Cement & Concrete Composites 31 (2009) 195–203

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Self-healing ability of fly ash–cement systems

Pipat Termkhajornkit [a,*], Toyoharu Nawa [b], Yoichi Yamashiro [c], Toshiki Saito [d]

[a] Lafarge Research Centre, Reactive Components Department, 95 Rue de Montmurier 38290, St. Quentin Fallavier, France
[b] Division of Solid Waste, Resources and Geoenvironmental Engineering, Graduate School of Engineering, Hokkaido University, N13 W8 Kita-ku, Sapporo 060-8628, Japan
[c] Civil Engineering Department, Hokuden-Kogyo Co., Ltd., Sapporo, Hokkaido, Japan
[d] Civil Engineering Department, Hokuden General Engineering Design and Consulting Company Inc., Sapporo, Hokkaido, Japan

ARTICLE INFO

Article history:
Received 30 July 2007
Received in revised form 9 September 2008
Accepted 28 December 2008
Available online 3 January 2009

Keywords:
Self-healing
Fly ash
Hydration reaction

ABSTRACT

Concrete is susceptible to cracking due to both autogenous and drying shrinkage. Nevertheless, most of these types of cracks occur before 28 days. Because fly ash continues to hydrate after 28 days, it is likely that hydrated products from fly ash may modify microstructure, seal these cracks, and prolong the service life. This research investigates the self-healing ability of fly ash–cement paste. Compressive strength, porosity, chloride diffusion coefficients, hydration reactions and hydrated products were studied. The research focuses on behavior after 28 days. According to the experimental results, the fly ash–cement system has the self-healing ability for cracks that occur from shrinkage. The self-healing ability increased when the fraction of fly ash increased.

1. Introduction

The self-healing ability of concrete has been researched for over a decade. Jacobsen and Sellevold [1,2] reported the self-healing of concrete after deterioration: concretes that lost as much as 50% of initial relative dynamic modulus during freeze/thaw cycling could recover almost completely during subsequent storage in water. Edvardsen [3] has reported autogenous healing of cracks in concrete during water flow: the experimental studies showed the formation of calcite in the crack to be the main reason for the autogenous healing. Reinhardt and Jooss [4] have reported permeability and self-healing of cracked concrete as a function of temperature and crack width. The mechanism involved water flow from an external supply. Neville [5] has reported that there are two major hypotheses regarding the reactions in self-healing mechanisms: the hydration of anhydrous cement available in the microstructure of hardened concrete and the precipitation of calcium carbonate $CaCO_3$. Granger et al. [6] have reported that the self-healing of cracks in an ultra high-performance cementitious material by mechanical tests and acoustic emission analysis.

From the literature review, in all cases, additional water is essential for the self-healing mechanism. This is not a problem for underground structures where water saturation generally exists. However, for aboveground structures, the availability of water is limited.

Meanwhile, fly ash is a pozzolanic material that reacts with $Ca(OH)_2$ from cement hydration and produces C–S–H gel. In fact, this reaction is less influenced by the availability of free water than the hydration reaction of cement [7].

Fly ash is also effective for improving various properties of concrete such as long term compressive strength, permeability and resistance to chloride diffusion. The C–S–H gel produced by the pozzolanic reaction of fly ash may seal micro cracks, and accordingly it is expected that the concrete made with cement and fly ash may show self-healing ability.

The objective of this research is to investigate the self-healing possibility of fly ash–cement systems. The factors in this study are compressive strength, chloride diffusion, the cracks and/or the porosity formation, the hydration of cement and fly ash and hydrated products such as C–S–H gel and $Ca(OH)_2$.

As for the hydration analysis, the individual hydrations of fly ash and cement were estimated by combination of selective dissolution and XRD-Rietveld analysis [7]. As for the cracks and/or the porosity formation, it is difficult to precisely measure the position and width of cracks in concrete because a multitude of factors influence the crack formation. In particular, in the case of a very small crack, the crack widths measured externally are not constant over the complete specimen height [4]. On the other hand, pore-structure modification can be detected by the mercury intrusion porosimetry. Jacobsen and Sellevold [1] have investigated the self-healing effects of conventional concrete by mercury intrusion porosimetry. Therefore, in this study, the pore modification measured by mercury intrusion porosimetry was used to analyze the cracks and the pore formation.

* Corresponding author. Tel.: +33 4 74 82 83 87; fax: +33 4 74 82 80 11.
E-mail address: pipat.termkhajornkit@lafarge.com (P. Termkhajornkit).

0958-9465/$ - see front matter Crown Copyright © 2009 Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconcomp.2008.12.009

2. Experiment

Ordinary Portland Cement (OPC) and fly ash type II following to JIS R5210 and JIS A6201 are used in this study. The physical and chemical properties of the fly ash and OPC are shown in Table 1. Paste samples were prepared with the water–binder ratio of 1.45 by volume. The cement was replaced with fly ash. The replacement ratios were 0%, 15%, 25% and 50% by volume, therefore, the water–binder ratio by weight are 0.48, 0.49 and 0.53, respectively. Samples were cured with a sealed curing condition so that there is no water exchange with the environment.

The compressive strength of the hardened pastes was measured until 182 days. The hydration degree and porosity were measured until 365 days. The compressive strength was the average value from three measurements and the porosity was based on one measurement. The standard method for compressive strength measurement in this study is JIS R5201. The effective chloride diffusion coefficient was measured at 28 and 91 days by acceleration method according to Japanese standard JSCE-G571-2003. This standard applies to concrete materials, but was adapted to paste specimens in this study. The paste was prepared in a cylinder mold with height and diameter of 200 and 100 mm, respectively. At each required age, the middle part of the specimens was cut. The thickness of specimen was 50 mm. The specimen was pre saturated with water for 24 h. The accelerated method was conducted under an applied electric potential of 15 V across samples. NaCl solution and NaOH solutions were prepared at cathode and anode with concentration 0.5 and 0.3 mol/L, respectively. The concentration of Cl ion in the solution at cathode and anode were measured by an ion chromatography. In this experiment, only FA 0% and FA 25% were tested.

At the required age, the samples were broken into 2.5–5.0 mm pieces by hammer, soaked in acetone to stop the hydration reaction, and further dried at 105 °C. A part of each of the samples was kept in a desiccator for mercury intrusion testing. The remaining material was ground in a disc mill until particles smaller than 75 μm were created. The determination of the amount of unhydrated fly ash was based on the selective dissolution method using HCl and Na_2CO_3 solutions [8]. It should be noted that the different cracking and drying methods can give the different results of the porosity and the hydration degree; however, these matters are outside the scope of this study.

