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Negative effect improvement of accelerated curing on chloride penetration resistance of ordinary concrete

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Abstract: Four mineral admixture concrete specimens were fabricated to study the negative effect improvements of accelerated curing on the chloride penetration resistance of ordinary concrete. After reaching different initial strengths, the specimens were placed in 40, 60, or 80 ℃ water tanks for accelerated curing. The Coulomb values of the specimens were measured with ASTM C1202 experiment at 28, 100, 200, and 300 d. Partial specimens were also selected for rapid chloride ion migration coefficient and mercury intrusion porosimetry experiments. The experimental results show that the accelerated curing for ordinary concrete linearly deteriorates the chloride penetration resistance, whereas the incorporation of mineral admixtures improves the concrete microscopic pore-structures and negative effects. An upper temperature limit of 60 ℃ of the accelerated curing is suitable for obtaining superior chloride penetration resistance for the mineral admixture concrete. Pre-curing at a normal temperature of 20 ℃ is beneficial for improving the negative effect, which is also alleviated with increasing testing age as a result of the successive hydration of binder materials in concrete.

Key words: negative effect improvement; chloride penetration resistance; ordinary concrete; accelerated curing

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Curing is fundamental for obtaining the strength and durability of concrete. Standard curing, natural curing, steam curing, and autoclave curing are the commonly used curing methods for concrete. Accelerated curing, such as steam curing and autoclave curing, is widely applied to precast concrete element plants because this method can shorten the required curing time, quickly obtain the designed strength, and increase the production efficiency[1-3]. However, the influence of accelerated curing on concrete performance is a double-edged sword.

Accelerated curing stimulates the activity of pozzolanic materials, promotes the speed and degree of hydration reaction of cementitious materials, increases the content of hydration products, and improves the compaction of concrete, concrete early age strength, and durability[4-6]. On the contrary, accelerated curing exacerbates the uneven distribution of hydration products, as well as increases porosity, micro-cracks, and defects due to the significant difference in the thermal expansion coefficient of each phase in concrete, which reduces the long term strength and durability of the concrete[7-10].

Some measures are studied to reduce or mitigate the negative effect of accelerated curing on concrete, such as partially substituting the mineral admixtures, prolonging the delay time, and setting the limit of curing temperature and duration. Aldea et al. [11] reported that the chloride permeability and penetrability of normal concrete are increased with steam curing and are reduced with the increasing replacement of slag. Hooton et al. [12] found that accelerated curing, ternary ordinary Portland cement, silica fume, and ground granulated blast-furnace slag binders did not have a detrimental effect on chloride penetration resistance. Sha et al. [13] found that prolonging the pre-curing time can increase the chloride resistance of steam-cured concrete, and the chloride resistance of standard-cured concrete is achieved when the pre-curing time reaches 6 h. Toutanji and Bayasi[14] found that steam curing can enhance the chloride resistance of silica fume concrete, and this effect is more significant with the increasing content of silica fume. Li et al. [15] revealed that the carbonation resistance of mineral admixture concrete can gradually improve with the increasing curing temperature until the upper limit of 60 ℃ and then it sharply declines.

Initial accelerated curing usually lasts for a short time, and most of the current studies focus on concrete performances at a short period of time after curing. Thus, these studies cannot reflect the real long-term performances of concrete as a result of the successive hydration of cementitious materials with the growth of concrete age. Khatib et al. [16] reported that curing substantially influences the chloride penetration in concrete at early periods of exposure, whereas the effect of curing is considerably reduced after a long period of exposure. Chen et al. [17] also suggested that the chloride diffusion coefficient of concrete depends on time, concrete types, and curing conditions.

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Hence, further study is needed to determine the influences of accelerated curing on ordinary concrete long-term durability performances. Chloride ion resistance is one of the major durability performances of concrete and one of the most important factors leading to steel bar corrosion[18-19]. This paper aims to study the long-term development of concrete chloride resistance after accelerated curing and to obtain some effective measures to reduce the negative effect of accelerated curing.

