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Cement and Concrete Research 37 (2007) 856–865

Cement and Concrete Research

A case history: Effect of moisture on the setting behaviour of a Portland cement reacting with an alkali-free accelerator

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Received 17 January 2005; accepted 22 February 2007

Abstract

Flash setting accelerators are a class of admixtures commonly used for sprayed concrete during tunnel excavation. They allow an immediate set of concrete which can bind to the substrate without dangerous collapses. Such a coating layer prevents the section convergence that is its tendency to squeeze. The early strength development (till 1 h) of the sprayed concrete can be connected to the final set time of cement pastes admixed with the accelerator. The lower is the final set time, the higher should be the early strength. Two main methods are used to project concrete: wet and dry. Today, for safety reasons and to obtain more homogeneous concrete layers, the wet method is becoming more diffused. This technique requires the use of liquid flash setting accelerators which are pumped to a nozzle and immediately projected onto the rock wall. In the European market, two kinds of setting accelerators are mainly available: alkali-rich and alkali-free. Recently, for several reasons, the demand of alkali-free accelerators is growing very rapidly. They are water solutions of aluminium sulphate with a total alkali metal content (expressed as equivalent of Na_2O) lower than 1%. In order to develop new and more performing accelerators, several studies are in progress to elucidate their action mechanism and the factors affecting the setting of accelerated concretes.

During an experimental study on the setting behaviour of several cement pastes reacting with an alkali-free accelerator, we found a cement showing, as time proceeded, a persistent setting time reduction. We discovered that the effect was connected to the cement exposure to the moisture. A mineralogical investigation performed on this particular cement revealed the presence of hemihydrate as setting regulator. In order to study the interaction between the alkali-free accelerator and this moist aged cement, some morphological (ESEM-FEG), crystal-chemical (XRD), physical–chemical (hydration temperature profile) and chemical (ICP) analyses on cement paste samples were carried out.

This study showed a significant setting time reduction of cement paste samples admixed with an alkali-free accelerator when they are composed of a Portland cement containing β-hemihydrate that was previously exposed to moisture. Such an effect seems to be related to the reduction of the β-hemihydrate dissolution rate.

Keywords: Accelerators; Alkali-free; β-Hemihydrate; Shotcrete; Sulphates

1. Introduction

1.1. General considerations

Since 1911, when C.E. Akelei [1] patented an equipment for spraying mixtures of cement and water, many advances were carried out in shotcrete technology. Today, two main spraying methods are available which are commonly defined as dry and wet. The former is the oldest one and arises from the Akelei's invention: cement and dry sand are conveyed by compressed air through a hose, and the water needed for hydration is introduced at the spraying nozzle. The wet process was introduced after the end of the second world war: mortar or concrete are pumped to a nozzle and pneumatically projected onto a substrate. However, due to poor/inefficient equipment, lack of know-how, and lack of experience, the quality of the first "generation" wet sprayed concrete was extremely low. Only recently, with the development of more sophisticated spraying machines (automated dosing and powerful pumps), advanced robotics and experience, wet sprayed concrete is becoming increasingly more attractive. The advantages of wet method in comparison to the dry one can be summed up as follows: 1) lower dust production;

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0008-8846/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.cemconres.2007.02.020

Table 1
Sample compositions

	Exposure time	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	K1	K2	K3	K4	K5	K6	K7	K8
Cement	No exposure	100	/	100	/	100	/	/	/	/	/	/	/	/	/	/	/	/	/
	10 min	/	/	/	/	/	100	/	/	/	/	/	/	/	/	/	/	/	/
	30 min	/	100	/	100	/	/	100	/	/	/	/	/	/	/	/	/	/	/
	2 h	/	/	/	/	/	/	/	100	/	/	/	/	/	/	/	/	/	/
	6 h	/	/	/	/	/	/	/	/	100	/	/	/	/	/	/	/	/	/
	24 h	/	/	/	/	/	/	/	/	/	100	/	/	/	/	/	/	/	/
Clinker	No exposure	/	/	/	/	/	/	/	/	/	/	97.8	97.8	/	/	97.8	97.8	/	/
	30 min	/	/	/	/	/	/	/	/	/	/	/	/	97.8	97.8	/	/	97.8	97.8
β-hemihydrate	No exposure	/	/	/	/	/	/	/	/	/	/	2.2	/	2.2	/	2.2	/	2.2	/
	30 min	/	/	/	/	/	/	/	/	/	/	/	2.2	/	2.2	/	2.2	/	2.2
Water	/	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35
Accelerator	/	/	/	2	2	7	7	7	7	7	7	2	2	2	2	7	7	7	7

2) higher spraying efficiency; 3) lower energy consumption; 4) better homogeneity of the concrete properties. This more efficient technology requires the use of liquid flash setting accelerators [2]. They should allow a rapid set of wet sprayed concrete thus determining a rapid concrete hardening and favouring overhead and vertical applications. The cementitious layer acts as a temporary consolidating shield, preventing dangerous falling rocks. Today, the requirement of thicker concrete layer and higher production rate, encouraged the demand for new more performing accelerators. Undoubtedly, they are the most important admixtures used in shotcrete and are mainly divided in two categories: alkali rich (composed of alkali metal hydroxides, alkali metal silicates or aluminates [2,3]) and alkali-free (which are water solutions or slurries of aluminium sulphate stabilised by inorganic or organic acids). Only recently the second type of accelerators was introduced in the market [4–6]. According to EN 934-5, a flash setting admixture can be defined as "alkali-free" when its alkali metal content (sodium and potassium), expressed as equivalent of Na_2O (% Na_2O + 0,658 × % K_2O), is lower than 1%.

1.2. Action mechanism of the alkali-free accelerators

Only few studies are available on the action mechanism of the alkali-free accelerators [7–10]. Bravo et al. [7] hypothesised that when the accelerator is added to a hydrating cement, Al^{3+} and SO_4^{2-}, coming from the admixture, could react with C_3A and Ca^{2+} to form immediately ettringite (in amorphous or crystalline state). Each mole of ettringite contains at least 32 moles of water [11]. Therefore, ettringite formation and water reduction enhance the solid/liquid ratio and the viscosity of the cementitious system thus determining a setting time shortening. The growth of ettringite crystals determines the early compressive strength development [12].