As for the XRD-Rietveld analysis, Cu Kα X-ray diffraction equipment was used. The experiments were carried out in the range of 5–70° in 2θ with 0.02 step scan and 1.00 s/step speed. The divergence slit, scattering slit and receiving slit were 1/2°, 1/2° and 0.3 mm, respectively. 10% of corundum was used as an internal reference. The sample and the internal reference were carefully mixed until a homogeneous color and texture were obtained. The Rietveld analysis program used in this study was the SIROQUANT version 3 software [9]. The hydration degree of cement and fly ash were measured until 365 days. The amount of C–S–H gel was calculated by combined method between the selective dissolution and XRD-Rietveld analysis [7,10,11].

An ignition loss was measured. The ignition loss of the sample is expressed as the weight loss of the sample between 105 °C and

Table 1
Physical and chemical properties of fly ash and OPC.

	Ignition loss (%)	Chemical composition from XRF analysis (mass)									Mineral composition from XRD-Rietveld analysis (mass)				Blaine surface area (m^2/kg)	Density (kg/m^3)
		SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	MnO (%)	C_3S (%)	C_2S (%)	C_3A (%)	C4AF (%)		
OPC	0.77	20.84	5.95	2.62	63.63	1.79	0.18	0.33	0.34	0.10	63.09	12.99	11.78	9.23	347	3150
Fly ash	0.90	59.90	29.60	4.80	1.30	0.60	0.00	0.70	0.00	0.00	–	–	–	–	376	2290

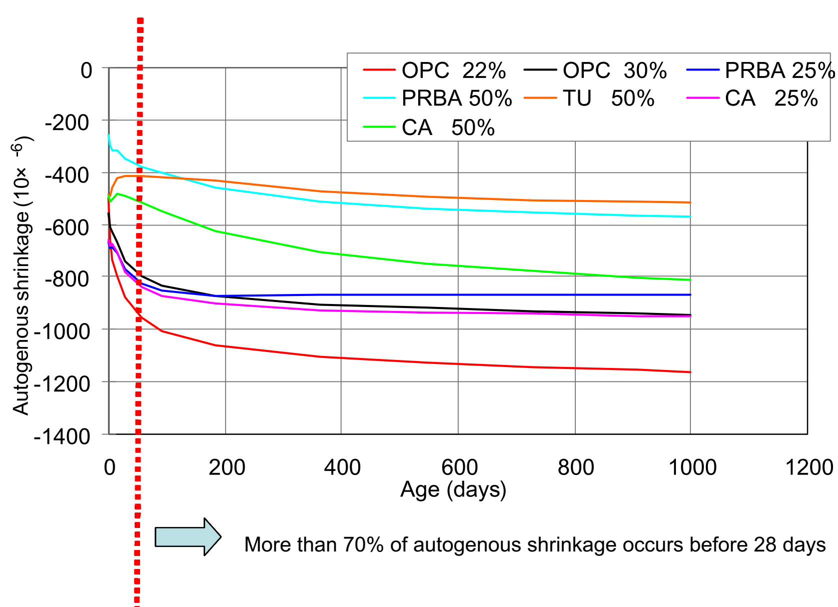

Fig. 1. Autogenous shrinkage of concretes.

950 °C divided by the weight of the sample after being burned at 105 °C.

3. Results and discussion

It must be noted that the artificial cracks were not generated in the experiment plan. Therefore, first of all, it is necessary to specify the meaning of self-healing in this study. In conventional concretes, micro cracks are typically induced by drying shrinkage [12,13]. On the other hand, high-performance concretes such as the high-strength and the self-compacting concretes may contain cracks due to autogenous shrinkage [14–17]. Many researchers have investigated and confirmed the benefits of shrinkage-reducing admixtures [18–20]. Nevertheless, it is difficult to completely avoid micro cracks in concretes. Holt and Leivo [13] have reported that both drying and autogenous shrinkage could be significant in certain early age scenarios.

In the author's previous research [8], similar results have been found. Fig. 1 elucidates the results of autogenous shrinkage. About 70% of the autogenous shrinkage occurred before 28 days. This amount should be similar for drying shrinkage.

If there are enough cementitious particles that can hydrate after 28 days, the self-healing ability may appear. Therefore, the definition of self-healing in this research is the ability to heal the cracks without extra treatment. Since the samples were prepared in a sealed curing condition, the source of the cracks was expected to be autogenous shrinkage. In this study, the changes of compressive

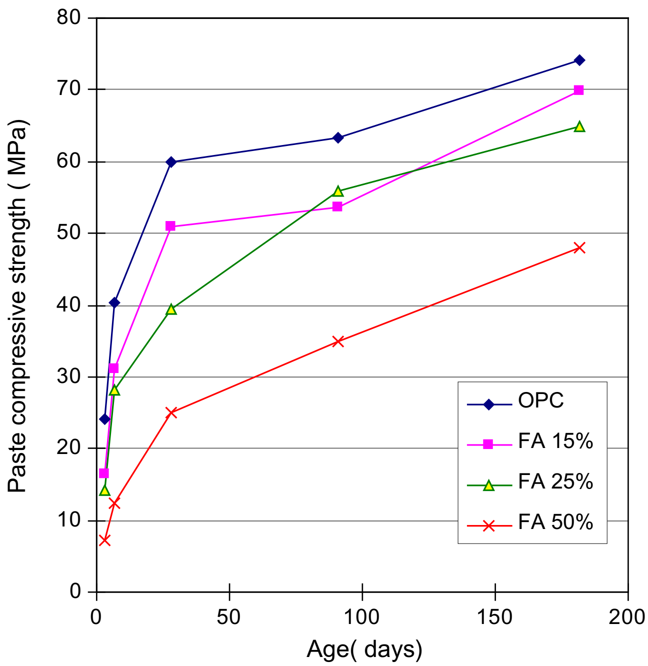

Fig. 2. Dependence of compressive strength on replacement ratio and time.

