

Effects of Curing Conditions on Carbonation of Concrete Containing Expansive Admixture

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ABSTRACT

The carbonation of concrete containing expansive admixtures in different curing conditions is investigated in this study. The compressive strength and carbonation rate of concrete containing fly ash (FA) and expansive admixture (EA) are measured at different ages. The $\text{Ca}(\text{OH})_2$, CaCO_3 and ettringite contents in concrete before and after the carbonation reaction are analyzed with TG-DSC technique. The total porosities of samples are analyzed with MIP test. The test results indicate that the compressive strength of concrete goes up while carbonation depth of concrete declines with the increased amount of expansive admixture, and there exists an approximate linear relationship between the compressive strength and carbonation depth of concrete in standard curing conditions. Standard curing is simulative for the ability of resistance to carbonation of concrete, while nature curing and water curing act on the opposite way.

1. INTRODUCTION

Expansive admixtures have been employed as an efficient way to counteract the shrinkage and accompanying cracking tendency in the hardening process of concrete (Neville, 1996) since the pioneering work of Lossier (1946). The volumetric compensating effects of expansive admixture depend highly on nature of the minerals generating the expansive potential and the curing history of the pre-mature concrete

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(Colleparidi et al. 2005). In any case the expansive potential should be dealt with great care as the period the expansion are critical, which may induce cracking of concrete and result in loss of strength (Taylor, 1997). Researches have shown that the curing condition affects strongly on the performance of concrete containing expansive admixture. Odler and Subauste (1999) found the extent of ettringite-related expansion depends on the conditions of curing. The expansion increases with increasing amounts of water taken up from the environment while ettringite is formed, indicating the participation of swelling phenomena in the expansion process. Subauste and Odler (2002) confirmed that magnitude of the expansive stresses brought by the formation of ettringite is significantly higher in pastes hydrating under water than in those hydrating just in humid air. The hydration of hard-burnt calcium oxide, another important source of expansive potential, causes a development of expansive stresses that remains constant after reaching the maximum value. Chen and Brouwers (2012) found that the volumetric shrinkage of mortar containing an ettringite-type expansive admixture is even greater than the blank reference if cured in the dry condition. The great water demand associated with the formation of ettringite renders it more sensitive to the moist supply than the neat Portland cement (Brouwers, 2005). Lobo and Cohen (1991) found that expansion of paste containing expansive admixture results in the formation of large pores (and/or microcracks) in the paste. Restraining the expansive cement paste results in the reduction of the size of large pores. However, even with a large degree of restraint, expansive cement paste is still more porous and contains larger pores than portland cement paste of the same age.

The carbonation of concrete is reported closely associated to the moist supply as well. Balayssac et al. (1995) have researched the effects of curing upon carbonation of concrete. Kwon and Song (2010) has analyzed relationship between CO₂ diffusion and relative humidity at different ratio of water to cement. CO₂ diffusion based on porosity saturation modeling has also been projected (Song and Kwon, 2007). Their researches have shown that porous of concrete have close connection with the concrete porosity. Borges et al. (2010) have investigated that the calcium carbonate phase formed appears to be determined by the amount of available Ca(OH)₂. He has considered that carbonation is associated with the amount of available Ca(OH)₂. Thus, when expansive admixture is used in concrete, how different curing humidity affects carbonation of concrete is not absolutely clear. These are the key points that this paper studies: the relationships among carbonation, expansive admixture and relative humidity.

This research is aimed to investigate the effects of four kinds of curing conditions on carbonation of concrete when different amount of expansive admixture (0%, 6% and 10%, respectively) is added. This paper also reports the lab results of compressive strength test and accelerated carbonation test after samples cured for 28 days and 56 days under different conditions. At the same time, the hydration products of expansive admixture are researched with XRD and SEM analysis. TG-DSC and MIP are also used to study hydration product content before and after carbonation together with porosity of

concrete structure to evaluate the potential relationship among them.

2. EXPERIMENTAL

2.1 Materials

The Portland cement (PC) used in the experiment was produced by the Huaxin Cement Co., Ltd classified as P.I 52.5. The fly ash (FA) was a type of coal fly ash supplied by the Wuhan Iron and Steel (Group) Corporation (WISCO) and the expansive admixture (EA) was produced by the Tianjin Baoming Co., Ltd. The oxide compositions and physical properties of the PC, FA and EA analyzed with the X-Ray Fluorescence Spectroscopy are listed in Table 1 and Table 2. A polycarboxylate-type superplasticizer (SP) (Brand LN-SP supplied by the Wuhan Harbour Engineering Design and Research Co., Ltd) was used to improve the workability of the mix. The fine aggregate used for the concrete mix was continuously graded river sand. The coarse aggregate was continuously graded crushed gravel with particle sizes ranging of 5~25mm.