1.3. Scope

The capability of concrete to adequately bind to the substrate is related to the reaction occurring between accelerator and hydrating cement phases. In particular, the higher is the early strength between concrete and substrate, the easier and safer are the spraying applications. The early strength is generally connected to the final set time of cement pastes admixed with the accelerator [13]. The lower is the final set time, the higher should be the early strength development of the projected concrete. The reaction between accelerator and hydrating phases could be governed by several cement characteristics such as the chemical composition, the calcium sulphate phase, the particle size distribution and the ageing. The influence of these parameters was not well explored. During an experimental evaluation of the final set time of several cement paste samples reacting with an alkali-free accelerator, it was found a cement with a very slow setting, showing a significant setting time shortening as time proceeded. It was observed that the phenomenon was related to its exposure to the moisture. Furthermore, an X-ray Diffraction analysis pointed out that hemihydrate was used as setting regulator. In particular, the cement producer declared that this hemihydrate was in the β form. The study was carried out to elucidate the effect of moist ageing of this type of cement on its reaction with an alkali-free accelerator. The weathering process was simulated by exposing fresh cement samples at 20 °C and 95% R.H.

XRD patterns were collected on fresh and aged cement, to detect possible changes of crystalline phase composition. The final set time was measured on mixtures prepared with fresh and weathered cement, admixed with several dosages of the alkali-free accelerator. Setting was also determined on samples prepared with cement having different ageing times (from 10 min

Table 2
Chemical and physical characteristics of cement (analyses performed according to ENV 196/2)

CaO (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	SO_3 (%)	Cl (%)	SO_3 (%)	Free CaO (%)	Na_2O equivalent (%)	Density (kg/m^3)	Blaine specific surface area (m^2/g)
61.2	21.5	5.8	2.7	1.7	2.2	0.01	2.2	0.15	0.7	3160	400

Table 3
Phase composition (expressed as %) of fresh cement (upper line) and clinker (lower line- standard deviation is indicated between brackets)

C_3S	C_2S	C_3A	C_4AF	β-hemihydrate	CaO	$Ca(OH)_2$	$CaCO_3$
$67.8_{(+/-0.1)}$	$9.7_{(+/-0.3)}$	$10.4_{(+/-0.2)}$	$6.9_{(+/-0.2)}$	$2.2_{(+/-0.1)}$	$0.5_{(+/-0.05)}$	$0.7_{(+/-0.08)}$	$1.8_{(+/-0.2)}$
$68.9_{(+/-0.1)}$	$11.4_{(+/-0.3)}$	$9.1_{(+/-0.2)}$	$8.2_{(+/-0.2)}$	/	$0.7_{(+/-0.05)}$	$0.5_{(+/-0.08)}$	$1.5_{(+/-0.2)}$

to 24 h). A comparative study on the interactions between the accelerator and both fresh and aged cement was performed by thermo-chemical hydration profile, ESEM-FEG (Environmental Scanning Electron Microscopy–Field Emission Gun), XRD (X-ray Powder Diffraction), ICP-AES (Induced Coupled Plasma–Atomic Emission Spectroscopy). The effect of humidity was evaluated by analysing the conductivity of water mixtures containing fresh and weathered β-hemihydrate and by measuring the setting time of paste samples composed of a clinker, aged or fresh β-hemihydrate, water and the alkali-free accelerator.

2. Experimental

Cement pastes (Table 1) were prepared by mixing fresh and aged cement type I 42,5 (ENV 197/1; Tables 2 and 3) and water (W/C=0.35). The alkali-free accelerator (trade name Mapequick AFK 777 J produced by Mapei; Al_2O_3= 17% and SO_3=40%) was added directly to the fresh made cement pastes and mixed for 10 s. The moist ageing was carried out exposing a cement layer (500 g — thickness 3 mm) at 20 °C and 95% R.H. for different times (10 min, 30 min, 2 h, 6 h and 24 h). A clinker (whose phase composition is reported in Table 3) and a β-hemihydrate ("Lages" Italy; SO3: 53%; CaO: 38.6%; medium particle size: 19.4 μm) were also used.

2.1. Mechanical tests

The final set time of the samples indicated in Table 1 was performed by Vicat needle method (ENV 196/3 — each result is an average of three measurements).

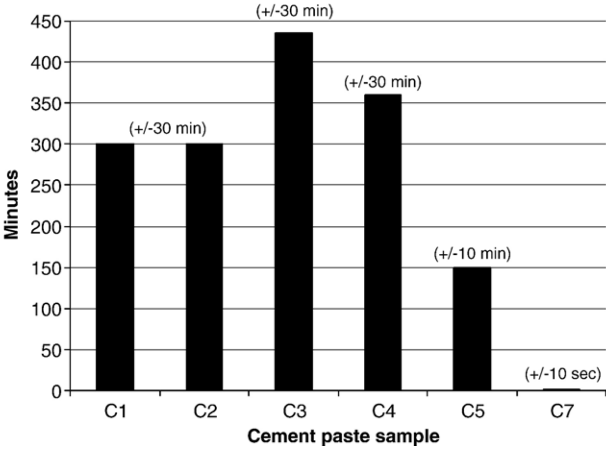

Fig. 1. Final setting time of cement pastes (standard deviation is indicated between brackets).

In order to evaluate the accelerating effect of the alkali-free accelerator (dosed at 2% and 7% by cement mass) on fresh and weathered (30 min) cement, the setting time of samples C1, C2, C3, C4, C5 and C7 was evaluated.

The influence of ageing time was studied by measuring the final set time of paste samples containing the cement which was kept in a moist environment (at the conditions already mentioned) till 24 h and admixed with 7% of the alkali free accelerator (C5-C10).

The effect of the moist curing on both clinker and β-hemihydrate, was analysed by setting time determinations of samples prepared by mixing a fresh or weathered clinker; a fresh or weathered β-hemihydrate, water and 2% or 7% (by cement mass) of the accelerator (K1–K8).

2.2. Physical–chemical analyses

In order to measure the amount of water absorbed by cement, its mass increase during moist curing was measured by a digital balance type Mettler AE 260 (each result is an average of three determinations).

