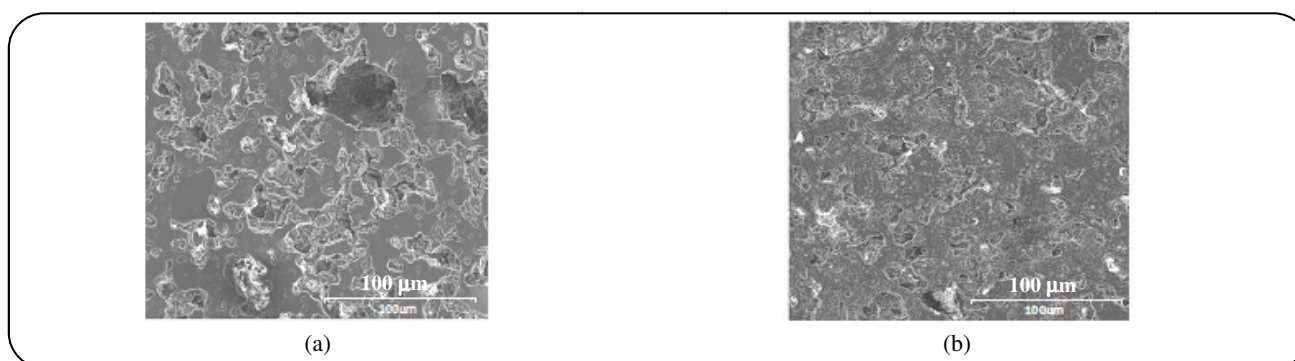
The data presented in Table 2 concerns the compressive strength for samples after 4 days and 6 months aging. Compared to samples prepared without carboxylic acid, the presence of the latter has beneficial effects on the mechanical strength. This is due to the increase of the density according to the acid content as shown in Fig. 10.

CONCLUSIONS

The effect of addition of carboxylic acid on rheological properties of a high alumina cement mortar has been studied. We found that acid can be a retarder and a water reducer in the high alumina cement mortar. The retarding effect of the acid could be attributed to the adsorption of cationic species that delays the dissolution reaction. It was found that the rheological behavior of pastes containing carboxylic acid is Newtonian. This acid decreases the viscosity of suspension for very low content and improves its dispersion. It also induces a densification and strengthening effect of the material. Pastes with 0 and 0.1% additive have the same setting duration and water consumption but a large difference in viscosity. It's therefore more interesting to choose the rate of 0.1% acid in our batches. Aging effect of samples containing carboxylic acid during 4 days and 6 months ameliorates the mechanical characteristics.

Table 2: Mean compressive strength obtained from sets of 03 samples, after 4 days and 6 months aging for high alumina cement mortar prepared with increasing mass percentages of carboxylic acid and kept at 20°C and 98% of relative humidity.

	Compressive strength (MPa)	
$(w_{acid}/w_{ciment}) \times 100$ (%)	4 days	6 months
0	4.76	5.01
0.1	6.16	6.32
0.3	6.25	6.87
0.5	6.97	7.12
1	8.95	9.10

(a)   (b)

Fig. 11: SEM micrographs of samples with respectively (a) 0% and (b) 0.1% acid content.

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