Table 1 Chemical compositions of Portland cement and expansive admixture (wt %)

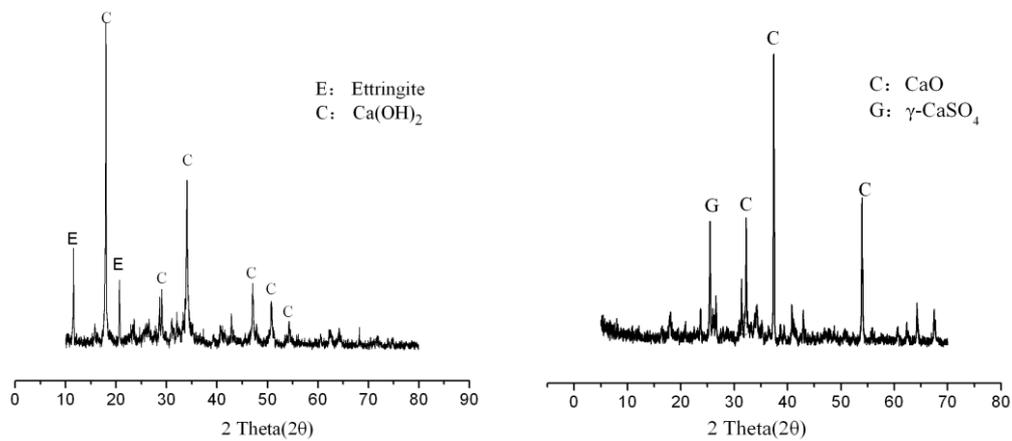
Materials	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	SO ₃	L.O.I. (%)
PC	19.37	3.69	3.92	68.3	1.61	0.81	1.09
EA	18.87	1.77	15.22	48.38	2.56	7.71	3.96

Table 2 Physical properties of Portland cement, fly ash and expansive admixture

Materials	Physical properties	
	Blaine surface area (m ² ·kg ⁻¹)	Density (kg·m ⁻³)
PC	336	3109
FA	326	2105
EA	300	2702

2.2 Material hydration products

The hydration characters of expansive admixture are studied in this experiment with X-ray diffraction analysis (XRD) and scanning electron microscope (SEM). The XRD patterns of the original expansive admixture used in this experiment before hydration (Fig. 1(a)) and its hydration products after hydrated for 3 days (Fig. 1(b)) are both showed in Fig. 1. The SEM images are showed in Fig. 2.



(a) Expansive admixture (b) Hydration products
 Fig. 1 XRD patterns of expansive admixture and its hydration products

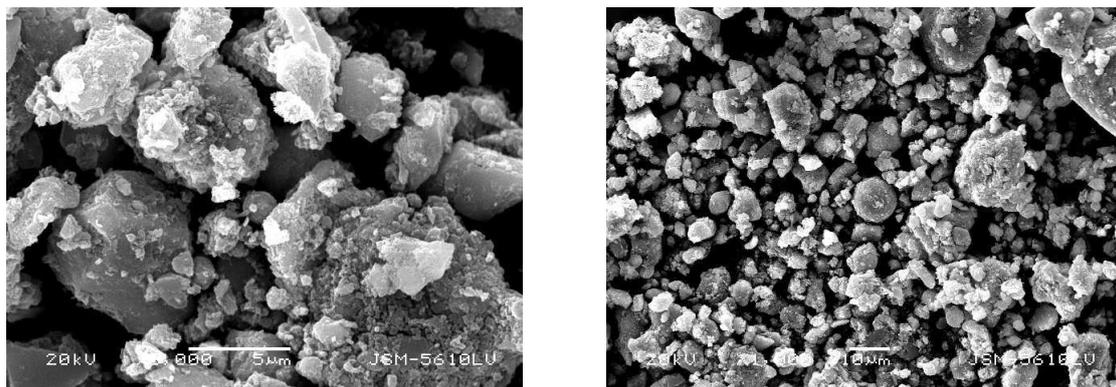


Fig. 2 SEM images of expansive admixture hydration products

From the XRD patterns (Fig. 1), the major diffraction peaks of expansive admixture indicate CaO and γ -CaSO₄. After 3 days hydration, the main diffraction peaks observed in the pattern turn to Ca(OH)₂ and ettringite. The microstructures of hydration products are also observed from Fig. 2, where plenty of Ca(OH)₂ crystals are found. Combined with the XRD analysis, the main expansive potential energy of this expansive admixture comes from the expansion of Ca(OH)₂ and ettringite.

2.3 Specimen preparation

Three mix proportions of the concrete were designed in the experiment, of which the

replacement levels of the Portland cement with the fly ash and the expansive admixture were different and all cement pastes were mixed with water to binder ratio (w/b) of 0.37. The similar slump and slump flow ensured all concretes have the similar workability and density. The proportions of the concrete mix are listed in Table 3.