During the first 3 h, the conductivity of water mixtures containing fresh and moist cured β-hemihydrate (water/powder ratio: 10) was measured by a conductivity-meter model WTW LF 538.

All the physical-chemical analyses performed on the cement pastes were carried out without any previous treatment to stop hydration, as it has not been clarified yet if and how the use of organic solvents to stop hydration could modify the crystalline

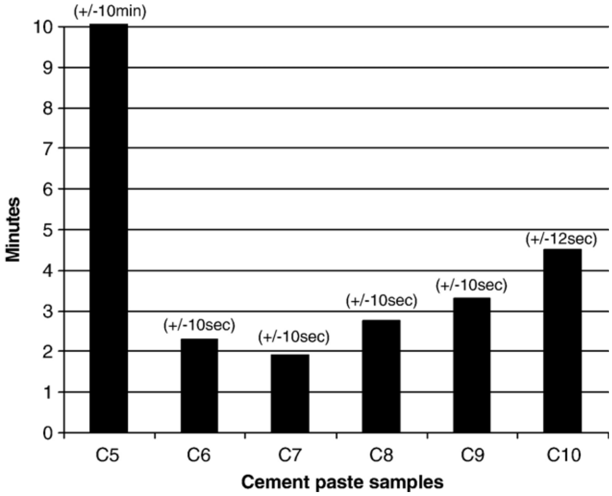

Fig. 2. Final setting time of samples containing cement at increasing exposure time (the real value associated to the first peak, C5, is 150 min; standard deviation is indicated between brackets).

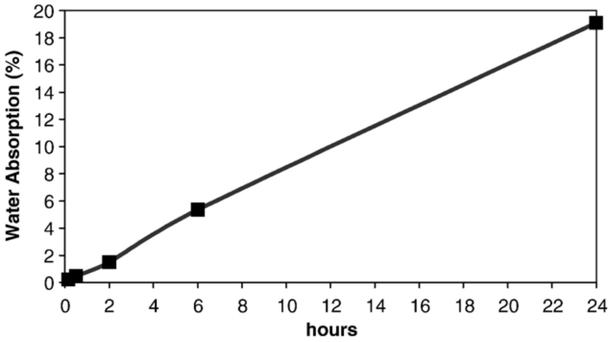

Fig. 3. Water absorption of cement exposed to moisture.

structure of the system involved. During hydration, the samples were kept at 20 °C and 95% R.H.

The hydration temperature profile was measured keeping the cement paste sample (0.5 kg) in a thermostatic bath (20 °C) and registering the temperature during the first hour by a digital thermometer type Testo mod. 781.

Soluble ions (Al^{3+} and SO_4^{2-}) concentration of hydrating cement was measured according to the following procedure: cement paste samples were grounded after 5 min, 30 min, 3 h and 20 h of hydration; the resulting fine powder was dipped in water (water/powder ratio: 2.5) and mixed for 15 min, in order to dissolve soluble ions.

ICP spectroscopy (Induced Coupled Plasma by Liberty 220 Varian Spectrometer) was employed to detect the soluble ions concentration (each result is expressed as % by cement mass, as the average of three measurements).

The mineralogical composition of fresh cement, aged cement and clinker was determined by XRD analyses (Philips PW 1830 Diffractometer with Cu(Kα) Radiation). The patterns were collected in the 5–90° 2θ range, using a step size of 0.02° 2θ and a counting time of 12 s per step. The powder diffraction pattern was refined by the Rietveld method [14], using GSAS computer package [15]. The lattice constants, the phase fractions of all minerals and the coefficient corresponding to zeropoint correction were also refined. The peak profiles of C_3S, C_2S, C_3A and C_4AF were modelled using a pseudo-Voight function; one gaussian and one lorentian coefficients were refined.

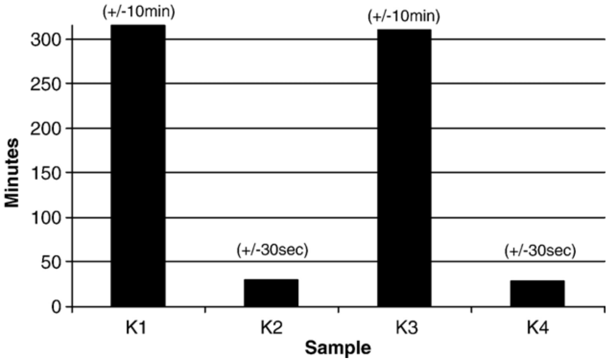

Fig. 4. Final setting time of samples composed of clinker and β-hemihydrate (fresh and aged), accelerator (2% by powder mass) and water (standard deviation is indicated between brackets).

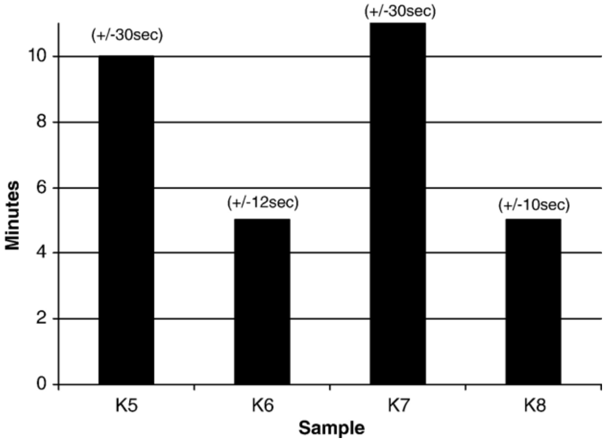

Fig. 5. Final setting time of samples composed of clinker and β-hemihydrate (fresh and aged), accelerator (7% by powder mass) and water (standard deviation is indicated between brackets).

A spherical harmonic (ODF) preferential orientation function was refined only for the C_3S. The goodness of the fit, evaluated as X^2, was 9.944.

In order to avoid the carbonation effect on young cement pastes, XRD patterns, in this case, were collected in the range between 5° and 40° 2θ in a short time (11 min). The samples were analysed after 30 min, 8 h and 24 h of hydration.

