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Cement and Concrete Research 35 (2005) 2244 – 2251

Cement and Concrete Research

Combined effect of expansive and shrinkage reducing admixtures to obtain stable and durable mortars

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Received 18 August 2003; accepted 23 November 2004

Abstract

In order to improve the dimensional stability of cement based mortars, the effects produced on cement hydration of a shrinkage reducer (propyleneglycol ether based—SRA) and an expansive admixture (calcium oxide based—EXP) were investigated. Mortar samples (prepared without admixtures or with SRA or EXP or SRA and EXP) were compared through compressive strength measurements, water evaporation, restrained shrinkage and restrained expansion measurements. Setting time and free expansion were also detected on cement paste specimens.

A synergistic effect on the shrinkage reduction was observed when the shrinkage reducing admixture and the expansive agent were used together. In order to clarify this phenomenon, the hydration of cement pastes containing these kinds of admixtures was followed by ESEM-FEG (environmental scanning electron microscopy–field emission gun), TG (thermogravimetry), specific surface area measurements (by BET—Brunauer–Emmet–Teller-method) and XRDS (X-ray diffraction spectroscopy).

Keywords: Calcium oxide; Expansion; Expansive admixture; Shrinkage; Shrinkage reducing admixture

1. Introduction

The exposure of a cement based system to non-saturated environment (RH < 100%) causes drying shrinkage due to water evaporation [1]. Shrinkage is one of the main reasons of mortar failures like curling, cracks formation and debonding. Many authors have underlined the importance of dimensional stability to extend the service life of concrete structures [2,3]. Today, several methods are available to limit shrinkage: (1) expanding and non-shrinking cements [4], (2) surface treatments [5], (3) shrinkage reducing admixtures (SRA) [6] and (4) expansive admixtures [7]. In the present paper, only the last two techniques will be evaluated as a means to obtain cement systems with high dimensional stability.

2. Experimental

The study was performed by detecting mechanical, morphological and chemical properties of mortars or cement pastes having variable composition: without admixtures, with 3% (by cement mass) of an expansive agent, with 3% of a shrinkage reducing admixture and with 3% of both admixtures. The mortar specimens were characterised measuring compressive strength development, air content, unit weight, mass loss during hardening, restrained shrinkage and restrained expansion. Setting time and free expansion were determined on cement paste samples. Furthermore, restrained shrinkage and restrained expansion were also followed on other mixture compositions: 8% (by cement mass), 6%, 4%, 2% of an expansive agent; 4%, 3.5%, 2%, 1.5% of a shrinkage reducer; and different their combinations. The influence of such chemicals on cement hydration was studied by: ESEM-FEG (environmental scanning electron microscopy–field emission gun), specific surface area measurements (BET—Brunauer–Emmet–Teller-method),

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doi:10.1016/j.cemconres.2004.11.021

Table 1
Clinker mineralogical composition (determined according to ENV 196/2)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
22.1%	3.2%	4.9%	65.2%	2.0%

thermogravimetric analysis (TG) and XRDS (X-ray diffraction spectroscopy).

2.1. Raw materials

A cement type I 52,5 (according to ENV 197/1—Table 1), a propyleneglycol ether as shrinkage reducing admixture (SRA) and a calcium oxide based expansive agent (EXP) were employed for mortar and cement paste preparation. The selected properties of the admixtures are shown in Table 2. A standard (ENV 196/1) silica sand (0–2.5 mm) was used.

2.2. Mechanical tests

The mixture compositions are reported in Table 3. The mortar specimens were prepared and stored according to ENV 196/1 (40 × 40 × 160 mm). Compressive strengths were determined at 24 h, 7 and 28 days (each result is an average of six measurements). Air content (DIN 18555—each result is an average of three measurements) and unit weight (by picnometer—each result is an average of three measurements) were detected on fresh made mortar samples (0% admixture, 3% EXP, 3% SRA and 3% EXP + 3% SRA). Restrained expansion was measured according to UNI 8148 (drawn from ASTM C 845-90) by a digital length comparator Mitutoyo Model IDC 112B: three (80 × 80 × 240 mm) samples provided with metallic reinforcement (made of a 240 mm steel rod, passing through the specimen and welded to two metallic plates) were cured for 8 h at 20 °C and 95% RH; the specimens were demoulded and conditioned in water; the restrained expansion data were calculated with respect to the initial steel rod length and measured from 24 h until 28 days after mixing. Restrained shrinkage was carried out as already described for the restrained expansion test with the difference that, after 8 h at 20 °C and 95% RH, the specimens were kept in a dry environment (23 °C and 50% RH). Water evaporation was determined by mass loss measurements on cylindrical samples (each result is an average of two measurements—