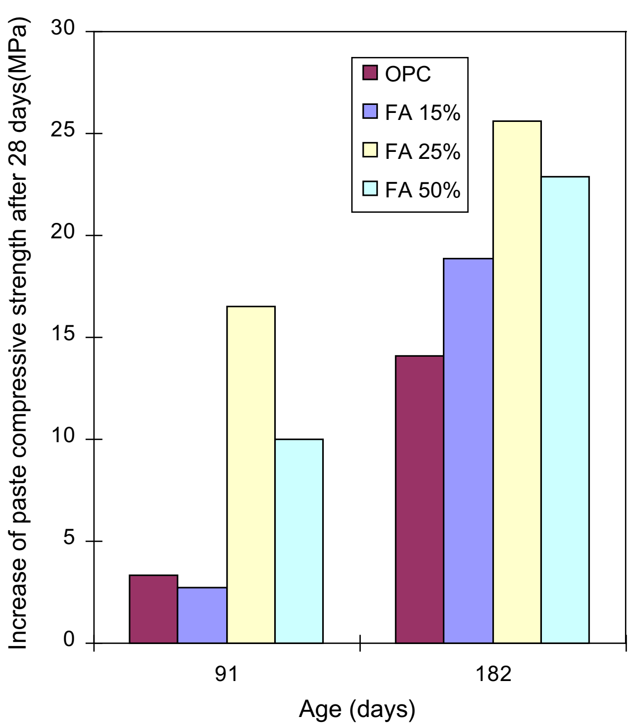

Fig. 3. Increase of paste compressive strength after 28 days.

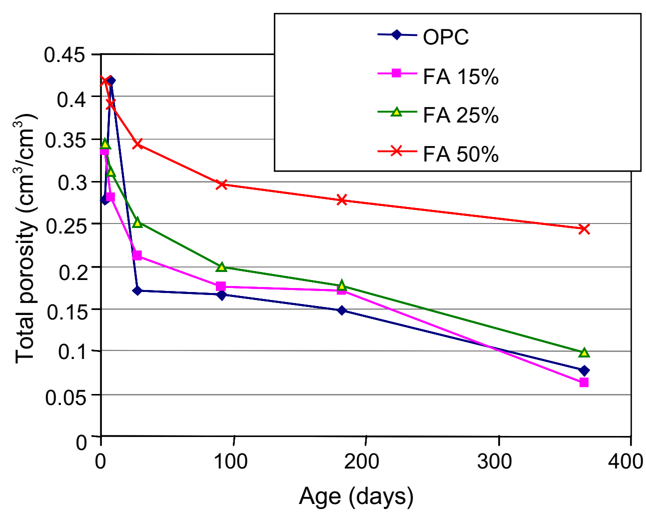

Fig. 4. Total porosity of specimens.

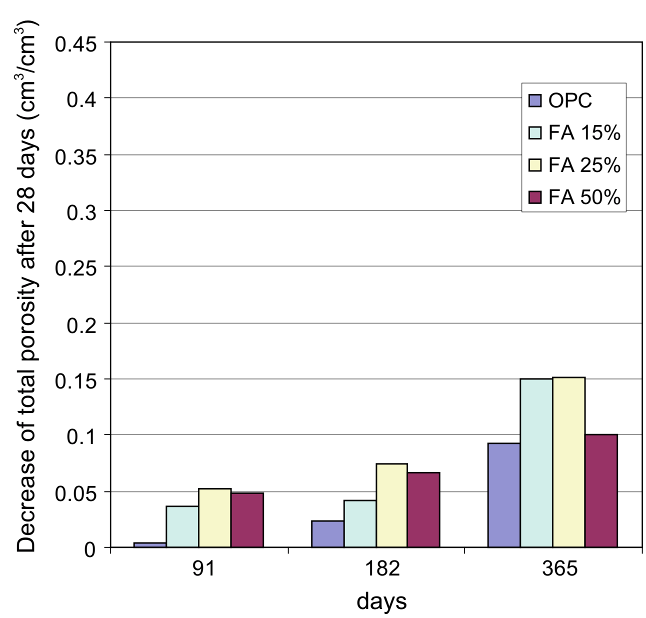

Fig. 5. Decrease of total porosity after 28 days.

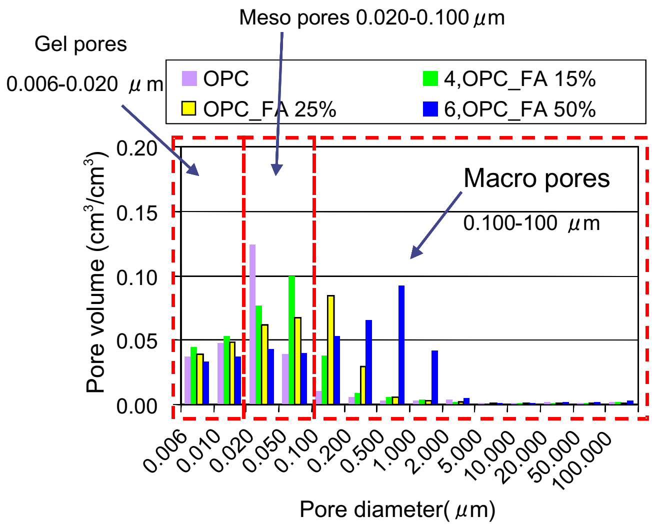

Fig. 6. Pore size distribution of specimens at 3 days.

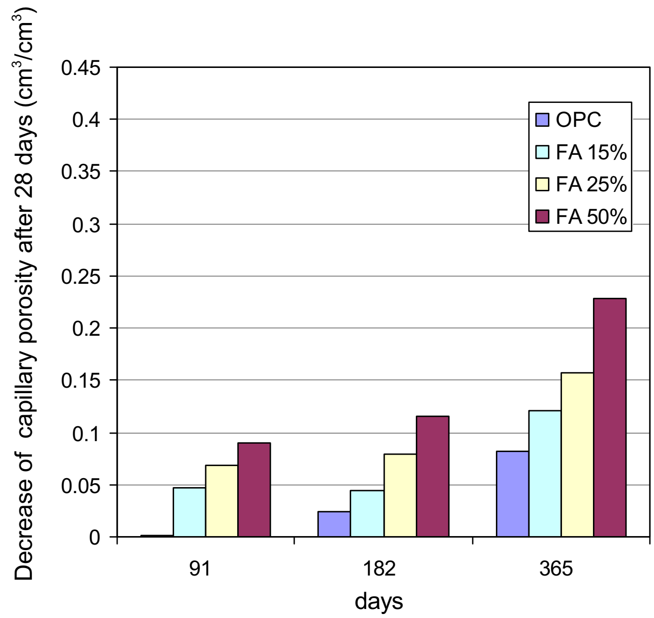

Fig. 8. Decrease of capillary porosity after 28 days.

strength, porosity, effective chloride diffusion coefficient, hydration reaction and hydrated products after 28 days are emphasized.