2.3. Morphological analyses

An Environmental Scanning Electron Microscope (Philips mod. XL30 ESEM-FEG) was used to analyse the morphology of hydrating cement pastes. The special instrumental configuration of the ESEM-FEG allowed to work in low vacuum setting (6 Torr), with a 10 kV voltage, at a temperature of 5 °C. Therefore, we could analyse the sample in the presence of significant amounts of residual water. The study was performed till 1 h of curing.

3. Results

3.1. Mechanical tests

The results, reported in Fig. 1, show that aged cement favours a significant setting time reduction of the accelerated

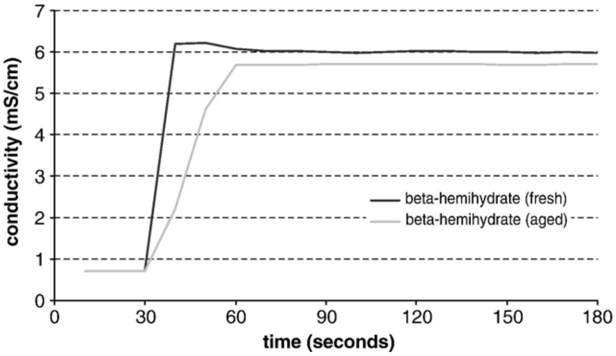

Fig. 6. Conductivity of water mixtures containing fresh and aged β-hemihydrate.

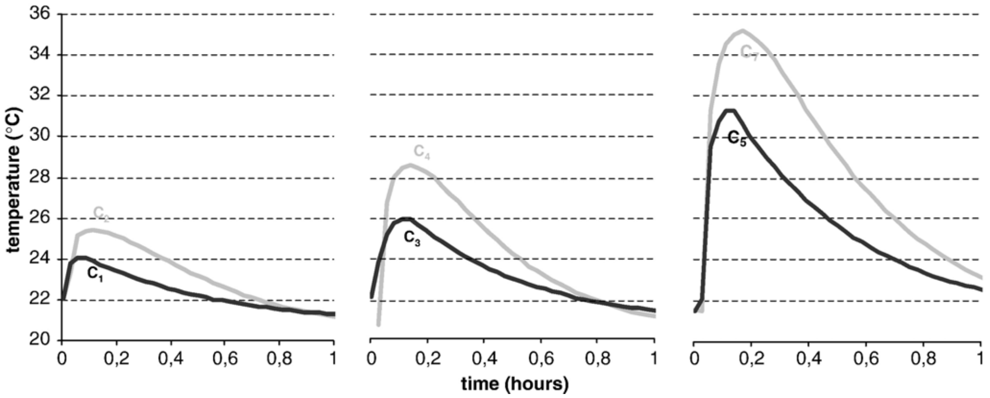

Fig. 7. Hydration temperature profile.

cement paste samples. In fact, the final set time of samples C4 (2% accelerator, 30 min aged cement) and C7 (7% accelerator, 30 min aged cement) is shorter than the one measured on samples C3 (2% accelerator, fresh cement) and C5 (7% accelerator, fresh cement).

As already reported in literature [7], the use of low accelerator dosage (for example 2% by cement mass) determines a retarding effect: the final set time of samples C3 and C4 is longer than the one measured on samples C1 and C2.

Fig. 2 shows that the shortest setting was found after half an hour of moist curing (C7), which corresponded to a water absorption of about 0.5% (Fig. 3). Cement components involved during the water absorption should be both the β-hemihydrate and the anhydrous cement phases.

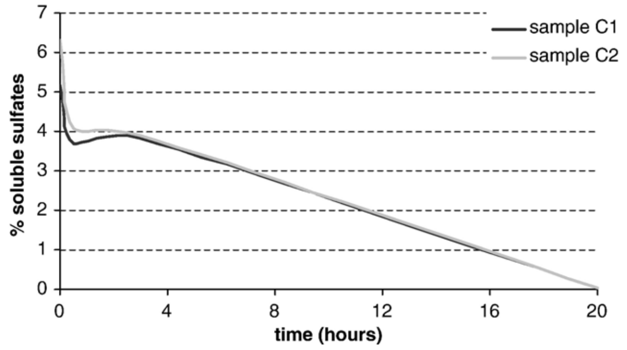

Fig. 8. Soluble ions concentration of C1 and C2 (standard deviation: 1%).

The results of Figs. 4 and 5 emphasise that moist curing of β-hemihydrate plays a key role in the setting time reduction. For example, the final set time of the sample composed of fresh clinker, fresh β-hemihydrate and 2% of the accelerator (K1) is significantly longer in comparison with the one measured on fresh clinker, aged β-hemihydrate and 2% of the accelerator (K2).

3.2. Physical–chemical analyses

The results, reported in Fig. 6, point out that the weathering of β-hemihydrate causes a drastic water conductivity reduction. This effect could be related to a lower dissolution rate of the aged calcium sulphate. It was already demonstrated that the moist ageing of β-hemihydrate can influence the accelerator reactivity (Figs. 4 and 5), therefore the calcium sulphate dissolution rate could be a physical parameter affecting the reaction between alkali-free accelerator and hydrating cement.

The hydration temperature profile is associated with the rate of heat release [7,16]. The exothermic peak, revealed during the first hour of hydration (Fig. 7 — standard deviation: +/− 0.5 °C), is due to early cement hydration and hydrated sulphoaluminate formation. A temperature rise is observed at increasing admixture dosages (as already published [7]) due to the formation of ettringite. In fact, as already mentioned, aluminium sulphate,

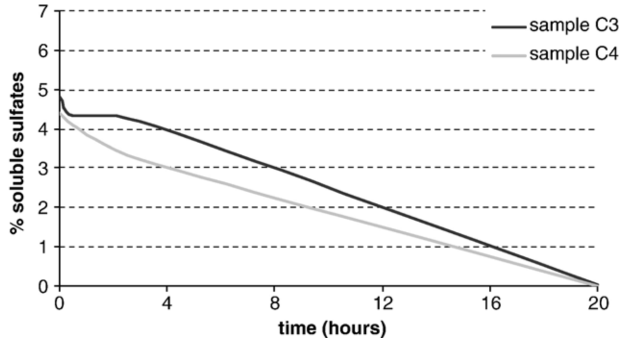

Fig. 9. Soluble ions concentration of C3 and C4 (standard deviation: 1%).