Table 3 Proportions and fresh properties of the concrete mix[#]

Mix	Mix proportions (Kg/m ³)							EA% [†]	Slump (cm)	Slump Flow (cm)
	PC	FA	EA	Sand	SP	Gravel	Water			
S0	200	200	0	714	2.4	1165	148	0	16	26
S6	176	200	24	714	2.4	1165	148	6	17.5	22
S10	160	200	40	714	2.4	1165	148	10	16	25

Notes: #: The water/binder mass ratio of all the mix was 0.37.

†: Mass percentage of expansive admixture in the binder.

2.4 Curing type arrangement

Four curing types were designed in this experiment; each included different curing procedure and curing humidity. Standard curing type (CT1) was that concrete samples were kept in fog-spraying curing room at 20±3°C and relative humidity was 90±5%. While nature curing type (CT2) was that samples were kept in a certain room at 20±3°C and relative humidity was 60±5%. The other two types were that samples were immersed in water for 3 and 7 days (referred to CT3 and CT4, respectively), and then shifted to nature curing room for further curing. The specific curing type arrangements were shown as Fig. 3.

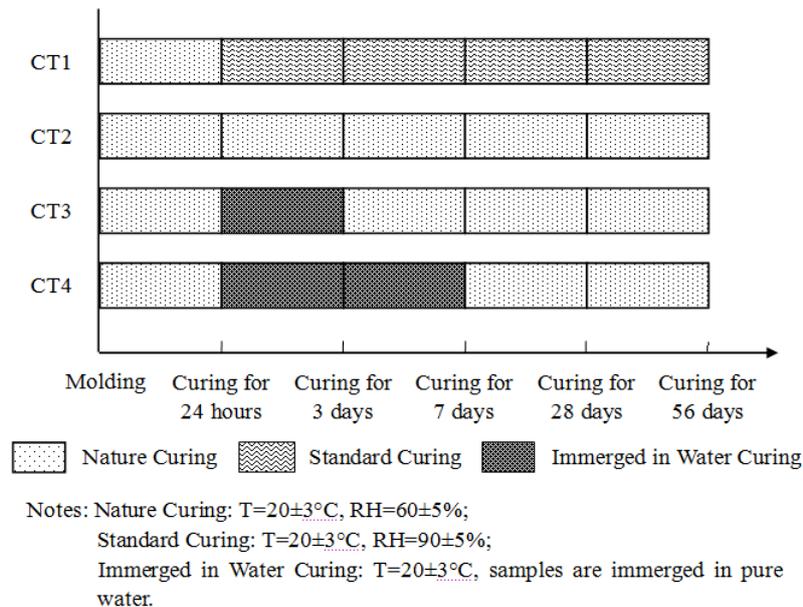


Fig. 3 Curing type arrangements of concrete

2.5 Compressive strength measurement

Specimen of size 100 mm × 100 mm × 100 mm were used in the compressive strength test. All samples for compressive strength tests were subjected to the different curing room according to different curing type arrangement. After curing for 28 and 56 days, the compressive strengths were measured by MCC 82 system machine (CONTROLS srl, Italy).

2.6 Carbonation depth measurement

The accelerated carbonation test also employed concrete specimens of the size 100 mm × 100 mm × 100 mm, which were cured for 26 days after molding in certain rooms as different curing types, and were then dried for 48 hours in oven at 60°C. Two opposite sides of the samples were retained and the remaining surface were sealed with mineral wax, and then carbonated in the accelerated carbonation chamber ($\text{RH}=70\pm 5\%$, $T=20\pm 3^{\circ}\text{C}$, concentration of CO_2 equaled to $20\pm 3\%$) for 28 and 56 days.

2.7 TG-DSC analysis

Cement pastes were extracted from the different concrete mix before and after carbonation 7 days and then analyzed with a simultaneous thermogravimetry – differential scanning calorimeter (TG-DSC) (model: STA 449c, manufacture: Netzsch–Gerätebau GmbH). The samples were kept in protective nitrogen gas and the heating rate was 10 K per minute.

2.8 Mercury intrusion porosimetry (MIP) analysis

The concrete specimens were crushed and small particles were taken for the MIP test. The particles were firstly dried at 105°C for 1 hour and then tested with the AutoPore IV 9500 system.

3. RESULTS AND DISCUSSIONS

3.1 Compressive strength test

The compressive strength results of the concrete cubes at 28 and 56 are shown in Fig. 4 and Fig. 5. By comparing the compressive strength of concrete samples at 28 days in different curing types, we can know that, in the condition of standard curing and nature curing, the compressive strength of concretes increases when expansive admixture is mixed in concrete, especially when 10% of expansive admixture is blended in the mix. However, the compressive strength of concrete sample does not clearly improve with the increase of expansive admixture blended in concrete after immersed in water curing for 3 or 7 days, S6 of which, however slightly decreases. Meanwhile, it is more evident that curing types have greatly influenced the compressive strength of samples as more amount of expansive admixture is mixed in concrete, based on the compressive strength of samples at 28 days (Fig. 4). When samples are cured in different curing types for 56 days, there are similar change disciplines at 56 days to those at 28 days (Fig. 5).