Table 2
Admixture properties

Admixture type	Characteristics	
Expansive (EXP)	Chemical composition (%)	90 CaO, 10 $CaCO_3$
	Specific gravity (kg/l)	0.8
	Material retained on a 80 μm sieve (%)	98
Shrinkage reducing (SRA)	Chemical composition (%)	100 propyleneglycol ether
	Density (kg/l)	0.91

Table 3
Mixture compositions

Component	Mortars																Cement pastes			
	0% Admixture	8% EXP	4% SRA	8% EXP+ 4% SRA	6% EXP	3.5% SRA	6% EXP+ 3.5% SRA	4% EXP	2% SRA	4% EXP+ 2% SRA	3% EXP	3% SRA	3% EXP+ 3% SRA	2% EXP	1.5% SRA	2% EXP+ 1.5% SRA	P (0% admixture)	P (3% EXP)	P (3% SRA)	P (3% EXP+ 3% SRA)
Cement (g)	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Normalised sand (g)	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	–	–	–	–
EXP (g)	–	8	–	8	6	–	6	4	–	4	3	–	3	2	–	2	–	3	–	3
SRA (g)	–	–	4	4	–	3.5	3.5	–	2	2	–	3	3	–	1.5	1.5	–	–	3	3
Water/cement ratio	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.35	0.35	0.35	0.35

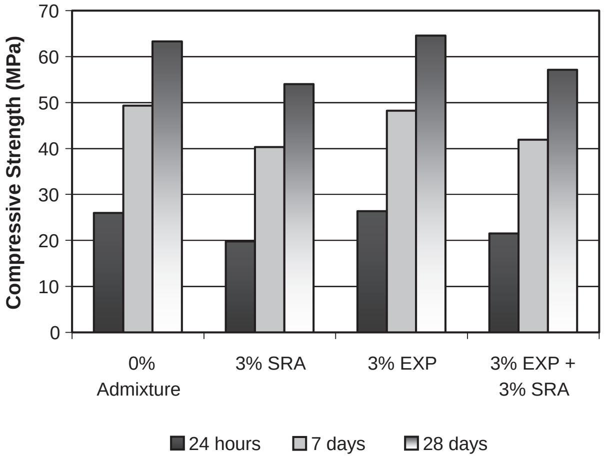

Fig. 1. Compressive strengths development.

20 × 200 mm height × diameter) stored at 23 °C and 50% RH, by a digital balance type Mettler PM 4800. Free expansion during the first 8 h was carried out on fresh prepared cement pastes (each result is an average of three measurements) determining their volume change occurring in a cylindrical metallic container (120 × 99 mm height × diameter) by two micrometric screws placed on the opposite faces of a prismatic bridge (more details are described in the Italian norm UNI 8996). Setting time (ENV 196/3) was detected on cement pastes at 23 °C and 50% RH (each result is an average of two measurements).

2.3. Physical, morphological and chemical analyses

All the investigations were performed on cylindrical cement paste samples (135 g) prepared at 23 °C and 50% RH and stored in sealed plastic containers.

An ESEM (Model XL30 ESEM-FEG—Philips) study was performed after 2 h of hydration (vapour pressure of 6.0 Torr and 5 °C by means of a Peltier stage).

The following analyses were carried out on samples ground with a mill to a particle size lower than 63 μm; the hydration was stopped replacing the physically bonded water by acetone and keeping the resulting powder at 105 °C for 24 h.

The specific surface area (BET method—each result is an average of three measurements) was measured by an instrument type Coulter Model SA 3100 after 24 h of curing. Calcium hydroxide formed after 2 and 24 h was determined by thermogravimetry (Model STA409 Netzsch). XRD patterns were also detected (Diffractometer Model PW 1830, Philips, Cu Kα radiation).