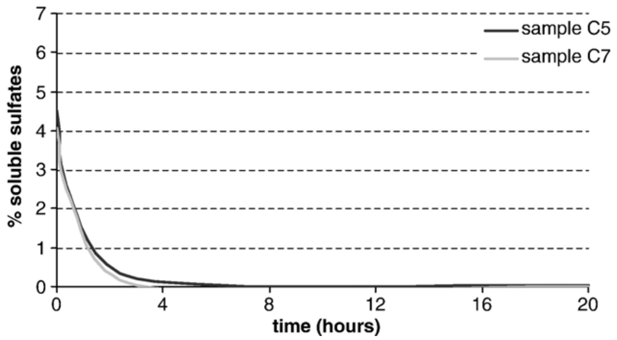

Fig. 10. Soluble ions concentration of C5 and C7 (standard deviation: 1%).

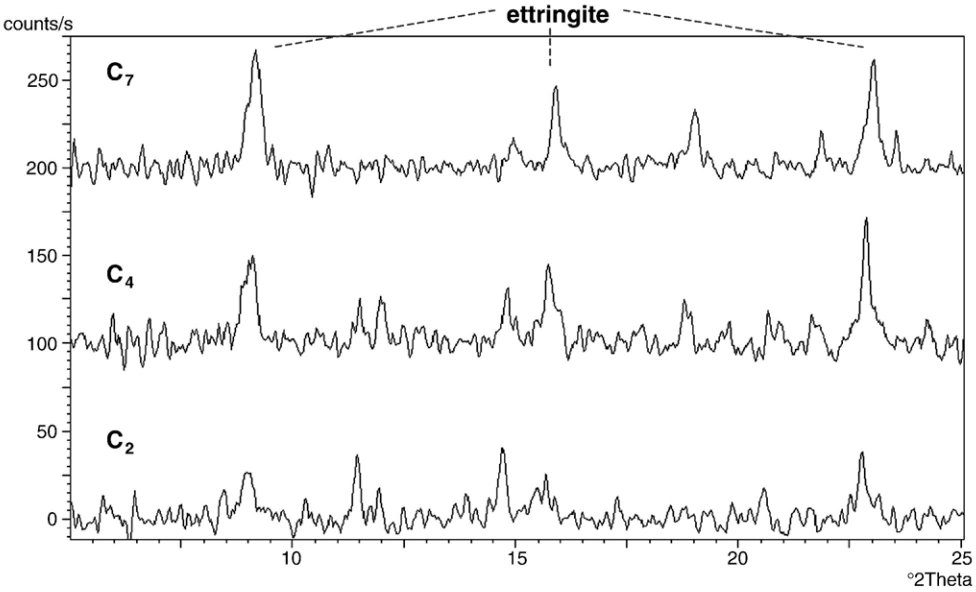

Fig. 11. XRD after 30 min of hydration: The intensity of ettringite peaks at 9°, 15.7° and 22.9° 2θ increases by increasing the admixture dosages.

contained in the accelerator, supplies a considerable amount of Al^{3+} and SO_4^{2-} to the cementitious pore solution, thus favouring a massive ettringite formation [8,9]. Cement weathering causes a significant increase of peak height (samples C2, C4, C7 compared to C1, C3, C5 in Fig. 7) suggesting that the alkali-free accelerator, reacting with the hydrating aged cement, produces a higher amount of ettringite.

A significant drop of soluble sulphates content is visible in all samples (Figs. 8–10). On the contrary, after 5 min, soluble aluminium ions are totally consumed due to a likely rapid formation of water insoluble precipitates (for example ettringite). Initially, a rapid decrease of soluble sulphate concentration is evident in the reference samples (C1 and C2 — Fig. 8). The effect could be due to a fast reaction between sulphates (coming from the β-hemihydrate) and aluminates (normally present in cement phases such as C_3A and C_4AF) to produce a protective layer of ettringite [17]. The sulphate decrease slows down during the dormant period (from 30 min to 3 h of hydration). The coating layer could possibly stop further reaction between hydrating cement phases and sulphates.

Samples C3 and C4 do not show the initial rapid sulphate decrease (between 5 and 30 min of hydration — Fig. 9) observed in the reference samples (C1 and C2 — Fig. 8). The effect can be explained assuming that soluble aluminium ions, coming from the admixture, could immediately interact with soluble sulphates (originated by the β-hemihydrate and the

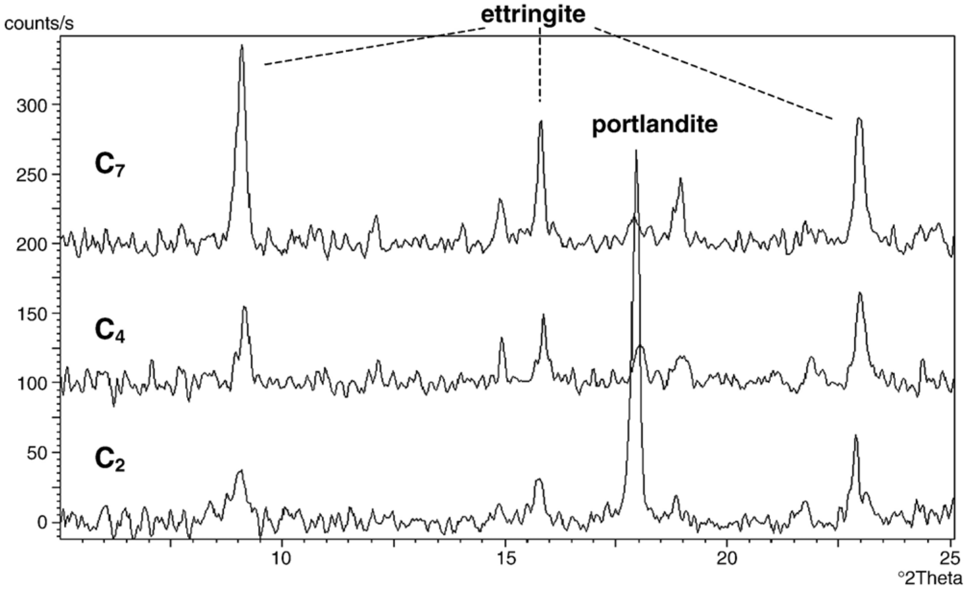

Fig. 12. XRD after 8 h of hydration: The intensity of ettringite peaks at 9°, 15.7° and 22.9° 2 increases by increasing the admixture dosages.