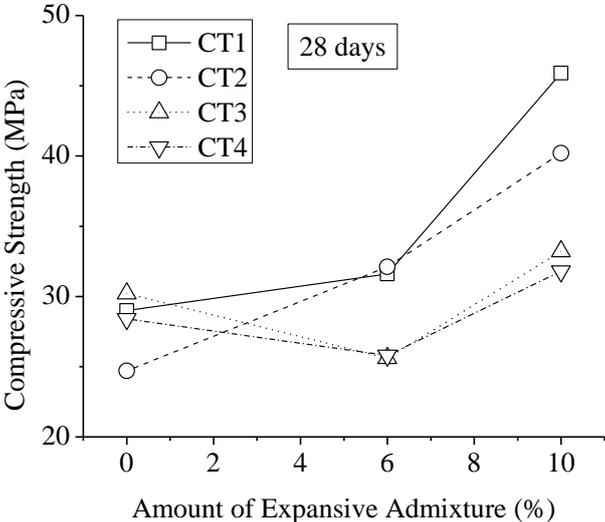


Fig. 4 Concrete compressive strength at 28 days in different curing types

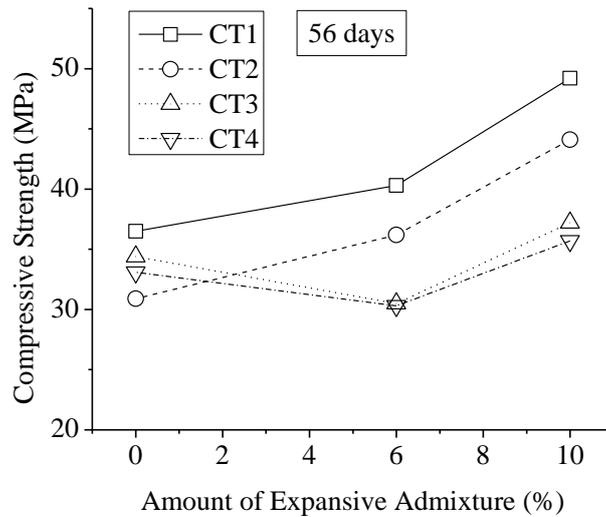


Fig. 5 Concrete compressive strength at 56 days in different curing types

3.2 Carbonation depth test

It can be known from Fig. 6 that different curing types affect the carbonation depths of concrete containing different expansive admixture seriously at 7 and 28 days. In CT1, the carbonation depths of concrete at 7 and 28 days slightly decrease with the increase of amount of expansive admixture. While, in CT2, 6% of expansive admixture mixed in concrete accelerates the carbonation of concrete greatly, yet the carbonation depth of concrete including 10% of expansive admixture is very close to that without it. What's more, carbonation depth of samples in CT4 is less than that in CT3. After immersed in water curing for 3 and 7 days, S6 and S10 reduce the carbonation depth markedly in comparison with S0. Moreover, the improving effect of S6 is better than S10 (Fig. 6(a)). Totally, the effect discipline of different curing types and different amount of expansive admixture mixed in concrete on carbonation depth of concrete at 28 days is similar with that at 7 days (Fig. 6(b)).

