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Water-entrained cement-based materials II. Experimental observations☆

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Abstract

This paper concerns a new concept for the prevention of self-desiccation in hardening cement-based materials. The concept is based on using fine, superabsorbent polymer (hydrogel, SAP) particles as a concrete admixture. This permits a controlled formation of water-filled macropore inclusions—water entrainment—in the fresh concrete. Consequently, the pore structure is actively designed to control self-desiccation. In the paper, experimental observations in relation to this technique are described and discussed. The observations show that self-desiccation can be controlled by water entrainment. The paper forms the second part of a series. In the first part, the theoretical background was presented [Cem. Concr. Res. 31(4) (2001) 647]. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Curing; Shrinkage; Admixture; High-performance concrete; Water entrainment

1. Introduction

The development of high-performance concrete (HPC) in the early 1980s was a significant progress in concrete technology. Initially, attention focused on the increased strength potential of HPC, but today HPC is considered to be a concrete with various properties useful for many different applications. The industrial use of HPC, however, showed that early-age cracking is a considerable problem for these concretes. Subsequent research in the 1990s showed that self-desiccation shrinkage is the major cause of crack formation in HPC. A solution to this problem is very important for the further development within this field. A historical overview including an explanation of terminology has been published previously [2].

This paper suggests a possible solution to this problem: so-called water entrainment by means of incorporation of superabsorbent polymer (SAP) particles in the cement-based material. This leads to a controlled formation of water-filled macropore inclusions in the fresh concrete, which prevents self-desiccation shrinkage of the hardening concrete. The principles and theoretical background of water entrainment were described in a previous paper [1]. The present paper reports experimental observations with focus on autogenous deformation, autogenous relative humidity (RH) change, and stress development during restrained hardening. A closer examination of other important properties, especially mechanical properties, is presently being carried out.

2. Materials and methods

2.1. Materials

White Portland cement was used with a Blaine fineness of 420 m^2/kg and the following Bogue-calculated phase composition (in wt.%): C_3S: 66.1, C_2S: 21.2, C_3A: 4.3, C_4AF: 1.1, $C\bar{S}$: 3.5, free CaO: 1.96, Na_2O eq.: 0.17.

The silica fume was added as a dry powder at a rate of 20 wt.% of cement. The specific surface of the silica fume is 17.5 m^2/g (BET method). The chemical composition is (in wt.%): SiO_2: 94.1, Fe_2O_3: 1.00, Al_2O_3: 0.13, MgO: 0.71, SO_3: 0.43, and Na_2O eq.: 1.09.

The superplasticizer was added at a rate of 1.0 wt.% of cement+silica fume. The superplasticizer is a naphtalene-based dry powder.

☆ A patent application on the concept *water-entrained cement-based materials* has been filed by the company Densit, Aalborg, Denmark. However, the opinions expressed in this paper are entirely the responsibility of the authors.

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Quartz sand 0–2.5 mm with a water absorption of 0.1% was used for the mortars. By volume, the mortars contain 60% aggregate.

Two different SAPs were used. The SAPs were added at a rate of 0–0.6 wt.% of cement. Both SAPs are covalently cross-linked acrylamide/acrylic acid copolymers: (1) SAP Type A is suspension polymerized, spherical particles with an average particle size of approximately 200 μm, (2) SAP Type B is solution-polymerized and after crushing sieved to particle sizes in the range of 125–250 μm. The given particle sizes apply to the dry state. The size of the swollen SAP particles in the cement pastes and mortars is about three times larger due to pore fluid absorption. The swelling time depends especially on the particle size distribution of the SAP. For the two types of SAP, Fig. 1 shows that more than 50% swelling occurs within the first 5 min after water addition. The water content in SAP at reduced RH is indicated by the sorption isotherm in Fig. 2.

Demineralized water was used for the cement pastes and mortars. The basic water-to-cement ratio (w/c) is 0.30 in all mixes—i.e., the w/c ratio not including entrained water. The w/c is by weight and does not include silica fume. Mixes with SAP additionally contain entrained water. An amount of entrained water equal to $(w/c)_e=0.05$ was added at an SAP addition of 0.4% for SAP Type A and 0.3% for SAP Type B. At other SAP additions, proportional amounts of water were entrained, i.e.,

$$(\mathrm{w/c})_\mathrm{e} = K(\mathrm{SAP/c});$$
$$K = \begin{cases} 12.5\ \mathrm{g/g\ dry\ gel\ for\ SAP\ Type\ A} \\ 16.7\ \mathrm{g/g\ dry\ gel\ for\ SAP\ Type\ B} \end{cases} \qquad (1)$$

where (SAP/c) is the weight ratio of dry SAP to cement and K is the actual water uptake of SAP in the cement paste.