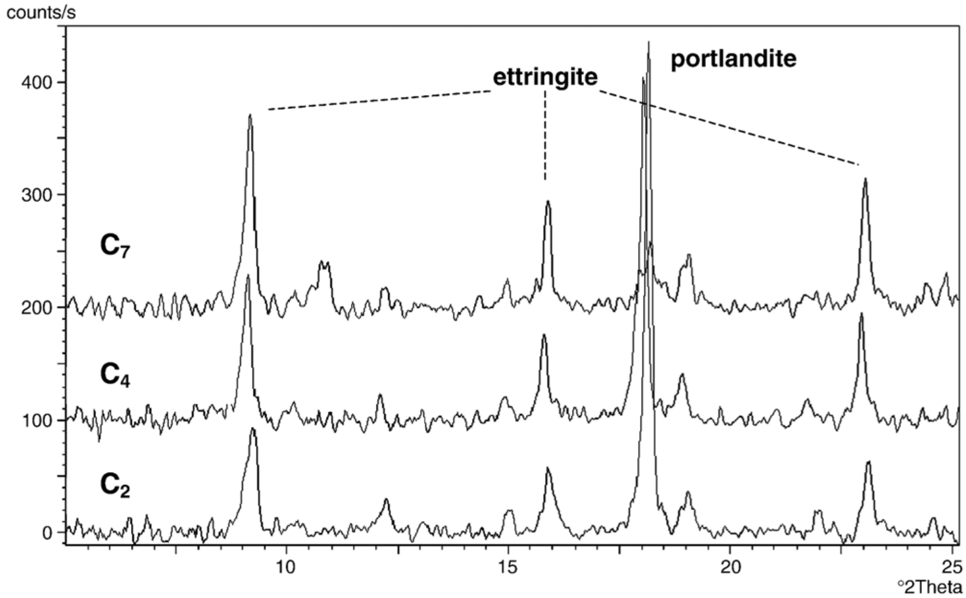

Fig. 13. XRD after 24 h of hydration: The intensity of ettringite peaks at 9°, 15.7° and 22.9° 2θ increases by increasing the admixture dosages.

accelerating admixture) and calcium hydroxide (produced during cement hydration), accelerating the initial formation of the ettringite layer [7], thus anticipating the dormant period.

The cement paste admixed with the highest amount of accelerator (7%) determines a sharp decrease of the sulphate content (Fig. 10). A high amount of soluble aluminium, due to an increased accelerator dosage, could react rapidly with all the available sulphate ions causing a fast concentration decrease due to the formation of a thick layer of ettringite. Sulphate concentration profiles do not emphasise significant differences between aged and fresh cement.

Signals of crystalline ettringite are visible in XRD patterns of cement pastes admixed with the alkali-free accelerator (Figs. 11–13). Ettringite content seems to raise at increasing admixture dosages (Figs. 11 and 12), as confirmed by literature [7–9]. Portlandite is clearly evident after 8 h of hydration in cement paste of sample C2 (Fig. 12). After 24 h of curing, ettringite may react with available aluminates to give hydrated calcium monosulphoaluminate (Fig. 13). XRD patterns of cement pastes made with fresh and aged cement do not show significant differences (an example is reported in Fig. 14).

3.3. Morphological analyses

The ESEM micrographs of reference pastes C1 and C2 do not show significant morphological differences.

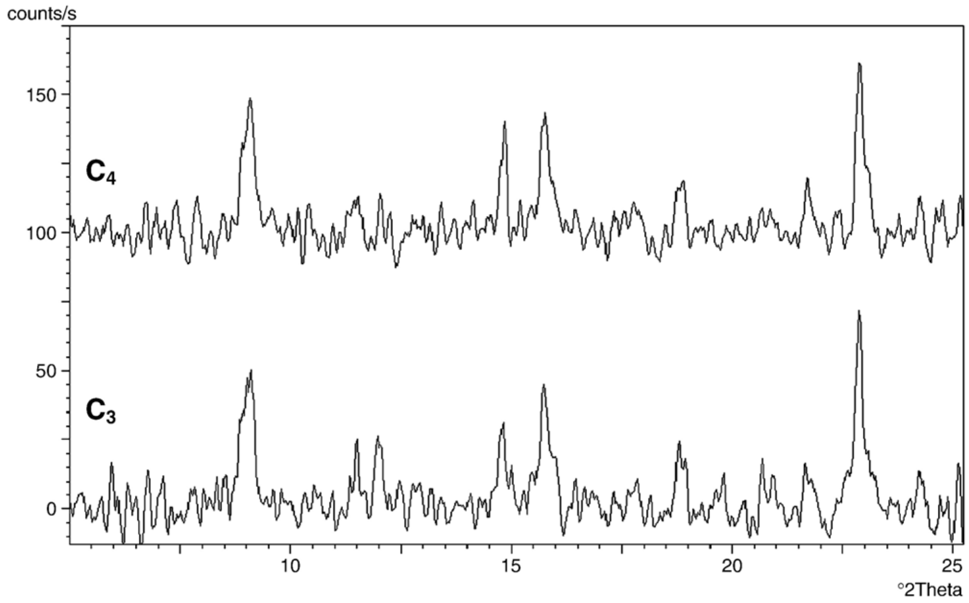

Fig. 14. XRD after 30 min of hydration of samples C3 and C4: The intensity of ettringite peaks at 9°, 15.7° and 22.9° 2 is the same.

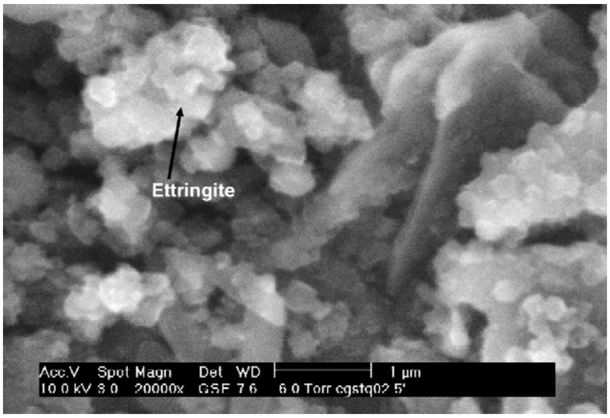

Fig. 15. ESEM micrograph of C3 after 5 min of hydration (unit length 1 μm).