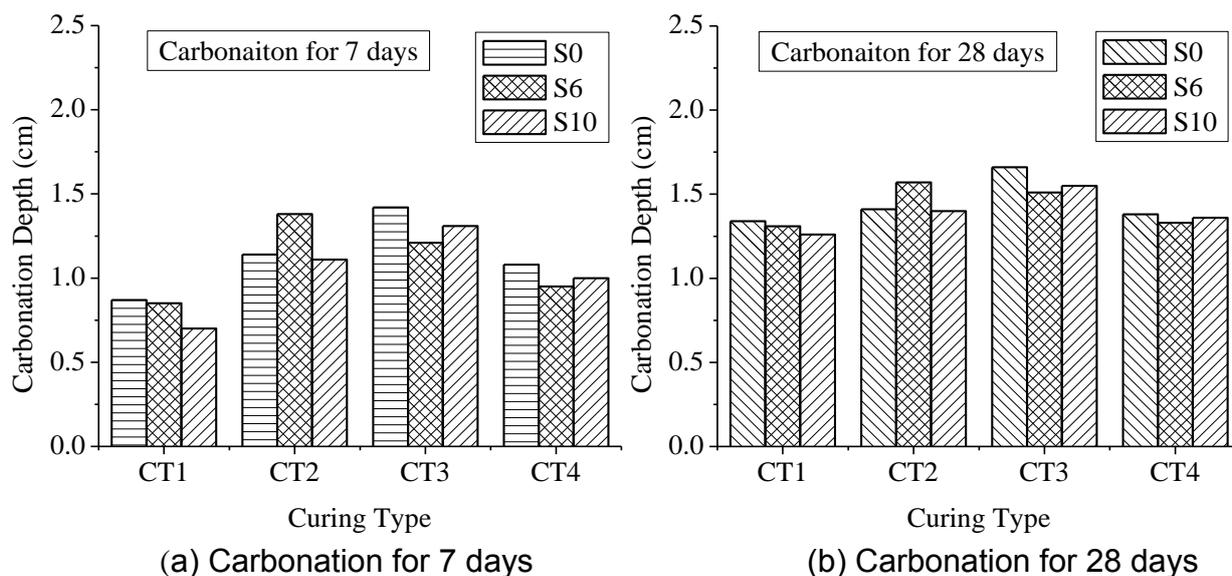
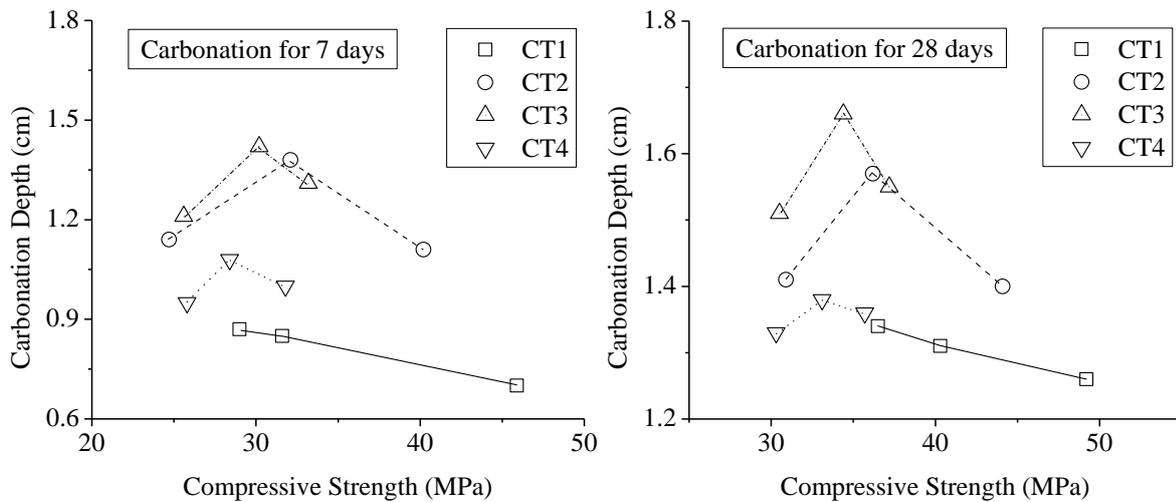


Fig. 6 Concrete carbonation depth after carbonated in different curing type

3.3 Relationship between compressive strength and carbonation depth

Owing to the analogous hydration age between compressive strength at 28 days and carbonation depth of concrete at 7 days, as well as the resemblance compressive strength at 56 days and carbonation depth of concrete at 28 days, the relationships between compressive strength and carbonation depth are contrastively analyzed in different curing types, as is shown in Fig. 7. In CT1, we can know from the Fig. 7, there is an approximate linear relationship between compressive strength of concrete and carbonation depth. The carbonation depth of concrete is smaller accordingly as the compressive strength of concrete is higher. However, carbonation depth and compressive strength have no clear relationship among CT2, CT3 and CT4 because water has great influence to cement hydration process of concrete.



(a) Carbonation depth at 7 days vs. compressive strength at 28 days

(b) Carbonation depth at 28 days vs. compressive strength at 56 days

Fig. 7 Relationship between carbonation depth of concrete at 7 and 28 days and compressive strength at 28 and 56 days in different curing types

This phenomenon demonstrates that relative humidity of CT1 is beneficial to inner hydration process of concrete. Interior structure of concrete has been improved gradually with the development of hydration process — forming a well inner pore structure, and compressive strength of it is enhanced simultaneously (Alsayed and Amjad, 1994). In addition, total porosity of concrete also enlarges if the amount of expansive admixture increases, which is good for carbonation of concrete, but the content of calcium hydroxide in concrete also goes up accordingly, compared with that without expansive admixture (Table 4 and Table 5). The ability of resistance carbonation of concrete thus improves slightly by the interaction between them (Fig. 7(a)). Nevertheless, it is completely different to samples cured in CT2. 70% of relative humidity results in that the free water provided to hydration of concrete is not enough, because plenty of water is required to secondary hydration of fly ash and generation of ettringite, which reduces the degree of fly ash secondary hydration reaction and the forming of ettringite (Batic et al., 2000). Therefore, carbonation depth of concrete is deeper in nature curing type than that in standard curing type, and it is the same to compressive strength. On the one hand, S10 enlarges the total porosity more though there is a higher content of calcium hydroxide than S6 in the two curing types respectively. Consequently, S10 severely accelerates the carbonation of concrete, compared with S6 (Fig. 6 and Table 5). On the other hand, when 10% of expansive admixture is added in concrete, more calcium hydroxide is supplied after expansive admixture hydration, which promotes the secondary hydration of fly ash. This is the reason why concrete containing 10% of expansive admixture has higher compressive strength than that blended with 6%

of expansive admixture, although it also accelerates the carbonation of concrete.