Table 4
Physical properties

Sample	Air content (%—DIN18555, Part 2)	Unit weight (kg/m^3—by picnometer)
0% Admixture	4	2250
3% EXP	4	2240
3% SRA	5	2238
3% EXP+3% SRA	5	2236

Table 5
Setting time

Sample	Setting time	
	Initial	Final
P (0% admixture)	2 h 30 min	5 h
P (3% EXP)	2 h	3 h
P (3% SRA)	4 h	6 h 30 min
P (3% EXP+3% SRA)	3 h 30 min	6 h

3. Results and discussion

3.1. Physical mechanical properties

The results reported in Fig. 1 (standard deviation: 3%) showed that the specimens added with SRA (3% SRA, 3% EXP+3% SRA) were characterised by lower compressive strengths than the reference (0% admixture). These data also suggested that EXP did not influence the compressive strength development (3% EXP and 0% admixture have similar values).

The air content among the samples was very similar (Table 4—standard deviation: 10%) and, therefore, it cannot affect the compressive strength values.

The data reported in Table 5 (standard deviation: 9%) indicated that SRA acted as a setting retarder. In water, the samples containing the expansive agent showed a significant expansion (Table 6—standard deviation: 4%). Whereas, the samples admixed with SRA were characterised by dimensional variations similar to the reference (0% admixture).

After 28 days, the restrained shrinkage test showed that a large part of the mortar bars (stored at 50% RH) were subjected to a significant dimensional contraction (Table

Table 6
Restrained expansion test (time after mixing)

Sample	24 h (μm/m)	7 days (μm/m)	28 days (μm/m)
0% Admixture	16	20	16
8% EXP	828	956	912
4% SRA	28	32	24
8% EXP+4% SRA	792	900	925
6% EXP	628	672	708
3.5% SRA	30	25	39
6% EXP+3.5% SRA	612	640	648
4% EXP	428	490	520
2% SRA	42	36	31
4% EXP+2% SRA	415	479	502
3% EXP	308	428	436
3% SRA	0	4	12
3% EXP+3% SRA	340	428	428
2% EXP	220	316	362
1.5% SRA	7	15	11
2% EXP+1.5% SRA	232	296	349

Table 7
Restrained shrinkage test (time after mixing)

Sample	24 h (μm/m)	7 days (μm/m)	28 days (μm/m)
0% Admixture	−80	−264	−525
8% EXP	534	292	88
4% SRA	−14	−142	−282
8% EXP+4% SRA	706	570	410
6% EXP	300	−128	−368
3.5% SRA	−20	−190	−310
6% EXP+3.5 SRA	524	250	187
4% EXP	122	−148	−332
2% SRA	−60	−215	−417
4% EXP+2% SRA	340	120	−52
3% EXP	64	−172	−475
3% SRA	−52	−200	−400
3% EXP+3% SRA	192	112	−100
2% EXP	43	−210	−490
1.5% SRA	−68	−220	−430
2% EXP+1.5% SRA	100	6	−203

7—standard deviation: 4.4%). This shrinkage was less pronounced for the specimens containing both admixtures (EXP and SRA). In order to verify if, at a time t after mixing, the shrinkage reduction, due to the contemporary use of SRA and EXP, arises from a synergistic interaction between the admixtures, the following considerations could be carried on (for example assuming $t=28$ days and for the system 3% SRA+3% EXP)

S_{rt}=28 days shrinkage of 0% admixture: −525 μm/m;
S_{st}=28 days shrinkage of 3% SRA: −400 μm/m;
S_{ext}=28 days shrinkage of 3% EXP: −475 μm/m;
S_t=28 days shrinkage of 3% EXP+3% SRA: −100 μm/m.