1 Experimental

1.1 Raw materials

P·O 42.5R ordinary Portland cement, class Ⅰ low calcium fly ash (type F), S105 ground granulated blast-furnace slag, and silica fume were adopted, and their properties are shown in Tab. 1. Natural river sand with fineness modulus of 2.63 and specific gravity of 2.64, crushed limestone with particle sizes from 5 to 20 mm and specific gravity of 2.71, and tap water were also used. In addition, a polycarboxylate superplasticizer was used as a water reducing agent. The following four mixtures of concrete were designed for comparison: fly ash concrete (FAC); fly ash and slag concrete (FSC); fly ash, slag, and silica fume concrete (FSSC); and ordinary Portland cement concrete (OPC). The detailed concrete mix proportions are presented in Tab. 2.

Tab. 1 Chemical composition of cementitious materials

Item	$w(SiO_2)/\%$	$w(Al_2O_3)/\%$	$w(Fe_2O_3)/\%$	$w(CaO)/\%$	$w(MgO)/\%$	$w(TiO_2)/\%$	Loss on ignition	Specific gravity
Cement	22.30	5.05	3.16	64.78	0.92		1.32	2.92
Fly ash	40.6	25.6	19.5	2.77	3.21	2.43	2.43	2.13
Slag	32.6	13.43	2.75	38.46	8.73	1.58	1.58	2.65
Silica fume	95.64	0.82	0.63	0.25	0.68	1.13	1.13	1.70

Tab. 2 Concrete mix proportions kg/m^3

Item	Cement	Fly ash	Slag	Silica fume	River sand	Crushed stone	Water	Water reducer
OPC	398	0	0	0	680	1 157	215	7.5
FAC	279	119	0	0	663	1 133	215	7.5
FSC	239	80	80	0	665	1 136	215	7.5
FSSC	218	80	80	20	660	1 129	215	7.5

1.2 Fabrication of concrete specimens and curing methods

Concrete was mixed by a forced mixer and was compacted by a table vibrator. Cylindrical specimens with 100 mm diameter and 200 mm height were fabricated and demolded at 24 h after casting. Considering that water is indispensable for cement hydration, specimens were applied in different temperature water tanks, such as 40, 60, and 80 ℃, for accelerated curing. The water temperature of each tank remained constant during the curing process. Specimens were also cured in 20 ℃ water for 28 d for comparison.

Specimens were initially kept in 20 ℃ water for pre-curing until a certain degree of strength (i.e., pre-cured strength) was obtained prior to the accelerated curing. In the current paper, FSSC specimens were designed with three pre-cured strengths at 7, 10.5, and 14 MPa. In addition, FSSC specimens with no pre-curing and having a compressive strength of 4.45 MPa were also designed for comparison. Other specimens were designed with a pre-cured strength of 14 MPa. Specimens were cured in different temperature water tanks until the designed strength of 35 MPa was obtained. The different curing times needed to achieve the specific strength for each specimen category were obtained based on previous experiments[20]. After the accelerated curing, specimens were removed from water and stored in a natural indoor environment with an annual average temperature of (20 ± 5) ℃ and an average relative humidity of (70 ± 10)%.

1.3 Chloride resistance experiment

The ASTM C1202 experiment measures the resistance of concrete to chloride ion penetration and is often used to evaluate the concrete resistance from chloride penetration. In this paper, specimens were investigated with ASTM C1 202 experiments at the age of 28, 100, 200, and 300 d to study the accelerated curing on concrete chloride resistance performances. Specimens were cut off at the two ends with about 25 mm in length using a rock-cutting machine and subsequently into three pieces of 50 mm in height before soaking in distilled water for 24 h in a vacuumed water tank. Afterward, the specimens were placed in a standard ASTM C 102 experimental device for testing. A direct current of 60 V was applied to the specimens and kept for 6 h. During testing, the intensity of current passing through each specimen was periodically recorded. The average value of three specimens was selected as the representative value. The risks of probability of chloride ion penetration for concrete with different Coulomb values are found in the evaluation standard of ASTM C1202. The Coulomb value Q of each specimen is calculated by

$$Q = 900(I_0 + 2I_{30} + 2I_{60} + \ldots + 2I_{330} + I_{360}) \qquad (1)$$

where I_0, I_{30}, and I_{60} are the current intensities corresponding to the subscript moment, accurate to mA.