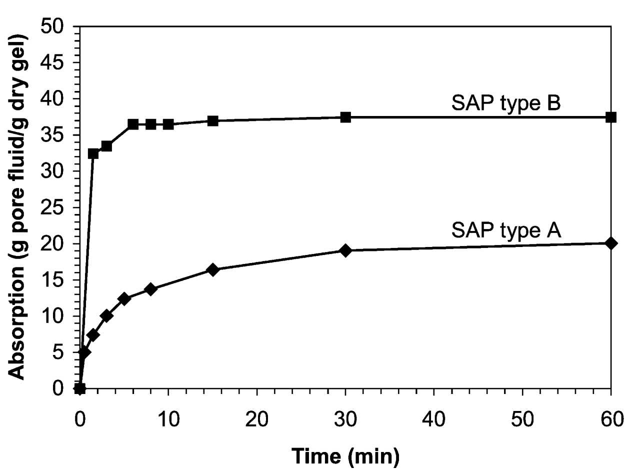

Fig. 1. Absorption kinetics for two SAPs in synthetic pore fluid with the following composition (see e.g., Ref. [3] (mmol/l): $[Na^+]=400$, $[K^+]=400$, $[Ca^{2+}]=1$, $[SO_4^{2-}]=40$, $[OH^-]=722$. Observations of SAP swelling in cement pastes indicate that the total absorption is about half the amount shown here for synthetic pore fluid. The dry weight at 105 °C is the reference.

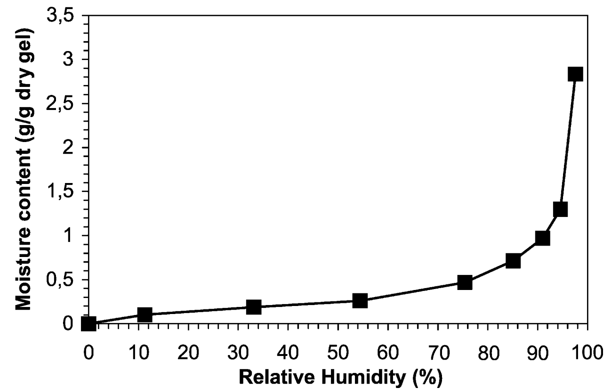

Fig. 2. Absorption and desorption isotherm (identical) for SAP Type B. The RHs were controlled by saturated salt solutions. The free liquid uptake amounts to approximately 350 g/g in distilled water and 37 g/g in synthetic pore fluid (cf. Fig. 1 and Ref. [1]). The dry weight refers to oven drying at 105 °C.

2.2. Mixing and sample preparation

The ingredients were mixed in a 5-l epicyclic mixer. Before water addition, all other components were mixed dry for 1 min followed by water addition and 5-min wet mixing for the pastes and 10-min wet mixing for the mortars. The water was added in two steps to assure the homogeneity of the mix and the dispersion of the silica fume. The temperature of the ingredients was approximately 20 °C at mixing.

For cement pastes with SAP Type A, the SAP particles tended to separate due to their lower density compared to the bulk cement paste. This problem was not encountered with the mortars or with cement pastes with SAP Type B. A stable paste could be created by assuming a slightly lower K for SAP Type A, since this would increase the viscosity of the paste. However, in the present case, rotation was used instead; after casting of the cement pastes with SAP Type A, the samples were slowly rotated for 7 h. At that time, the pastes were viscous enough to prevent separation of the SAP.

The setting time for the pastes was measured by the temperature rise and the Vicat needle test in separate samples. The setting time was 9–10 h at 20 °C, both for pastes with and without SAP.