From these values, the following differences can be calculated:

Shrinkage difference between 3% SRA and 0% admixture=$\Delta SRA=|S_{st}-S_{rt}|=125$ μm/m;

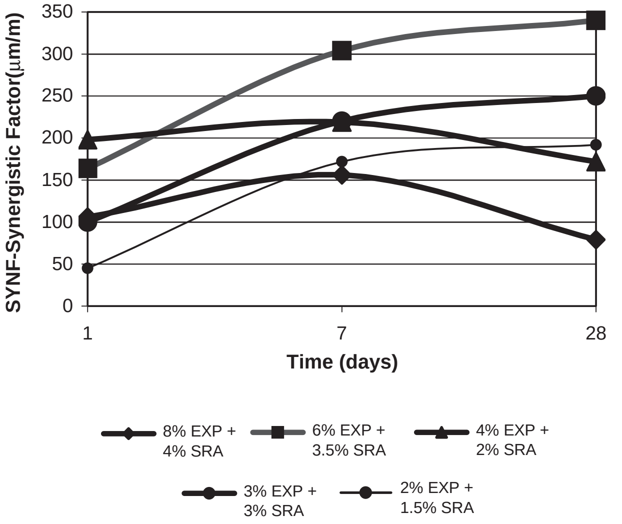

Fig. 2. Synergistic factor for different systems.

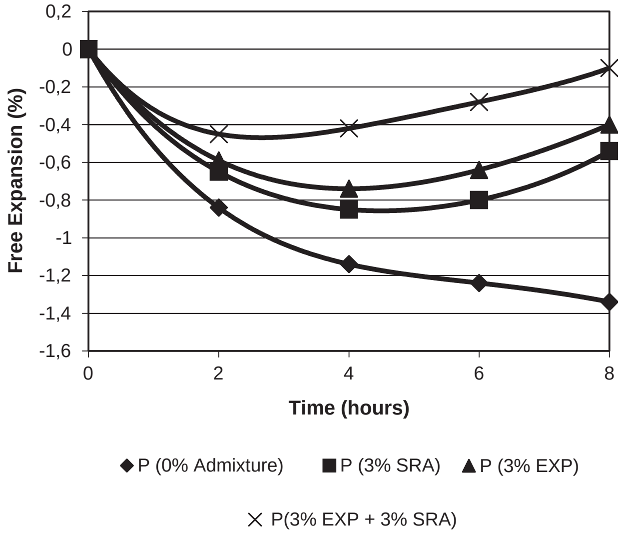

Fig. 3. Free expansion test.

Shrinkage difference between 3% EXP and 0% admixture=$\Delta EX=|S_{ext}-S_{rt}|=50$ μm/m;
Shrinkage difference between 3% EXP+3% SRA and 0% admixture=$\Delta S=|S_t-S_{rt}|=425$ μm/m.

Defining $\Delta=\Delta EX+\Delta SRA=175$ μm/m, if $\Delta=\Delta S$, the shrinkage reduction is due to the sum of the two individual admixture contributions. However, since $\Delta S>\Delta$(425 μm/m>175 μm/m), the interaction between SRA and EXP could be considered synergistic. The magnitude of synergistic effect could be connected to the difference: SYNF (synergistic factor)=$\Delta S-\Delta$. This parameter was calculated for all the systems at 24 h, 7 days and 28 days. The results (Fig. 2) demonstrated that the interaction between EXP and SRA is synergistic at all curing times and for different admixture rates.

This trend was also confirmed by the free expansion test (Fig. 3—standard deviation: 10%). The water evaporation test (Fig. 4—standard deviation: 1%) showed that, after 2 days, the admixtures slightly reduced water evaporation. This effect could contribute to the higher

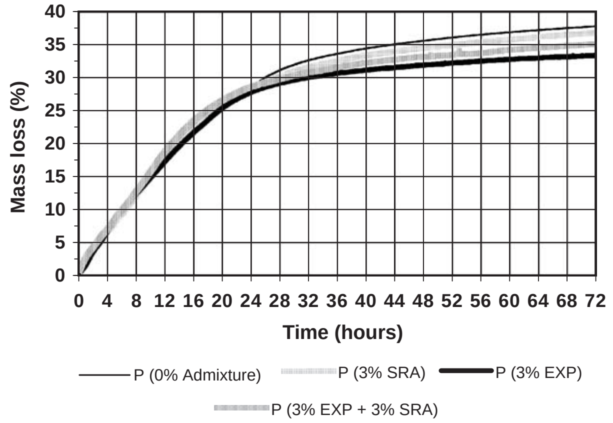

Fig. 4. Water evaporation test.