In addition, as supplement and verification of Coulomb electric flux experiment, rapid chloride ion migration coefficient (RCM) experiments were also conducted for partial specimens of OPC and FAC at 28 d according to the Chinese code of GB/T 50082—2009.

1.4 Microscopic experiment

Partial specimens of OPC and FAC at 28 d were selected and subjected to mercury intrusion porosimetry (MIP) experiments to analyze the concrete micro-structures. An AutoPore IV 9510 mercury intrusion apparatus was adopted. In consideration of the specimen size requirement for microscopic experiment and to obtain the representative result, the mortar obtained from original concrete specimens was used to prepare the samples that were immersed in a bottle of anhydrous ethanol to prevent hydration. Mortar samples were extracted the day before testing, dried at (60 ± 5) ℃ to a constant weight (about 24 h), and sealed in a bottle until use.

2 Results and Discussion

2.1 Influence of curing temperature on concrete chloride resistance

Based on the data obtained from different testing ages, the developments of the Coulomb values of specimens under different curing temperatures are presented in Fig. 1. The values are similar except for OPC, and all exhibit nonlinear changes. In the curing temperature range of 20 to 60 ℃, the Coulomb values of all mineral admixture concrete, including FAC, FSC, and FSSC, exhibit a generally descending trend. The chloride resistance of mineral admixture concrete increases with the increase in curing temperature. As the curing temperature continuously increases (higher than 60 ℃), the Coulomb values exhibit a sharp increase, and thus, the concrete chloride resistance begins to sharply decrease. Corresponding to the specimen at 300 d, when the curing temperature increases from 20 to 60 ℃, the Coulomb values of FAC, FSC, and FSSC specimens decrease by 46.3%, 65.7%, and 64.5%, respectively. When the curing temperature increases from 60 to 80 ℃, the Coulomb values of FAC, FSC, and FSSC specimens increase by 47.0%, 55.9%, and 33.8%, respectively.

These phenomena are attributed to the pozzolanic activity of most mineral admixtures, such as fly ash, slag, or silica fume, which is very low at a normal temperature. Elevating the curing temperature can stimulate the pozzolanic activity, promote the hydration reaction speed, generate more hydrated gel products, and create a concrete denser[7-8]; thus, the resistance of concrete to chloride penetration is improved. The differences of expansion coefficient of each phase in concrete, such as aggregates,

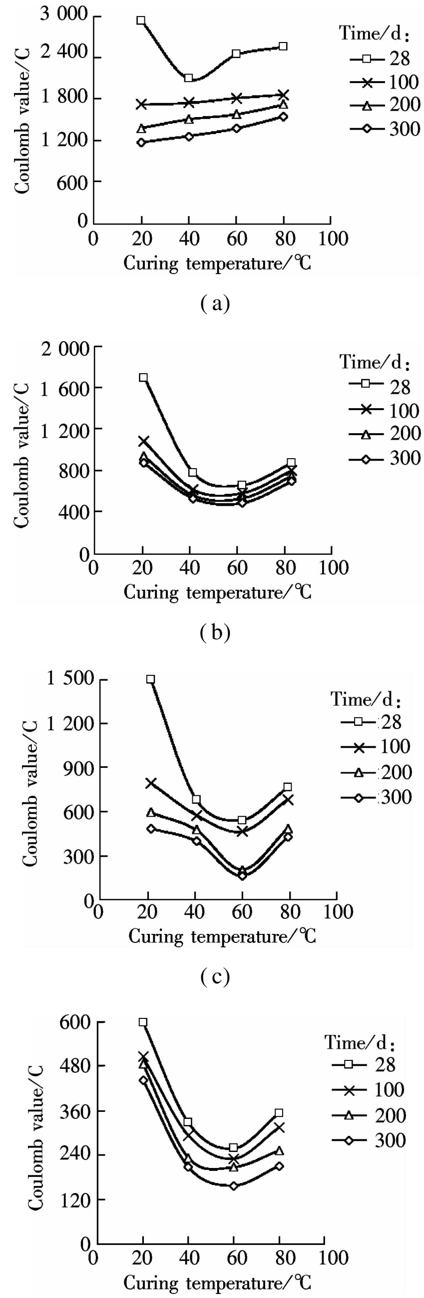

Fig. 1 Coulomb values of specimens under different curing temperatures. (a) OPC; (b) FAC; (c) FSC; (d) FSSC