3.1. Compressive strength

Until now, the compressive strength is still the major factor to control the quality of concrete in practice. The results in Fig. 2 confirm the known dependence of compressive strength as a function of replacement ratio of fly ash and time. The compressive strength decreased when cement was replaced by fly ash. However, the increase in compressive strength after 28 days is notable. As shown in Fig. 3, the increase of compressive strength after 28 days of FA 25% was highest, following by FA 50%, FA 15% and OPC, respectively. It is expected that the increase of compressive strength after 28 days is mainly due to the hydration of fly ash, as described in Section 3.4.

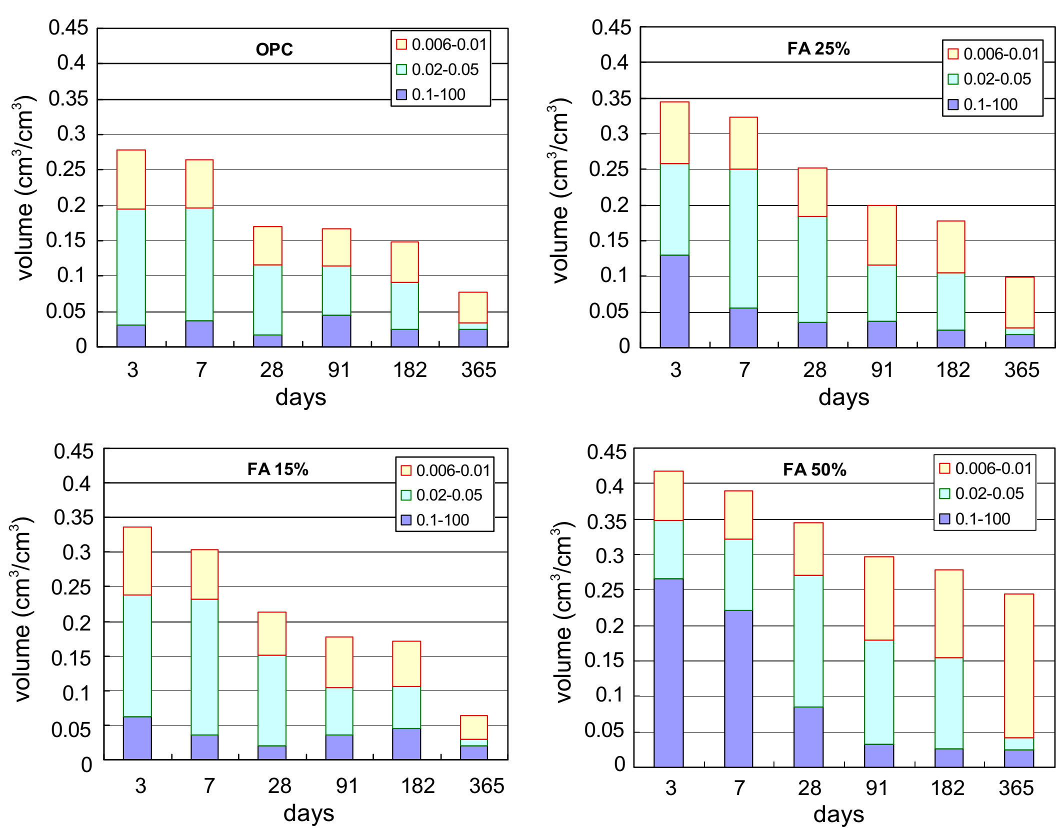

Fig. 7. Gel pore, meso-pore and macro-pore of cement and fly ash–cement pastes.

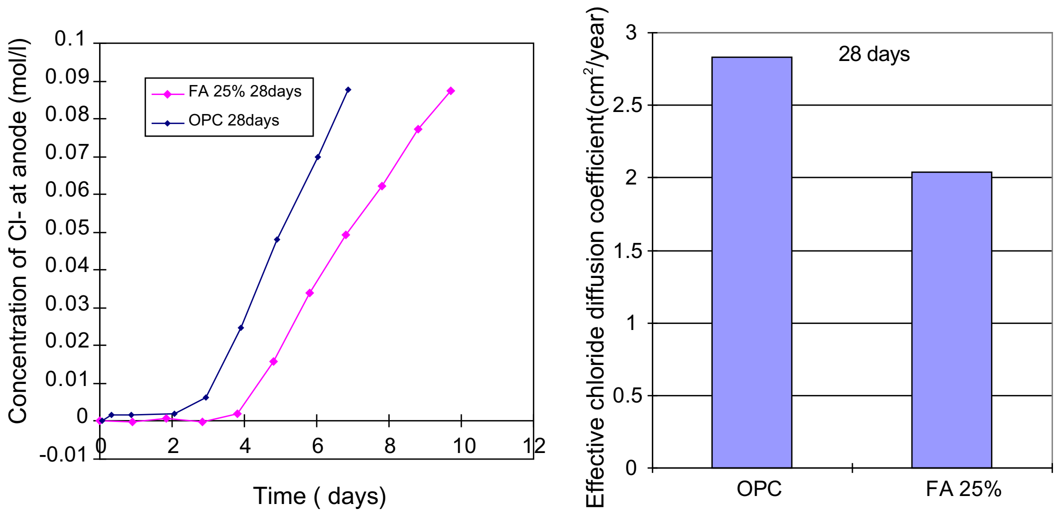

Fig. 9. Concentration of Cl^- at anode and the effective chloride diffusion coefficient at 28 days.