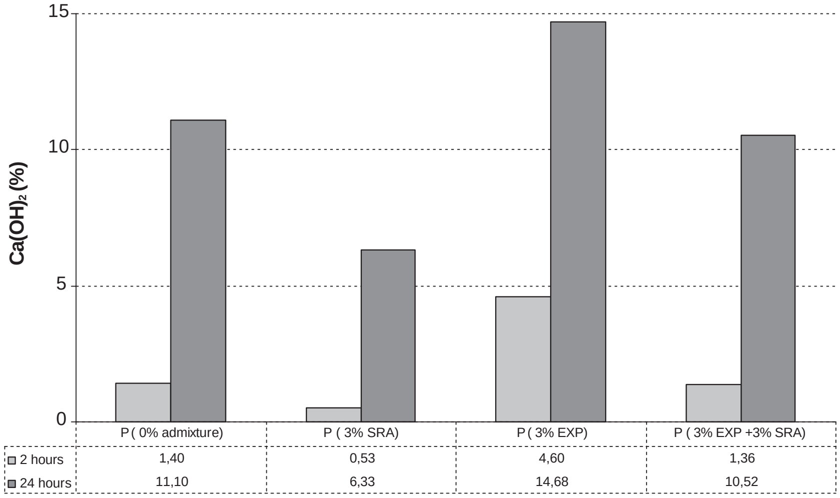

Fig. 5. Calcium hydroxide content determined by TG.

dimensional stability, at 50% RH, of 3% EXP, 3% SRA and 3% EXP + 3% SRA respect to the reference (0% admixture—Table 7).

3.2. Chemical–morphological analyses

TG analyses pointed out that SRA hindered calcium hydroxide formation (Fig. 5—standard deviation: 5%). This result is also confirmed by the literature [8].

On the contrary, as expected, the calcium oxide based admixture (EXP) significantly increased calcium hydroxide content due to the supplementary amount coming from calcium oxide hydration. After 2 and 24 h of hydration, the XRD patterns (Figs. 6 and 7) showed the formation of portlandite and crystalline ettringite. In P (3% EXP + 3% SRA), a different peak intensity between portlandite and ettringite was observed. This result could suggest a higher portlandite content compared to ettringite, for this kind of sample.

SRA increased the specific surface area of hydrating cement system (Table 8—standard deviation: 10%). Therefore, a significant effect, on the morphology of hydrating cement phases, could be expected.

In Fig. 8, an ESEM micrograph of the reference paste (0% admixture) after 2 h of hydration is presented. The typical morphology of hydrating Portland cement was evident: a gel-like material surrounding cement grains.

Typical hexagonal plates of likely portlandite were observed when only the expansive admixture was used (3% EXP—Fig. 9).

A dramatic morphology change was noted in cement pastes added with SRA (Figs. 10 and 11): some long prismatic needles were present on the material surface. According to XRD, these well-shaped prisms could be crystals of ettringite or, most probably, hydrated lime due to the fact that such crystalline formation was more pronounced when EXP was employed (which is a further source of hydrated lime—Fig. 11—3% EXP + 3% SRA).

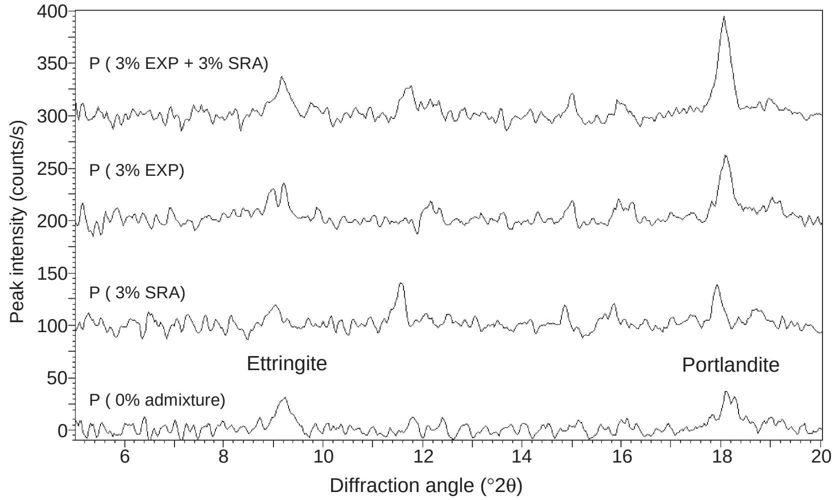

Fig. 6. XRD after 2 h of curing.