Table 4 Mass fraction of $\text{Ca}(\text{OH})_2$, CaCO_3 and ettringite in the paste of concrete containing 10% of expansive admixture after carbonation for 7 days

Items	Contents (%)			
	S10			
	CT1	CT2	CT3	CT4
$\text{Ca}(\text{OH})_2$ (before carbonation)	4.26	4.03	4.47	4.46
$\text{Ca}(\text{OH})_2$ (after carbonation for 7 days)	1.50	1.21	1.23	1.92
$\text{Ca}(\text{OH})_2$ (differentials value)	2.76	2.82	3.24	2.54
Ettringite (before carbonation)	0.46	0.43	0.49	0.51
CaCO_3 (before carbonation)	11.67	14.49	12.19	10.88
CaCO_3 (after carbonation for 7 days)	17.84	19.18	18.68	17.12
CaCO_3 (differentials value)	6.17	4.69	6.49	6.24

Table 5 The total porosity of concrete before carbonation in different curing types

Curing Types	Total porosities (%)	
	S0	S10
CT1	20.47	21.06
CT4	N.T.	23.22

Note: N.T.: Not Tested.

Meanwhile, to concretes containing the same amount of expansive admixture, CT3 and CT4 also have great effects on inner structure development of concrete. When cured in water, an amount of calcium sulfoaluminate hydrates completely and transfers into ettringite due to plenty of water that existed, thereby leading to the increase of total porosity and volume of solid phase. The riming stress destroys the points of junction formed in hydration process and broadens the pore structure, which reduces the compressive strength of concrete and the carbonation depth ascends accordingly (Sahamitmongkol and Kishi, 2011). Furthermore, it is more noteworthy that 10% of expansive admixture more greatly affects carbonation depth, compared with 6% of

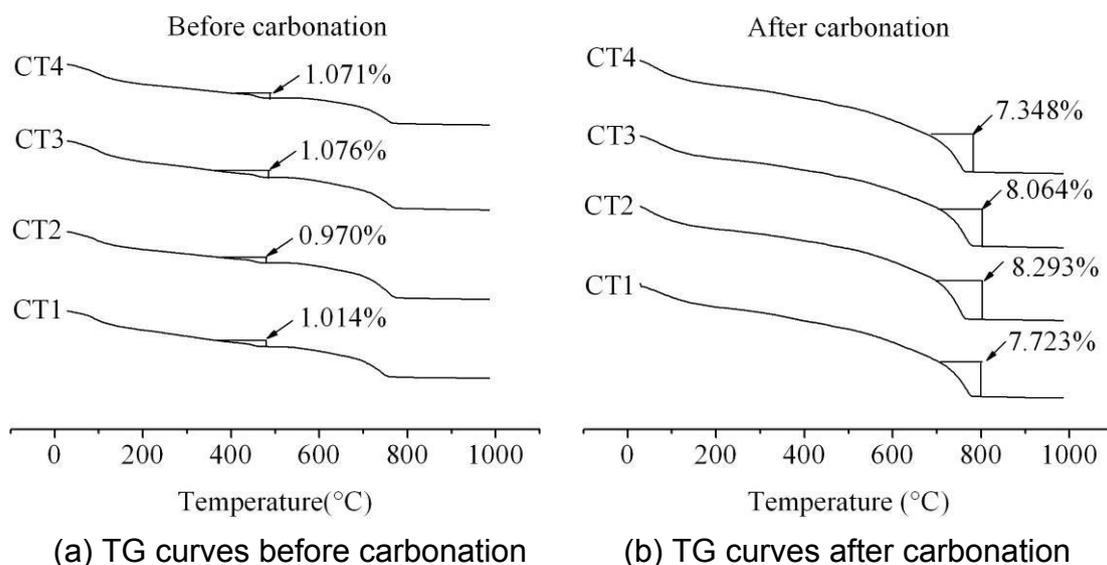
expansive admixture.