hardened cement, water, and air, increase the porosity and formation of micro-cracks in concrete[21], thereby increasing the risk of chloride ion intrusion. Based on experimental results, 60 ℃ is the most suitable curing temperature for the mineral admixture concrete in obtaining superior chloride resistance, and excessively elevated temperature (above 60 ℃) or lowered temperature (under 60 ℃) can decrease the chloride resistance of the concrete.

For OPC specimens, the development of the Coulomb values with the curing temperature of concrete at every age forms a nearly linear ascending trend, i.e., chloride resistances linearly decrease against curing temperatures, which confirms the negative effect of accelerated curing on chloride resistance for ordinary concrete. For example, corresponding to 300 d, when the curing temperature increases from 20 to 80 ℃, the Coulomb values increase from 1 167.3 to 1 543.9 C with an increment of 32.3%, which also suggests that the chloride resistance of concrete is reduced by 32.3% when the curing temperature increases from 20 to 80 ℃.

The chloride ion migration coefficients of OPC and FAC specimens based on the RCM results are shown in Tab. 3. The development of chloride ion migration coefficients of OPC and FAC specimens with the initial curing temperatures obtained from RCM experiments is consistent with the results obtained from the Coulomb electric flux experiments. As the curing temperature increases from 40 to 80 ℃, the chloride ion migration coefficients of OPC specimens exhibit an ascending trend from 2.09×10^{-9} to 3.68×10^{-9} m^2/s, whereas that of FAC specimens first exhibit a descending and then ascending trend. The lowest chloride ion migration coefficient corresponds to the initial curing temperature of 60 ℃.

Tab. 3 Chloride ion migration coefficients $10^{-9}m^2/s$

Item	Curing temperature/℃		
	40	60	80
OPC	2.09	3.15	3.68
FAC	1.92	1.29	2.03

2.2 Influences of mineral admixtures on concrete chloride resistance

The particle sizes of fly ash, ground granulated blast-furnace slag, and silica fume are generally smaller than those of cement particles. The incorporation of such materials optimizes the microscopic pore structures of hardened cement through the filling effect, as well as increases the compactness of concrete, thereby improving the resistance to chloride ions penetration[11, 15, 22–24]. Fig. 2 provides the comparison of the Coulomb values of specimens cured at different temperatures at 300 d.

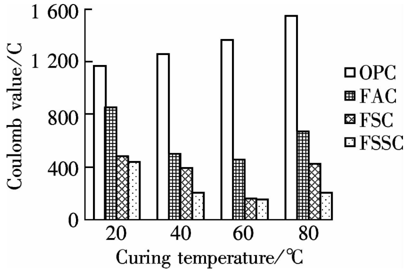

Fig. 2 Comparison of Coulomb values of different concrete mixtures

Although different Coulomb values of specimens are usually obtained at different curing temperatures for the same mixture, the order of these values is similar. The rating of chloride resistance of each mixture specimen whether under normal temperature or elevated temperature curing is FSSC > FSC > FAC > OPC.

Among these four mixtures, OPC specimens (as the control for comparison) have the poorest chloride resistance. The chloride resistance of FAC specimens is improved with 30% fly ash replacement ratio. The chloride resistance of FSC specimens is further improved with the binary incorporation of fly ash and slag with each replacement ratio of 20%. FSSC specimens exhibit the best chloride resistance with the ternary addition of fly ash (replacement ratio of 20%), slag (replacement ratio of 20%), and silica fume (replacement ratio of 5%). At corresponding 80 ℃ and 300 d, the Coulomb value of OPC is 1 543.9 C, which is considered low-grade in ASTM C1202 criterion. By contrast, the values for FAC, FSC, and FSSC are 674.3, 428.6, and 210.5 C, respectively, which are considered to have low probability of chloride penetration and are decreased by 56.3%, 72.2%, and 86.4% compared with OPC. This finding reveals that the addition of mineral admixtures can effectively improve the negative effect of accelerated curing on chloride resistance for ordinary concrete. Moreover, the effect of single addition is better than that of control, whereas the effect of binary addition is better than that of single addition, and the effect of ternary addition is better than that of the binary addition.