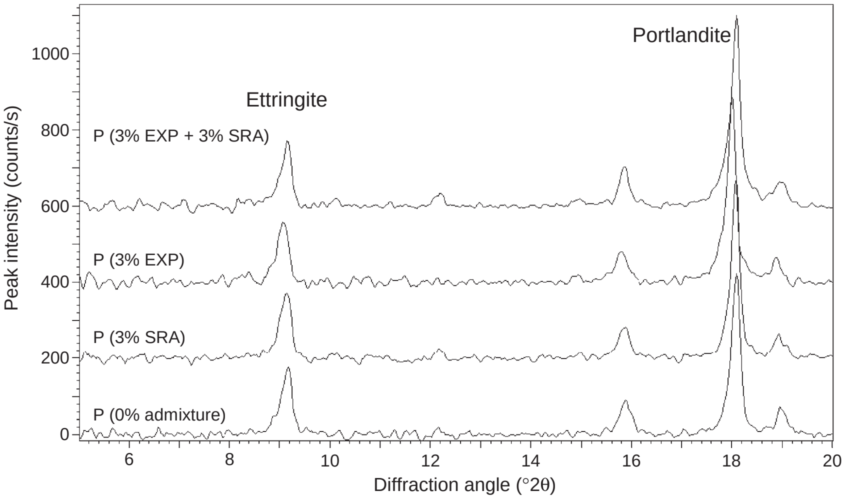

Fig. 7. XRD after 24 h of curing.

However, these crystals did not appear as hexagonal plates (c/a crystallographic axis between 0.5 and 1.5) [9], which is the normal morphological form of portlandite, but they seemed to be elongated prisms. Perhaps SRA could have influenced the morphology of precipitated calcium hydroxide. This supposition is supported by the work of Berger and McGregor [9] who investigated the morphology of calcium hydroxide developed in cement pastes admixed with many different chemicals. These crystals were too thin to be analysed by EDS (energy dispersion system) and their chemical composition was not determined.

3.3. Discussion

Today, the scientists generally agree that water evaporation is one of the main causes of material deformation through several possible mechanisms, depending on the environmental relative humidity [3,10,11]. For example, at a relative humidity higher than 40% and lower than 100%, water, in the partially filled mortar pores, can attract, by capillary pressure, the pore walls thus determining the material contraction. The lower is the capillary stress, the less pronounced is the shrinkage. A simplified expression of the capillary stress [12] is:

$$P = 2\gamma/r \tag{1}$$

where P = capillary pressure, γ = surface tension of the pore solution and r = radius of the meniscus.

Table 8
Specific surface area

Sample	Specific surface area (m^2/g)
P (0% admixture)	17.7
P (3% EXP)	18.4
P (3% SRA)	24.1
P (3% EXP+3% SRA)	23

High shrinkage may cause cracks and degradation of cementitious materials and it is a basic problem of building industry. Some admixtures, which are able to reduce shrinkage, are today commercially available [6]. Several studies [8,13] pointed out that SRA, being essentially a non-ionic surfactant, could reduce surface tension of cement pore solution. According to Eq. (1), the decrease of surface tension (γ) causes a capillary stress reduction with a consequent decrease of drying shrinkage. Our experimental results (Table 7) confirmed that SRA was able to reduce drying shrinkage at 23 °C and 50% RH. As a matter of fact, at all curing ages, the specimens with added SRA shrank less compared to the reference one (0% admixture). If the samples were cured in water (restrained expansion test—Table 6), SRA did not affect the dimensional variations of the cementitious system. The similarity of the dimensional behaviour of 0% admixture and the samples admixed with SRA (Table 6) suggested that, in this case, as the specimens were not subjected to evaporation, drying shrinkage and capillary

Fig. 8. ESEM micrograph of P (0% admixture) after 2 h of curing.

Fig. 9. ESEM micrograph of P (3% EXP) after 2 h of curing.