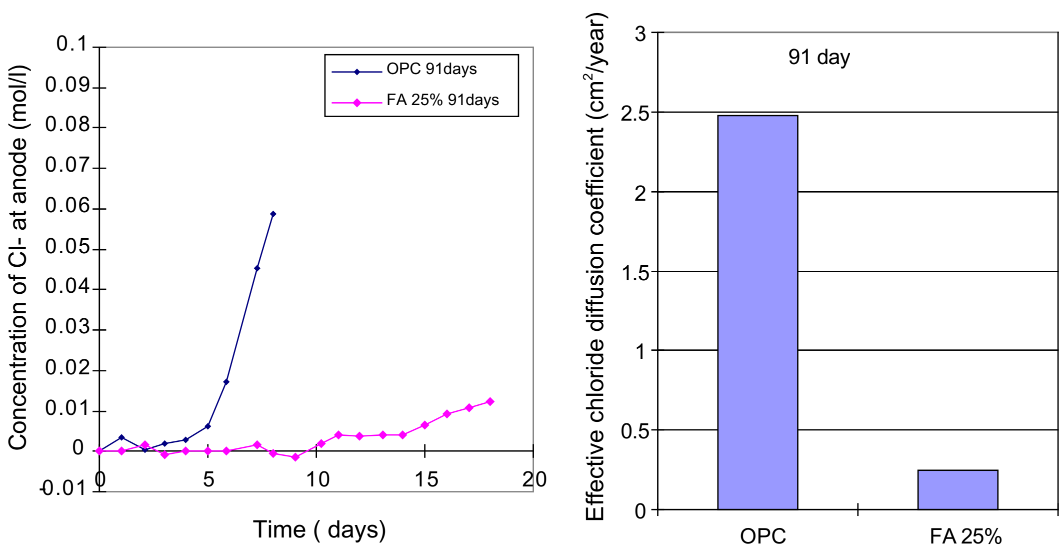

Fig. 10. Concentration of Cl^- at anode and the effective chloride diffusion coefficient at 91 days.

3.2. Porosity

Total porosity is shown in Fig. 4. These are also common results: the total porosity decreased when the replacement ratio of fly ash increased. However, for the decreasing of total porosity after 28 days, those containing fly ash were better than OPC as shown in Fig. 5. The sequence corresponded to the compressive strength results.

Pore size distributions were further analyzed. For convenience, the pore sizes were separated into three ranges; 0.006–0.020 μm (gel pores), 0.020–0.100 μm (meso-pores) and larger than 0.100 μm (macro-pores) (Fig. 6). The meso-pores and the macro-pores are considered as capillary pores. The results are shown in Fig. 7. At early age, the volume of meso-pores plus macro-pores increased when the replacement ratio of fly ash increased. The fraction of gel, meso- and macro-pores changed as age increased. From 182 days to 365 days, the volume of meso- and macro-pores decreased markedly for FA 25% and 50%.

Fig. 8 elucidates the capillary pores that decreased after 28 days. The reductions of total capillary pores after 28 days in fly ash–cement paste were higher than those in Portland cement paste. They increased with an increase of the replacement ratio of fly ash.

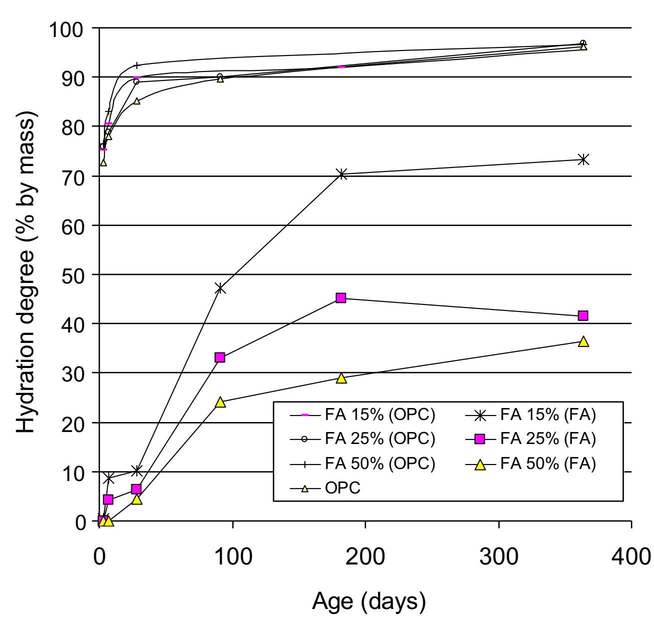

Fig. 11. The hydration degree of cement and fly ash as a function of time.

3.3. Effective chloride diffusion coefficient

Figs. 9 and 10 show the concentration of Cl^- at the anode and the effective chloride diffusion coefficients of OPC and FA 25% at 28 and 91 days, respectively. The effective chloride diffusion coefficient was calculated as follows:

$$D = \frac{J_{Cl} \times R \times T \times L}{Z_{Cl} \times F \times V \times C_{anode}} \times 100 \quad (1)$$

$$J_{Cl} = \frac{V_{anode}}{A} \times S \quad (2)$$

In which D is an effective chloride diffusion coefficient (cm^2/year); J_{Cl} is a flux of chloride ion (mol/cm^2 year); R is the gas constant (J/(mol K)); T is absolute temperature (K); L is the length of specimen (mm); $Z_{\ Cl}$ is 1 for chloride ion; F is Faraday constant (C/mol); V is electrical potential (V); C_{anode} is the concentration of chloride ion at anode (mol/l); V_{anode} is the average volume of solution at anode (l); A is cross-section of specimen (cm^2); and S is a slope of the curve between concentration of chloride ion at anode and time (mol year/l).

At 28 days, the effective chloride diffusion coefficient of FA 25% was slightly lower than that of OPC. The difference was greater at 91 days. At both ages, the effective chloride diffusion coefficients of OPC are higher though the total porosity is lower.

From 28 to 91 days, the effective chloride diffusion coefficients of OPC somewhat decreased, however, for those of FA 25%, a

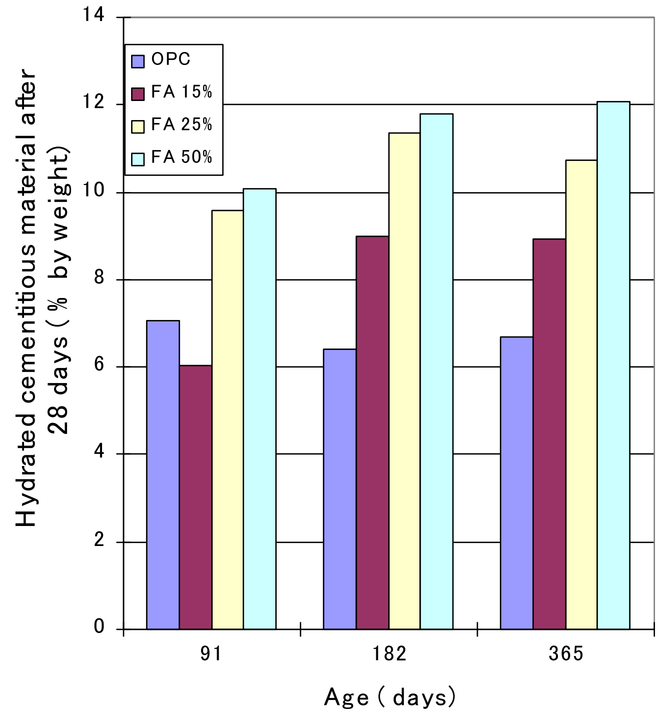

Fig. 13. The amount of cementitious particles that hydrate after 28 days.