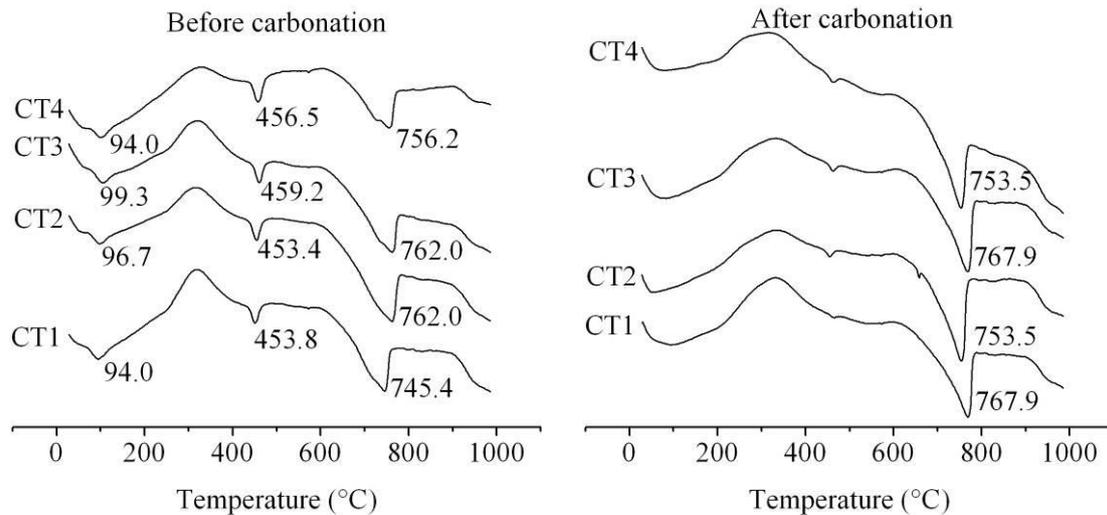
Though the content of calcium hydroxide mount up with the increase of expansive admixture, the effect of pore structure increase caused by expansive admixture works on carbonation depth of concrete much further. It is opposite, however, in standard curing condition, 90% of relative humidity can not only provide the water needed by hydration of expansive admixture, which makes ettringite form, but also it is not excessive expanded. As a result, it can enhance the compressive strength of concrete and advance the ability of resistance carbonation of concrete.

3.4 TG-DSC analysis

Coupled thermal gravimetric and differential scanning calorimetry (TG-DSC) analysis is used to calculate the hydration production content in concrete based on the different quality change of material at different temperature. The samples of concrete containing 10% of expansive admixture in different curing types are investigated with TG-DSC analysis in this paper. In the course of the temperature increase, free water loses below 100°C and pore water and interlayer water are driven off from the material between 100°C and 400°C. The ettringite decomposes at about 90~100 °C (Shimada and Young, 2004). The decomposition of $\text{Ca}(\text{OH})_2$ takes place at 450~550°C, and the mass loss is about 24.5% in this reaction. CaCO_3 decomposes at about 700~900°C (Alarcon-Ruiz et al., 2005).

There are endothermic peaks at about 90~100°C and there are also similar peaks between 400°C and 500°C before carbonation, which demonstrates that amounts of ettringite and $\text{Ca}(\text{OH})_2$ exist in concrete (Castellote et al., 2004). Whereas, at 700~800°C, the peaks belonged to CaCO_3 are also obvious after carbonation (Handoo et al., 2002). The results of TG-DSC curves are listed in Fig. 8.





(c) DSC curves before carbonation (d) DSC curves after carbonation
 Fig. 8 TG and DSC curves of concrete samples before and after carbonation for 7 days

It can be seen from the contents of samples before carbonation (Table 4) that, curing in water and standard curing are propitious to the hydration of cement paste, which can help form more $\text{Ca}(\text{OH})_2$ in concrete. Moreover, the hydration of expansive admixture, also bringing to $\text{Ca}(\text{OH})_2$, is influenced by curing types a lot. After carbonated for 7 days, $\text{Ca}(\text{OH})_2$ contents in the cement paste decline dramatically. It can be seen that, if cured in CT2, almost all of the $\text{Ca}(\text{OH})_2$ in carbonation regions are converted into CaCO_3 . Meanwhile, curing in CT4 shows an obvious improvement relatively to natural curing. It is also equivalent to that in standard curing. However, CT3 shows hardly any improvement to carbonation resistance ability.

The $\text{Ca}(\text{OH})_2$ contents of S10, seen from the Table 4, are 4.47% and 4.46% after cured in CT3 and CT4, which are higher than others significantly. Meanwhile, more ettringite are formed in hydration process when the ages immersed in water are longer, as a result of enough water provided in this environment. It is opposite to the ettringite content in nature curing condition, the least among them since 70% of relative humidity is the lowest correspondingly. The amount of $\text{Ca}(\text{OH})_2$ which is consumed in carbonation reaction form Table 4, has prodigious difference among these four curing types. There is 3.24% of $\text{Ca}(\text{OH})_2$ used up in carbonation process, which is much higher than the others. More precisely, the ability of resistant carbonation of concrete in this curing type is much worse because of the increase of total porosity even though the available content of $\text{Ca}(\text{OH})_2$ supplied to be carbonated also ascends.

3.5 MIP analysis

Mercury Intrusion Porosimetry (MIP) is used to analyze the pore structure of concrete before carbonation process under different curing conditions. The results of

total porosity of concrete are listed in Table 5.