2.3. Measuring techniques

Autogenous deformation of cement pastes was measured by a special measuring technique, where the cement paste is encapsulated in thin, corrugated polyethylene moulds with *l*/*d* approximately 300:30 mm [4]. This ensures insignificant restraint of the hardening cement paste and permits measurements to commence at an early age. Two different dilatometers were used for the measurements: (1) a dilatometer equipped with a manual dial gauge for measurement of long-term deformation and (2) a dilatometer equipped with automatic data-logging and electronic linear

Fig. 3. ASG to evaluate the cracking susceptibility of mortars. Strain gauges are mounted on the inside of the inner steel ring to measure the deformation. During measurement, the top surface is covered with acrylic glass. The mortar ring has a cross-section of 50×50 mm [7].

displacement transducers for high-precision measurements during the first few weeks of hardening. With the manual dilatometer, the first measurement was taken 8.5 h after water addition, close to set. Measurements in the automatic dilatometer were commenced 7 h after water addition. A further description of the dilatometric technique can be found in the literature [4].

Autogenous RH change of cement paste was measured by a Rotronic Hygroscope DT (Rotronic, Basserdorf, Switzerland) equipped with WA-14TH and WA-40TH measuring cells, which are built into a thermostatically controlled box (±0.1 °C). Before and after every experiment, the equipment was calibrated with saturated salt solutions in the range 75–100% RH. Autogenous RH change was measured simultaneously on two identical samples. A thorough description of the Rotronic Hygroscope and the sample preparation is published elsewhere [5].

Cracking susceptibility was evaluated on mortars with an annular shrinkage gauge (ASG) (Fig. 3). Such a test is somewhat similar to a uniaxial test [6]. An inner steel ring of the ASG partly restrains the autogenous shrinkage. This gives rise to a uniform, radial pressure on the steel ring and induces tensile hoop stresses in the mortars. Due to the tensile stresses, the mortars may crack during the measurement. The stress build-up was followed by strain gauges on the inside of the inner steel ring. The ASG was thermostatically controlled to 20 °C, however, due to heat of hydration, the temperature in the mortar increased during an 8-h period by up to 4 °C.

3. Results and discussion

Fig. 4 shows the autogenous RH change in the investigated hardening cement pastes with different amounts of SAP. At no SAP addition, a significant autogenous lowering of the RH is observed. After 3 weeks of sealed hardening,

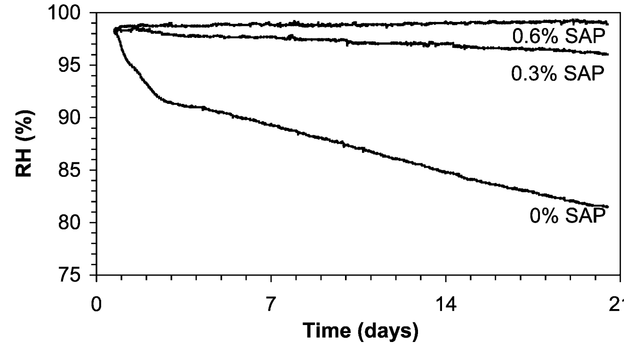

Fig. 4. Autogenous RH change of cement pastes with different amounts of SAP Type A and, consequently, different amounts of entrained water according to Eq. (1). SAP additions are given by weight of cement, where 0.6% corresponds to an entrained w/c of 0.075. Basic w/c is 0.3 for all mixes. Temperature: 20 °C.

the RH is approximately 80% due to the hydration reactions. Water entrainment based on SAP addition is seen to be efficacious in counteracting autogenous RH change: The autogenous RH change is counteracted partly at 0.3% SAP addition and fully at 0.6% SAP addition. The slight autogenous RH change to about 99% RH at 0.6% SAP addition can be accounted for by dissolved salts in the pore fluid [8].

Measured autogenous deformation of hydrating cement pastes with different amounts of SAP is shown in Fig. 5. For easy comparison, each deformation course has been adjusted to zero at the time of set, approximately 9 h after water addition [4].