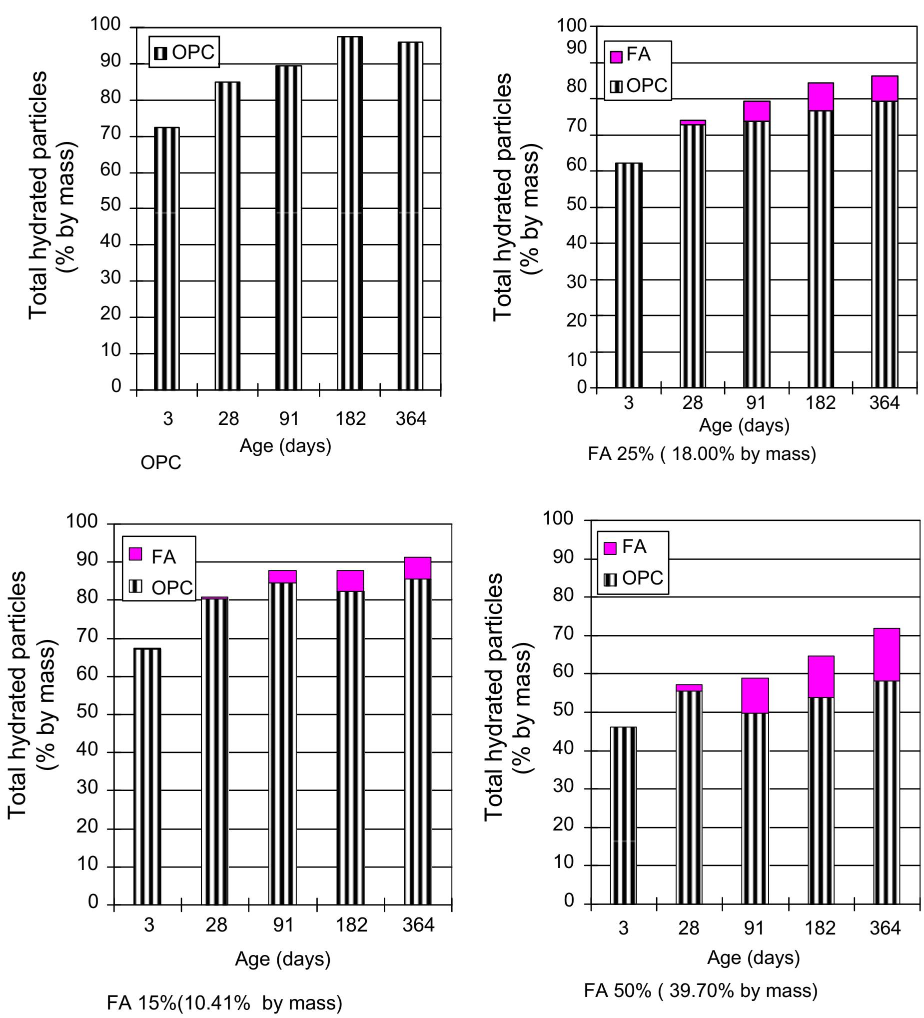

Fig. 12. The amount of hydrated cement and fly ash as a function of time.

remarkable decrease was observed. Fig. 10 shows that for the 91-day test, it took a long period of time before the concentration of Cl^- at anode of FA 25% started to increase. It is likely that the difference between effective chloride diffusion coefficients of FA 25% at 28 and 91 days came from the hydration of fly ash.

3.4. Hydration degree and hydrated products

Fig. 11 shows the hydration degree of the cement and fly ash as functions of time. The hydration degree of cement increased rapidly until 28 days and then became almost constant.

Comparing between the cement paste and the fly ash–cement paste, the hydration degree of cement in the cement paste was slightly lower than those in the fly ash–cement paste. Nevertheless, the difference could be neglected at higher ages. In contrast, the hydration degree of fly ash was very low before 28 days. However, from 28 days to 91 days, the hydration degree of fly ash increased rapidly and was still gradually increasing at later ages.

The hydration degree is defined as the amount of the hydrated part divided by the total amount before the hydration reaction. It is useful to compare the hydration degree among samples if the total amounts before the hydration reactions are equal. However, if the total amounts before the hydration reactions are not equal, comparing the amount of hydrated material may be more convenient.

Fig. 12 shows the amounts of hydrated cement and fly ash as functions of time. In Fig. 11, the hydration degree of fly ash in FA 15% was higher than those in FA 25% and FA 50%. In Fig. 12, however, the amount of hydrated fly ash in FA 50% was higher than those in FA 25% and FA 15%. The total hydrated particles (cement and fly ash) decreased when the replacement ratio of fly ash increased.

Fig. 13 shows the amount of cementitious particles that hydrated after 28 days. At 91 days, the specimen that had highest hydrated fraction after 28 days was FA 50%, followed by FA 25%, OPC and FA 15%, respectively. However, at 182 and 365 days, the sequence has changed corresponding to the replacement ratio of fly ash. Fig. 14 shows the fraction of cementitious particles that hydrated after 28 days. As the replacement ratio of fly ash increases, the hydrated fraction of fly ash increases.