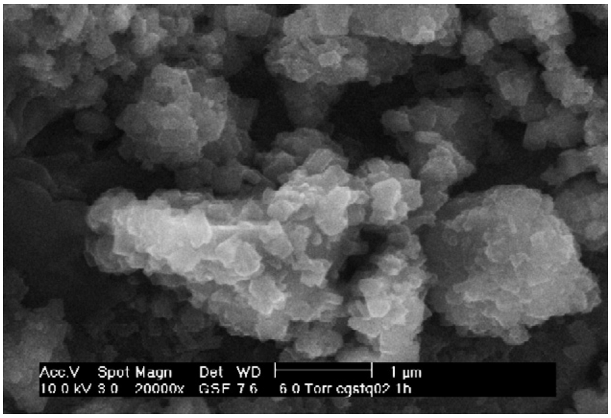

Fig. 17. ESEM micrograph of C3 after 1 h of hydration (unit length 1 μm).

In Fig. 15, the ESEM micrograph of C3 after 5 min of hydration is shown. Small rounded masses of likely ettringite are visible. At the same hydration time, the morphology of sample C4 (Fig. 16) appears more similar to its reference C2 but significantly different respect to C3. The well shaped rounded masses of sample C3 (Fig. 15) are less pronounced in the cement paste sample made with aged cement and 2% of accelerator (C4 — Fig. 16). These differences are still evident after 1 h of curing (Fig. 17 compared to Fig. 18).

ESEM micrograph of sample C5 after few minutes of hydration (Fig. 19) shows few prismatic needles and some globular masses. At similar hydration time, the morphology of C7 is completely different: a gel like material and several crystals of likely ettrigite with different dimensions are present everywhere (Fig. 20).

After 1 h, a significant increase and growth of ettringite needles is visible (Figs. 21 and 22). Nevertheless, size and amount of needles (Fig. 22) of the sample made with aged cement and 7% of the alkali-free accelerator (C7) appear significantly higher than those observed in Fig. 21.

4. Discussion

The results are in general agreement with the published literature [7–10]. As previously mentioned, the reaction between cement and water gives rise to a layer of hydrated solid phases which can cover cement grains thus slowing down further hydration (dormant period — [18]). After this stage, cement setting occurs due to a massive formation of portlandite and C–S–H (acceleration step). Alkali-free accelerators are commonly added during the dormant period, producing a layer of hydrated calcium sulphoaluminates (likely ettringite), as confirmed by the hydration temperature profile evaluation (Fig. 7), the XRD analyses (Fig. 11) and the ESEM-FEG tests (Fig. 20). Formation and growth of ettringite crystals (Figs. 20 and 22) could enhance the solid/liquid ratio and the viscosity of hydrating cement thus determining a setting time shortening. The use of high accelerator dosage (for example 7% by cement mass) favours the formation of larger amounts of ettringite (hydration temperature profile in Fig. 7; XRD in Figs. 11–13) and shortens cement paste setting time (samples C3 and C4 in comparison with respectively C5 and C7 in Fig. 1). In particular, it appears that the higher is the amount of ettringite the shorter is the final set time.

The exposure of β-hemihydrate to moisture reduces the setting time of accelerated samples (Figs. 4 and 5). This effect was investigated by evaluating β-hemihydrate water conductivity, a parameter related to the amount ionic species delivered during the dissolution process: at a fixed time, the higher is the conductivity, the faster is the salt dissolution rate. Fig. 6 shows

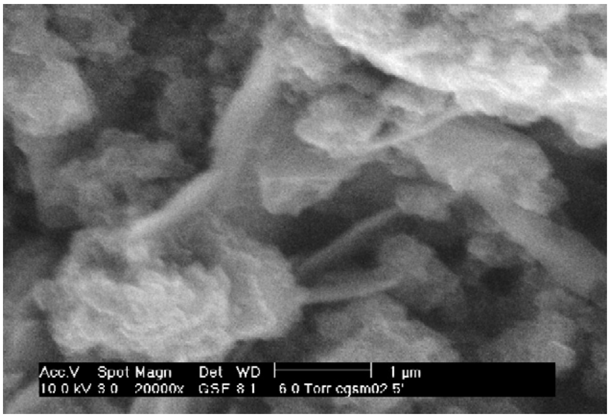

Fig. 16. ESEM micrograph of C4 after 5 min of hydration (unit length 1 μm).

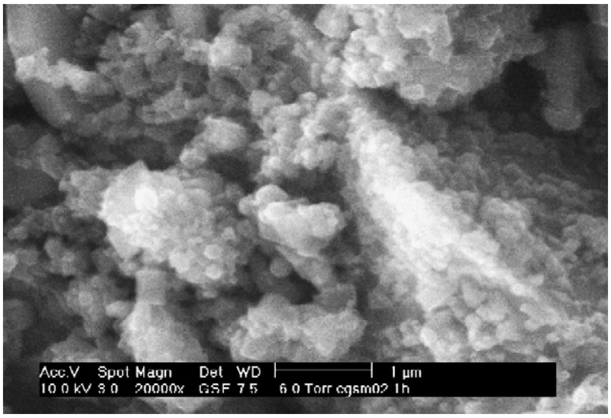

Fig. 18. ESEM micrograph of C4 after 1 h of hydration (unit length 1 μm).

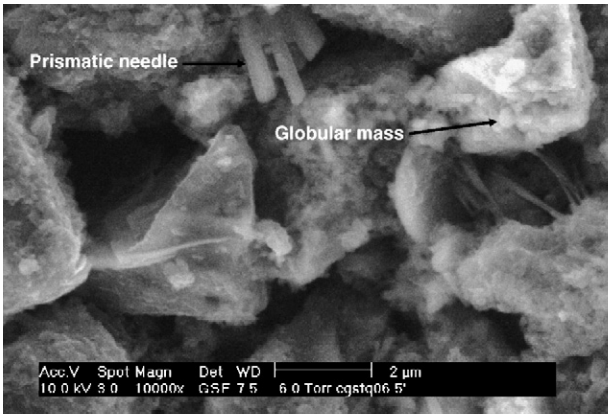

Fig. 19. ESEM micrograph of C5 after 5 min of hydration (unit length 2 μm).