Water entrainment based on SAP addition is seen to have a strong effect on the autogenous deformation after setting. At no SAP addition, a considerable shrinkage, approximately 3700 microstrain, is developed during 3 weeks of sealed hardening. Additions of 0.3% and 0.6% SAP led to a successive reduction of this shrinkage and even induced an expansion right after set. This expansion is a result of the internal water curing from the SAP; if there is a continuous supply of water to a concrete during hydration, it is well known that concrete expands. Powers explained this to be a result of absorption of water by the cement gel. The

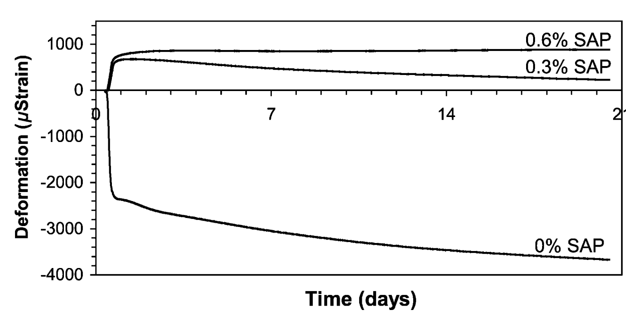

Fig. 5. Autogenous deformation from setting of cement pastes with different amounts of SAP Type A and, consequently, different amounts of entrained water according to Eq. (1). SAP additions are given by weight of cement, where 0.6% corresponds to an entrained w/c of 0.075. Basic w/c is 0.3 for all mixes. Temperature: 20 °C.

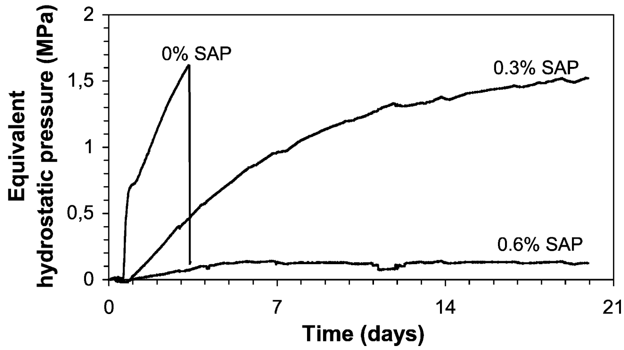

Fig. 6. Equivalent hydrostatic pressure developed in the ASG by mortars with different amounts of SAP Type A and, consequently, different amounts of entrained water (cf. Eq. (1)). SAP additions are given by weight of cement, where 0.6% corresponds to an entrained w/c of 0.075. Basic w/c is 0.3 for all mixes. Temperature: 20 °C.

expansion may amount to approximately 1000–2000 microstrain for a neat cement paste [9]. The observed expansion for the cement pastes in Fig. 5, approximately 1000 microstrain, is in agreement with this range. At 0.6% SAP addition, full shrinkage compensation is achieved. From 2 days to 3 weeks after water addition, an expansion of approximately 50 microstrain is measured. In relation to other deformation mechanisms, e.g., thermal deformation, this is negligible.

Fig. 6 shows the stress development during sealed, restrained hardening of mortars with different amounts of SAP. As can be seen, significant tensile hoop stresses are induced in the mortar without SAP addition: After approximately 3 days of hardening, this mortar cracks as indicated by the stress relief. Water entrainment based on SAP addition is seen to be efficacious in counteracting the stress build-up. The stress build-up is counteracted partly at 0.3% SAP addition and almost fully at 0.6% SAP addition. The slight stress, approximately 0.15 MPa, measured at 0.6% SAP addition may be induced by the slight temperature change during hydration (cf. Section 2.3). In any case, none of the two mortars at 0.3% and 0.6% SAP addition cracked within the 3-week period.

All the above observations are in agreement with one another; autogenous RH change (Fig. 4), autogenous deformation (Fig. 5), and stress build-up (Fig. 6) all indicate that SAP addition can prevent self-desiccation and consequently mitigate cracking during sealed, restrained hardening.

Digital image analysis of plane polished sections of cement pastes with SAP Type B was also carried out. The water-filled macropore inclusions due to the SAP particles were easy to identify, and based on this, the water uptake of the SAP in the cement pastes was calculated. In the cement pastes, the water uptake of SAP Type B was about 17 g/g dry gel—much lower than in synthetic pore fluid (cf. Fig. 1).

For SAP Type A, 0.4% addition corresponds to an entrained $(w/c)_e$ of 0.05 (cf. Section 2.1). According to theoretical considerations [1], a cement paste with a basic w/c ratio of 0.30 requires an entrained w/c of 0.05 to prevent self-desiccation. This seems to be in reasonable agreement with the results in Fig. 4: Above 0.3% SAP addition, almost no RH lowering is observed during the first 3 weeks of hardening. In any case, the calculated entrained w/c needed to prevent self-desiccation should be considered an estimate, since for example silica fume is not taken into consideration.