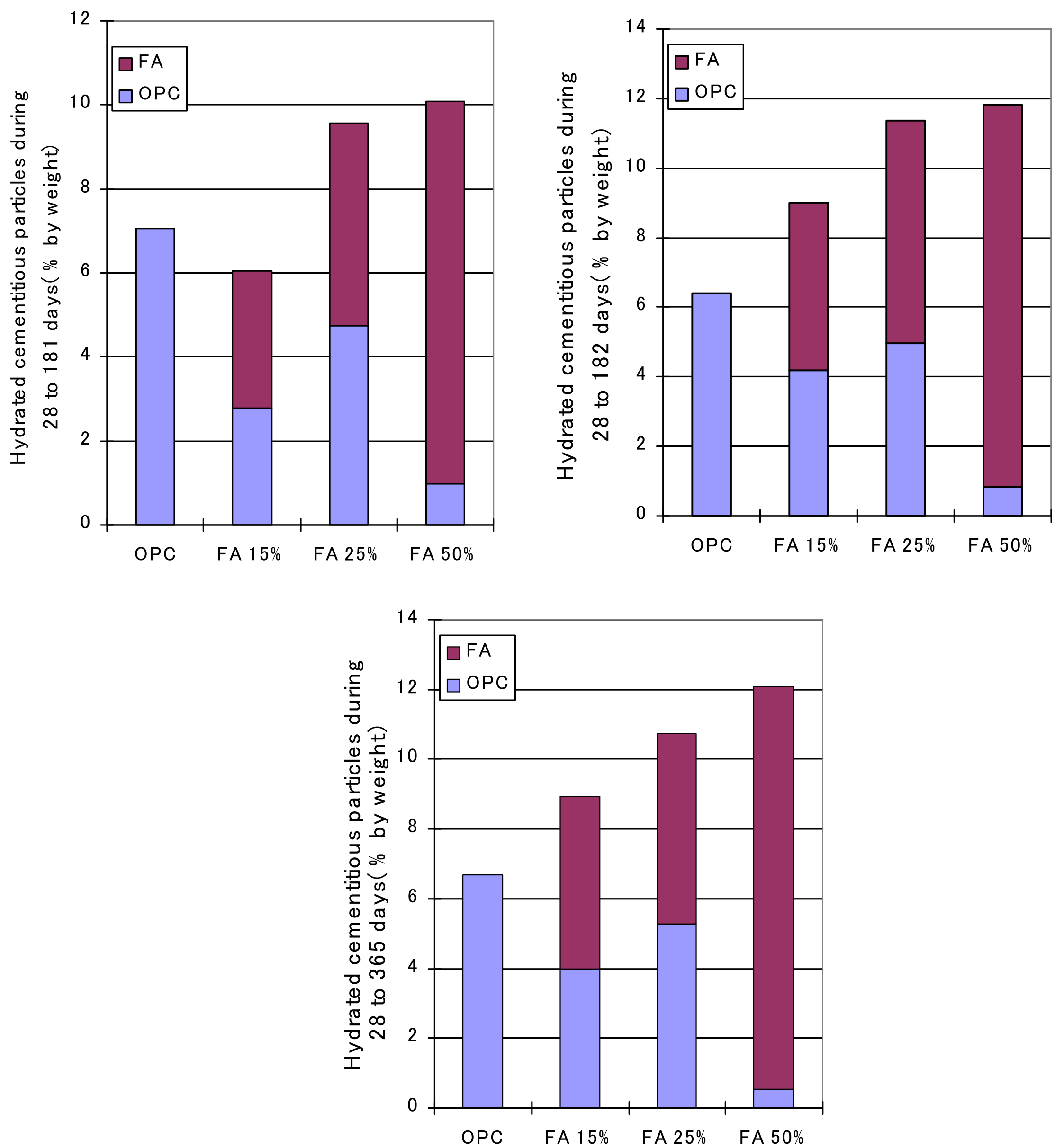

Fig. 14. Fraction of hydrated cementitious particles after 28 days.

Fig. 15 shows the amount of hydrated products, C–S–H gel and $Ca(OH)_2$ as a function of time. The decreasing of $Ca(OH)_2$ corresponds to hydration of fly ash. Until 91 days, the amount of C–S–H gel decreased as the replacement ratio of fly ash increased. However, after 91 days, the differences in OPC, FA 15% and FA 25% are very small. Fig. 16 shows the amount of C–S–H gel that is produced after 28 days. For greater amounts of fly ash, the amount of C–S–H produced after 28 days increased.

One may ask how long fly ash–cement system can maintain the self-healing ability. This should relate to how long fly ash can continue to hydrate. There are at least two factors: first, the available space for the hydrated products and second, the essential compounds for the self-healing reaction, anhydrate fly ash and $Ca(OH)_2$.

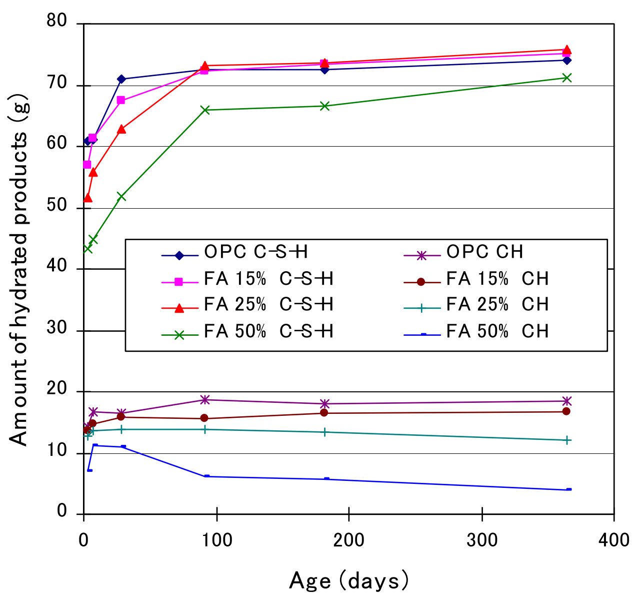

Fig. 15. The amount of hydrated products, C–S–H gel and $Ca(OH)_2$ as a function of time.

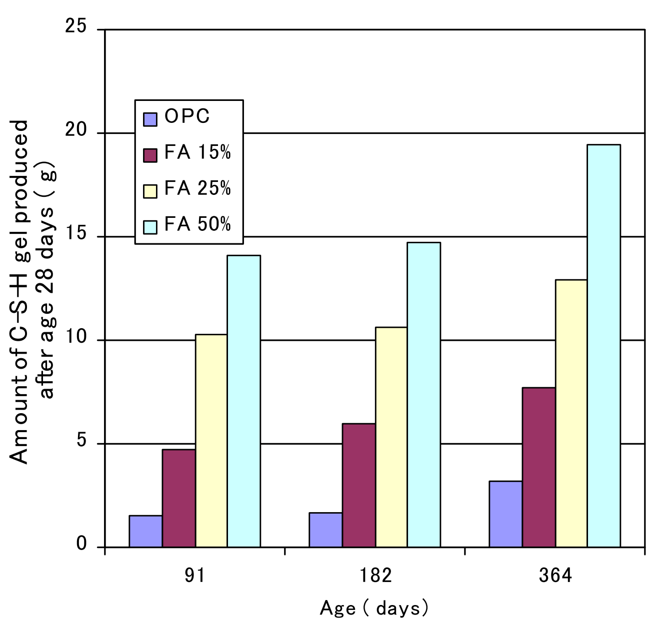

Fig. 16. Amount of C–S–H gel produced after 28 days.