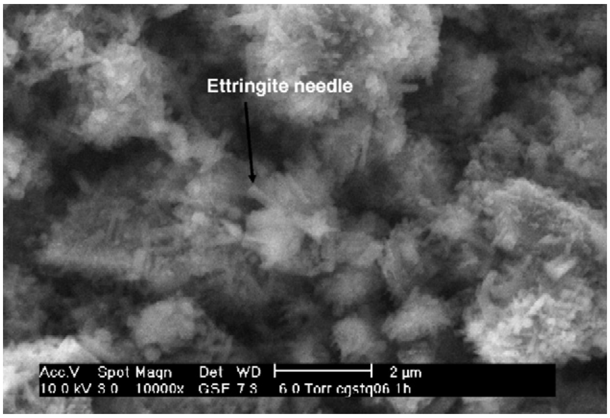

Fig. 21. ESEM micrograph of C5 after 1 h of hydration (unit length 2 μm).

an evident conductivity reduction after moist curing of the β-hemihydrate. Therefore, the dissolution rate of calcium sulphate could be a factor affecting the setting shortening. Likely, fresh and aged β-hemihydrate dissolve in water at different rates; this fact could influence the kinetics of ettringite formation and, therefore, the final set time of hydrating cement. The shift in conductivity of water mixtures which contain moist β-hemihydrate, could be connected to its transformation to gypsum, which is a phase characterised by a lower dissolution rate [19]. Nevertheless, XRD of fresh and aged cement do not show the formation of gypsum. Perhaps a partial superficial conversion occurs, which cannot be detected by XRD.

Fig. 1 shows that low accelerator dosage can retard cement setting (C3 and C4 compared respectively to C1 and C2). It was already mentioned that at early cement hydration times, aluminates and sulphates form a protective layer of ettringite [17,18] on cement grains. The retarding effect, due to the use of low accelerator dosage, could be explained supposing that the alkali-free accelerator can supply, to the cementitious pore solution, a low amount of Al^{3+} and SO_4^{2-}. Therefore, a further thin layer of ettringite could be formed. In these conditions, setting should be governed by the formation of C–S–H during the acceleration stage, and the thin coat of ettringite, arising from the alkali-free accelerator, could slow down the hydration of cement phases causing a retarded setting if compared to the samples without the accelerator.

At higher admixture dosage (7% by cement mass) a very fast setting was measured. In this case, setting mechanism is mainly connected to the formation and growth of ettringite, as confirmed by ESEM images (Figs. 19–22).

The final set time of cement pastes prepared with fresh cement and 7% of the alkali-free accelerator (C5) is longer than that measured on sample C7 (made with aged cement and 7% of the alkali-free accelerator). The ESEM micrographs (Fig. 19 in comparison with Fig. 20) and the hydration temperature profile (Fig. 7) point out a higher amount of ettringite in cement pastes made with aged cement (C7), which could be the main reason of its faster setting.

5. Conclusion

This study confirms that the action mechanism of alkali-free accelerators is mainly based on the formation and growth of ettringite crystals: they increase the solid/liquid ratio thus causing a viscosity increase of the cementitious matrix which results in a shortened final set. The early strength of the sprayed concrete is generally connected to the final set time of cement pastes admixed with the accelerator. In particular, the lower is

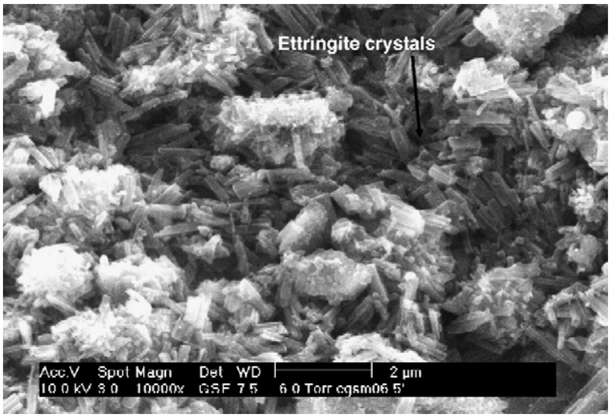

Fig. 20. ESEM micrograph of C7 after 5 min of hydration (unit length 2 μm).

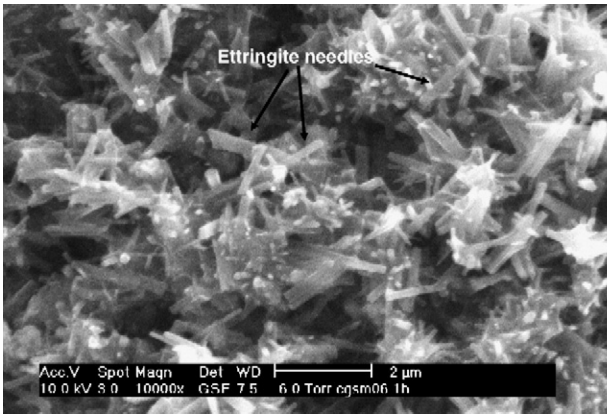

Fig. 22. ESEM micrograph of C7 after 1 h of hydration (unit length 2 μm).

the final set time, the higher should be the early bond strength. A significant setting time reduction of cement paste samples admixed with an alkali-free accelerator was observed when they are composed of a Portland cement containing β-hemihydrate that was previously exposed to moisture. Therefore, such an effect could improve the spraying operations. The phenomenon could be related to the reduction of the β-hemihydrate dissolution rate which influences the kinetics of the reaction between the alkali free accelerator (based on aluminium sulphate) and the hydrating cement phases thus affecting amount, morphology and growth of ettringite crystals. A further study is necessary to deeply investigate this phenomenon and to analyse the interaction between alkali free accelerator and Portland cements containing calcium sulphate phases with different dissolution rates.

Acknowledgements

We are grateful for the precious cooperation of Mr. Gurzì Pasquale, Mrs. Gulfo Maria Rosa of MAPEI SPA.

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