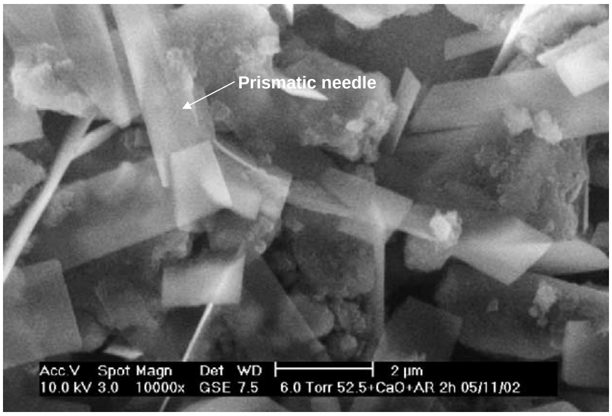

Fig. 11. ESEM micrograph of P (3% EXP + 3% SRA) after 2 h of curing.

stress were not operative and, therefore, SRA was not effective.

The use of expansive agents such as, for example, alkaline earth metal oxides (in particular calcium and magnesium oxide) [7], is another method commonly employed from the concrete admixture manufacturers, to reduce shrinkage. These chemicals reacting with water slowly produce an expansion due to the formation of the corresponding hydroxide. The transformation of calcium oxide to calcium hydroxide causes a molar solid volume increase of about 90% [14], which, at proper rates, could compensate material contraction. The mechanism of expansion has been already studied. Chatterji [14] described the expansion in terms of delayed calcium hydroxide formation. This compound, having a molar volume higher than calcium oxide, gives origin to a crystal growth pressure. According to the scientist, the expansion is strictly related to the solubility of calcium hydroxide: the higher the solubility, the more diffused is the migration of calcium ions, the higher is the distribution of calcium hydroxide and the lower is the expansion. The experimental results (Table 6 in comparison with Table 7) showed that the expansive agent is more effective for water immersed samples. Calcium oxide is strongly embedded in the cement matrix and likely the mixing water alone could not be enough to complete its reaction with water. Therefore, an external supply of water (through water immersion) could allow a better calcium oxide hydration, which favours a full expansion. On the contrary, at 23 °C and 50% RH, calcium hydroxide formation, due to the initial slight calcium oxide hydration, could not completely compensate shrinkage. In fact, after 28 days (Table 7), the specimens containing a lower dosage of EXP (6% EXP, 4% EXP, 3% EXP and 2% EXP) were characterised by a small shrinkage reduction respect to the reference (0% admixture). At 23 °C and 50% RH, when the admixtures were used together, a low shrinkage or an expansion were observed (Table 7). As already mentioned (Fig. 2), we demonstrated that the effect of shrinkage reduction is due to a synergistic interaction between EXP and SRA. A first hypothesis of this synergism could be the possible massive formation of elongated crystals (Fig. 11). These crystals could favour an initial expansion of the cement system, which could compensate the material contraction. The expansive effect due to crystal growth has been studied [14–17].

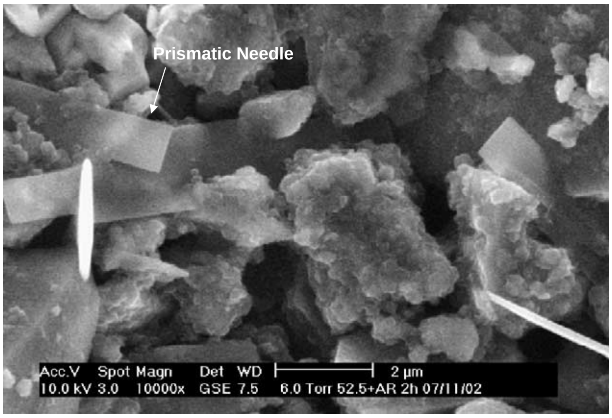

Fig. 10. ESEM micrograph of P (3% SRA) after 2 h of curing.

Furthermore, hypothesising that such crystals were mainly composed of portlandite, Chatterji [14] stated that the lower is the solubility of calcium hydroxide, the higher was the mortar expansion. SRA, being an organic hydrophobic molecule, could reduce the permittivity of water, and thus decreasing the ability of water to dissolve salts [18]. Therefore, SRA could reduce the water solubility of calcium hydroxide, which is already low, promoting the material expansion and compensating more efficaciously the shrinkage.

4. Conclusion

The use of an expanding agent (calcium oxide based) with a shrinkage reducing admixture (propyleneglycol ether based) allows to obtain mortars less sensitive to drying. A synergistic effect that was observed between the mentioned admixtures and some hypothesis were proposed to explain it.

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