It can be known that, the total porosity of concrete goes up from 20.47% to 21.06% if 10% of expansive admixture is blended in concrete in standard curing type. While, the total porosity of S10 cured in standard condition is smaller than that in CT4 significantly, which are 21.06% and 23.22%, respectively.

4. CONCLUSIONS

In different curing types, based on experimental results and the TG-DSC and MIP analysis above, the following conclusions can be drawn:

(1) In standard curing type, the compressive strength of concrete goes up and carbonation depth of concrete declines with the increased amount of expansive admixture. The higher the compressive strength is, the less the carbonation depth is. There is an approximate linear relationship between compressive strength and carbonation depth of concrete. However, carbonation depth and compressive strength have no clear relationship among nature curing type, immersed in water curing for 3 or 7 days type yet, because water has great influence on cement hydration process of concrete.

(2) By contrast with the concrete samples containing the same amount of expansive admixture in different curing conditions, nature curing is the worst option to the ability of resistance to carbonation of concrete due to the lack of water, while standard curing is the best choice.

(3) If samples are cured in water for 3 or 7 days, plenty of ettringite will form in hydration process and stresses generated in expansive reactions will also increase correspondingly, causing larger total porosity and lower compressive strength, which is good for accelerating carbonation process of concrete.

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REFERENCES

Alarcon-Ruiz, L., Platret G., and Massieu, E. (2005), “The use of thermal analysis in assessing the effect of temperature on a cement paste”, *Cement Concrete Res*, **35**(3), 609-613.

Alsayed, S.H. and Amjad, M.A. (1994), "Effect of curing conditions on strength, porosity, absorptivity, and shrinkage of concrete in hot and dry climate", *Cement Concrete Res*, **24**(7), 1390-1398.

Balayssac, J.P., Détriché, C.H. and Grandet, J. (1995), "Effects of curing upon carbonation of concrete", *Constr Build Mater*, **9**(2), 91-95.

Batic, O.R., Milanese, C.A. and Maiza P.J. (2000), "Secondary ettringite formation in concrete subjected to different curing conditions", *Cement Concrete Res*, **30**(9), 1407-1412.

Borges, P.H.R., Costa, J.O. and Milestone, N.B. (2010), "Carbonation of CH and C-S-H in composite cement pastes containing high amounts of BFS", *Cement Concrete Res*, **40**(2), 284-292.

Brouwers, H.J.H. (2005), "The work of Powers and Brownard revisited: Part 2", *Cement Concrete Res*, **35**(10), 1922-1936.

Castellote, M., Alonso C. and Andrade C. (2004), "Composition and microstructural changes of cement pastes upon heating, as studied by neutron diffraction", *Cement Concrete Res*, **34**(9), 1633-1644.

Chen, W. and Brouwers, H.J.H. (2012), "Hydration of mineral shrinkage-compensating admixture for concrete: an experimental and numerical study", *Constr Build Mater*, **26**(1), 670-676.

Colleparidi, M., Borsoi, A., and Colleparidi, S. (2005), "Effects of shrinkage reducing admixture in shrinkage compensating concrete under non-wet curing conditions", *Cement Concrete Comp*, **27**(6), 704-708.

Handoo, S.K., Agarwal, S. and Agarwal, S.K. (2002), "Physicochemical, mineralogical, and morphological characteristics of concrete exposed to elevated temperatures", *Cement Concrete Res*, **32**(7), 1009-1018.

Kwon, S.J. and Song, H.W. (2010), "Analysis of carbonation behavior in concrete using neural network algorithm and carbonation modeling", *Cement Concrete Res*, **40**(1), 119-127.

Lobo, C. and Cohen, M.D. (1991), "Pore structure development in type K expansive cement pastes", *Cement Concrete Res*, **21**(2-3), 229-241.

Lossier, H. (1946), "Cements with controlled expansions and their applications to pre-stressed concrete", *The Structural Engineer*, **24**(10), 503-534.

Neville, A.M. (1996), *Properties of concrete*. New York, Wiley.

Odler, I. and Subauste J.C. (1999), "Investigations on cement expansion associated with ettringite formation", *Cement Concrete Res*, **29**(5), 731-735.

Sahamitmongkol, R. and Kishi, T. (2011), "Tensile behavior of restrained expansive mortar and concrete", *Cement Concrete Comp*, **33**(1), 131-141.

Shimada, Y. and Young, J.F. (2004), "Thermal stability of ettringite in alkaline solutions at 80°C", *Cement Concrete Res*, **34**(12), 2261-2268.

Song, H.W. and Kwon, S.J. (2007), "Permeability characteristics of carbonated concrete considering capillary pore structure", *Cement Concrete Res*, **37**(6), 909-915.

Subauste, J.C. and Odler I. (2002), "Stresses generated in expansive reactions of cementitious systems", *Cement Concrete Res*, **32**(1), 117-122.

Taylor, H.F.W. (1997), *Cement chemistry*. London, Thomas Telford Ltd.