For the first factor, it seems that the meso- and macro-pores are the space for the hydrated products of fly ash. If there are no meso- and macro-pores or their volume is very small, the hydration reaction may stop. However, if there is space generated later by cracks, there is possibility that the hydration reaction might restart again.

For the second factor, from Figs. 11 and 15, it confirmed that anhydrate fly ash and $Ca(OH)_2$ still left in every fly ash–cement mixtures. As long as fly ash and $Ca(OH)_2$ are still available, there is good possibility for healing.

In very long term case, $Ca(OH)_2$ may not exist anymore due to carbonation. However, as long as anhydrate fly ash still exists, the self-healing ability might be activated by painting concrete with $Ca(OH)_2$ solution. This part needs further research to verify.

All the results in this study showed that the self-healing ability of fly ash–cement paste increased when the replacement ratio of fly ash increased from 0% to 50% by volume. However, it should be noted that when cement was replaced by fly ash, the compressive strength decreased. In real concrete, this problem may be overcome if fine aggregate instead of cement is replaced by fly ash.

4. Conclusions

This research has investigated the self-healing ability of fly ash–cement systems considering compressive strength, porosity, chloride diffusion coefficient, hydration reactions and hydrated products. The research focused on behavior after shrinkage cracking occurs or after 28 days. The amount of cracks was not measured directly but was implied by the amount of total porosity. The results showed that the increase of compressive strength after 28 days of samples containing fly ash was higher than those of ordinary cement paste. As for the porosity, the reductions of total capillary pores after 28 days in fly ash–cement paste were higher than those in cement paste. They increased with an increase of the replacement ratio of fly ash. As for chloride diffusion, the effective chloride diffusion coefficients of samples with 25% fly ash at 91 days were significantly lower than those of cement paste. From the view point of hydration, the amount of cementitious material hydrated after 28 days increased when the replacement ratio of fly ash increased. It can be concluded that fly ash–cement system has the self-healing ability for micro cracks that occur from shrinkage. Future directions of this work include a focus on larger cracks, which may need to be artificially generated, and also on cracks that appear at later ages.

References

[1] Jacobsen S, Sellevold EJ. Rapid freeze/thaw testing of concrete-pore structure changes by cracking and healing. In: Sakai K, Banthia W, Gjorv OE, editors. Concrete under severe conditions: environment and loading. E & FN SPON; 1995. p. 114–25.
[2] Jacobsen S, Sellevold EJ. Self healing of high strength concrete after deterioration by freeze/thaw. Cem Concr Res 1996;26(1):55–62.
[3] Edvardsen C. Water permeability and autogenous healing of cracks in concrete. ACI Mater J 1999;96(4):448–55.
[4] Reinhardt HW, Jooss M. Permeability and self-healing of cracked concrete as a function of temperature and crack width. Cem Concr Res 2003;33(7):981–5.
[5] Neville A. Autogenous healing – a concrete miracle? Concr Int 2002:76–82.
[6] Granger S, Loukili A, Pijaudier-Cabot G, Chanvillard G. Experimental characterization of the self-healing of cracks in an ultra high performance cementitious material: mechanical tests and acoustic emission analysis. Cem Concr Res 2007;37(4):519–27.
[7] Termkhajornkit P, Nawa T, Kurumisawa K. Effect of water curing conditions on the hydration degree and compressive strengths of fly ash–cement paste. Cem Concr Compos 2006;28(9):781–9.
[8] Termkhajornkit P, Nawa T, Nakai M, Saito T. Effect of fly ash on autogenous shrinkage. Cem Concr Res 2005;35(3):473–82.
[9] Taylor JC. Computer programs for standardless quantitative analysis of minerals using the full powder diffraction profile. Powder Diffract 1991;6(1):2–9.
[10] Termkhajornkit P, Nawa T, Kurumisawa K. A study of fly ash–cement hydration by Rietveld analysis and selective dissolution. JCI Annu Meet 2005:169–74.

[11] Termkhajornkit P, Nawa T, Kurumisawa K. Quantitative study on hydration of fly ash and portland cement. In: CONMAT, August 22–24, Vancouver; 2005.
[12] Barr B, Hoseinian SB, Beygi MA. Shrinkage of concrete stored in natural environments. Cem Concr Compos 2003;25(1):19–29.
[13] Holt E, Leivo M. Cracking risks associated with early age shrinkage. Cem Concr Compos 2004;26(5):521–30.
[14] Powers TC. Absorption of water by Portland cement paste during hardening process. Ind Eng Chem 1935;27(7):790–4.
[15] Sellevold EJ. The function of condensed silica fume in high strength concrete, FIP Notes, vol. 4. 1987; p. 11–4.
[16] Tazawa E, Miyazawa S. Autogenous shrinkage of concrete and its importance in concrete technology. In: Bazant ZP, Carol L, editors. Proceedings of the fifth international RILEM symposium on creep and shrinkage of concrete, E and FN Spon. London; 1993, p. 159–168.
[17] Wittmann FH. On the action of capillary pressure in fresh concrete. Cem Concr Res 1976;6(1):49–56.
[18] Bentz DP, Geiker MR, Hansen KK. Shrinkage-reducing admixtures and early-age desiccation in cement pastes and mortars. Cem Concr Res 2001;31(7):1075–85.
[19] Collepardi M, Borsoi A, Collepardi S, Olagot JJO, Troli R. Effects of shrinkage reducing admixture in shrinkage compensating concrete under non-wet curing conditions. Cem Concr Compos 2005;27(6):704–8.
[20] Rongbing B, Jian S. Synthesis and evaluation of shrinkage-reducing admixture for cementitious materials. Cem Concr Res 2005;35(3):445–8.