The experiments shown in Figs. 4, 5, and 6 refer to sealed curing of the pastes. However, in practice, a concrete has to equilibrate to the surroundings sooner or later. This will normally imply a desiccation of the concrete. The measurements shown in Fig. 7 elaborate this aspect. When the investigated cement pastes are exposed to drying at 50% RH after sealed curing for 4.5 months, a residual shrinkage is observed. The residual shrinkage depends systematically on the amount of entrained water. During 1 year of drying exposure, the cement paste without SAP addition exhibits 1100 microstrain of residual shrinkage, whereas the cement paste with 0.4% SAP shrinks 1900 microstrain.

The increased residual shrinkage of the water-entrained cement pastes is a consequence of the higher RH in these cement pastes after autogenous curing. As indicated by Fig. 4, the non-water-entrained cement paste will have an internal RH of approximately 75%, whereas the cement paste with maximum water entrainment will have an internal RH close to 100% after autogenous curing. Considering total shrinkage, the water entrainment is seen to have a significant effect: The effect of water entrainment on autogenous deformation completely overrides the effect of residual shrinkage.

During drying of the cement pastes in Fig. 7, differential stresses develop across the samples. The surface layer is subjected to tensile hoop stresses, whereas the interior is under compression. These stresses may potentially lead to cracking. However, a visual examination of the samples did not disclose any cracking within the considered time scale of approximately 1.5 years. Consequently, this simple test did not indicate an increased cracking potential during subsequent drying despite an increased residual shrinkage for the water-entrained cement pastes.

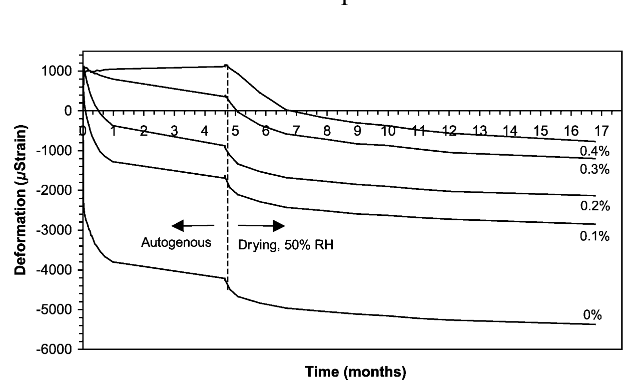

Fig. 7. Autogenous deformation from setting followed by drying shrinkage of cement pastes with different amounts of SAP Type B and, consequently, different amounts of entrained water (cf. Eq. (1)). Basic w/c is 0.3 for all mixes. After approximately 4.5 months, the corrugated moulds are removed and the pastes are exposed to drying at 50% RH. Temperature: 20 °C.

A number of parameters have been examined with respect to the shrinkage reducing effect of SAP. These include the amount of SAP addition as illustrated above and the SAP particle size, which will be discussed below. SAP chemistry is also important for their usability in cementitious systems, but this will not be addressed here.

The size of the SAP particles affect their performance in concrete, such as their mechanical stability during mixing and their influence on the rheology of the fresh concrete. With respect to the ability of SAP to reduce autogenous shrinkage, the SAP particle size is also of major importance. A series of preliminary autogenous deformation experiments indicated that an optimum SAP particle size exists; particles that are either smaller or larger than this optimum size are less effective in reducing autogenous shrinkage. Several phenomena may be involved in this.

If the SAP inclusions are large, they may not be able to fully supply every part of the cement paste with water during hydration. Computer simulations indicate that the water diffusion in a cement paste is effectively limited to distances of the order of 100–200 μm when the capillary pore space is depercolated [10]. Very large SAP particles may also have a reduced efficiency due to insufficient time for water uptake during mixing. On the other hand, if the SAP inclusions are small, their shrinkage reducing effect may be partly offset by filling with hydration products or a less active surface zone of the SAP particles compared to the bulk. These points are summarized in Fig. 8.

A number of concrete properties will be influenced by water entrainment. In addition to autogenous deformation, RH change and stress build-up during restrained hardening other properties should also be examined such as frost resistance and chloride ingress. Two additional observations will briefly be addressed here.

Potentially, SAP may influence the setting time and hydration development of cement due to leaching of extraneous substances from the SAP. In the present project, this effect has been registered by measurements of the semi-adiabatic temperature development in hardening cement paste samples. These measurements show that depending on the SAP type both acceleration and retardation may be observed. In this project, modifications of the setting time of less than 1 h were observed for the pastes and mortars.

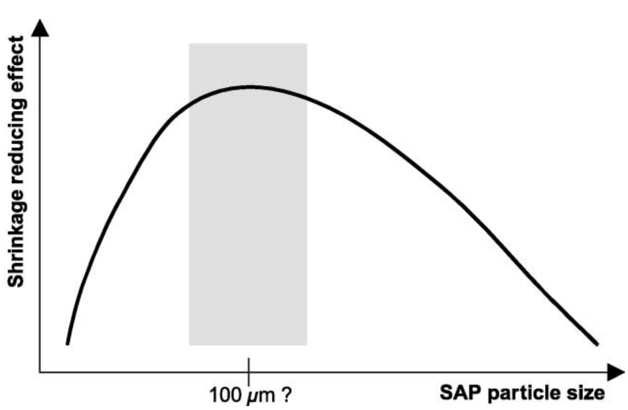

Fig. 8. Suggested schematic effect of SAP particle size on reduction of autogenous shrinkage. The suggested optimum size, about 100 μm, refers to the swollen state.

A preliminary test of the influence of water entrainment on the mechanical properties was also carried out. Compressive strength was measured on 45×90-mm mortar cylinders after 1 day of sealed curing followed by 27 days of water curing at 20 °C. The average of three samples was 134 MPa for a reference mortar (0% SAP) and 109 MPa for a water-entrained mortar (0.6% SAP), i.e., the strength was reduced by 19% due to the water entrainment.

According to a theoretical estimate [1], the maximum strength of the water-entrained mortar should be comparable to the strength of the reference mortar. However, the measured lower strength of the water-entrained mortars in the present case may be a result of the moisture condition of the samples. Two opposite extremes exist:

1. The water curing has resulted in complete saturation of both the water-entrained and the non-water-entrained samples. In that case, the samples should have achieved the same degree of hydration, and consequently the lower strength of the water-entrained mortar is due to the higher porosity induced by water entrainment. However, this is an unrealistic comparison, since in ordinary structures it is normally not possible to ensure water curing from an external source.

2. The permeability of the samples is too low to allow ingress of curing water into the samples. In that case, the samples will have a different moisture condition when tested for compressive strength: The water-entrained samples will be moist due to the water entrainment whereas the reference mortar will have a lowered RH due to self-desiccation (cf. Fig. 4). Bartlett and MacGregor [11] reported the effect of moisture condition on the compressive strength of a well-hardened HPC. The average strength after drying in laboratory air with RH<60% was 98 MPa whereas it was 76 MPa after soaking in water, i.e., a 22% lower strength compared to the dry condition.

It thus seems that the measured lower strength of the water-entrained mortar compared to the reference mortar may be caused by the moisture condition. If samples are cured in a realistic way and tested at identical moisture conditions, the water-entrained mortar may have a strength comparable to the reference mortar, as predicted. However, further experiments are needed to document this.

4. Conclusion

The results presented in this paper show that it is possible to avoid self-desiccation in hardening HPC by means of water entrainment. Autogenous RH change and autogenous shrinkage after setting, as well as cracking during restrained hardening, can be avoided when SAPs are used as a water-entraining admixture.

A large number of cement paste and concrete properties need to be examined before this technique can be implemented in practice. Mechanical properties such as compressive strength and cracking due to long-term shrinkage may be of primary interest. Potential problems with SAP addition include change of setting time and rheology, separation of SAP particles, and grinding of SAP particles during mixing due to aggregate particles. In the present case, these phenomena were not preventive for the usage of SAP.

Complete elimination of autogenous shrinkage based on water entrainment may not be necessary. Optimally, only the amount of water entrainment required to avoid cracking due to restrained autogenous shrinkage should be used. This will be more economically attractive and will minimize possible negative side effects such as residual shrinkage or adverse influence on the rheological properties.

Acknowledgments

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