2.3 Influences of pre-cured strength on chloride resistance of concrete

Pre-curing is usually conducted to allow the concrete to obtain a certain strength prior to the elevated temperature curing, which is beneficial for the concrete to resist the internal thermal stress caused by the accelerated curing. The delay period before steam curing or autoclave curing in the production of pre-cast concrete elements has a similar role in pre-curing. According to Ref. [25], higher strengths are obtained in a shorter time by delaying the steam curing operation by a period equal to the setting time of concrete. The Coulomb values of FSSC specimens cured at different pre-cured strengths and temperatures at 300 d are shown in Fig. 3.

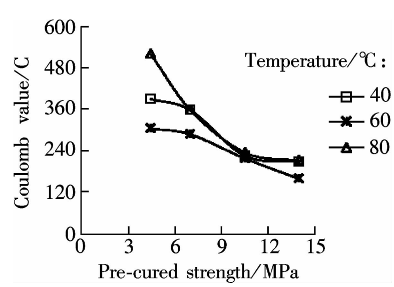

Fig. 3 Coulomb values of FSSC specimens at different pre-cured strengths

Corresponding to the same curing temperature, the Coulomb values of specimens with different pre-cured strengths are different, whereas the specimens with higher pre-cured strengths always correspond to lower Coulomb values. For example, compared with specimens with no pre-curing (4.45 MPa), the Coulomb values of specimens cured at 40, 60, and 80 ℃ decrease by 46.8%, 48.2%, and 59.5%, respectively, after obtaining a pre-cured strength of 14 MPa. The pre-curing at a normal temperature of 20 ℃ before accelerated curing is beneficial to the reduction of the negative effect on the chloride resistance of concrete. Moreover, higher pre-cured strength usually results in a greater improvement on the chloride resistance of concrete.

2.4 Influences of testing age on concrete chloride resistance

Generally, the duration of accelerated curing for precast concrete elements is relatively short, and the binder materials do not completely hydrate. Thus, even after curing, unhydrated cement particles or pozzolanic materials in concrete continue hydrating when free water remains in the concrete. This phenomenon affects the internal micro-pore structures and durability of the concrete. Fig. 4 provides the Coulomb values of four-mixture concrete species cured at 80 ℃ against different testing ages.

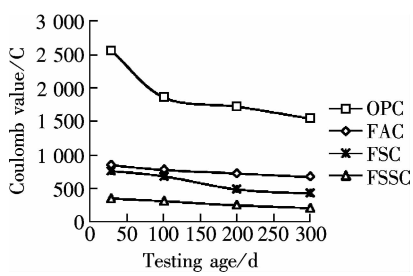

Fig. 4 Coulomb values of specimens with testing age

The finding in Fig. 4 is consistent with the previous theoretical analysis, which suggests that the Coulomb values of each mixture concrete gradually decrease with the increase in testing age, that is, the chloride resistance of the concrete gradually improves with increasing age. For example, the Coulomb values of OPC, FAC, FSC, and FSSC decrease by 39.7%, 20.8%, 43.9%, and 40.5% from the ages of 28 to 300 d. The average decreasing amplitude is 36.2%, and the smallest is FAC and the highest is FSC. This result is attributed to the activity differences of fly ash and slag. The pozzolanic activity at the normal temperature of the fly ash is lower than that of the slag. Thus, the long-term hydration of binder materials in FSC reaches a higher degree than that in FAC. This finding reveals that the negative effect of accelerated curing on concrete chloride resistance is alleviated with the increase of testing age.

2.5 Influences of curing conditions on concrete micro-structures

Most properties of hardened concrete are related to the quality and characteristics of pores in concrete[9,11]. Tab. 4 and Fig. 5 present the pore-size distribution results of FAC and OPC mortar samples at three curing temperatures of 40, 60, and 80 ℃ from MIP experiments at 28 d.

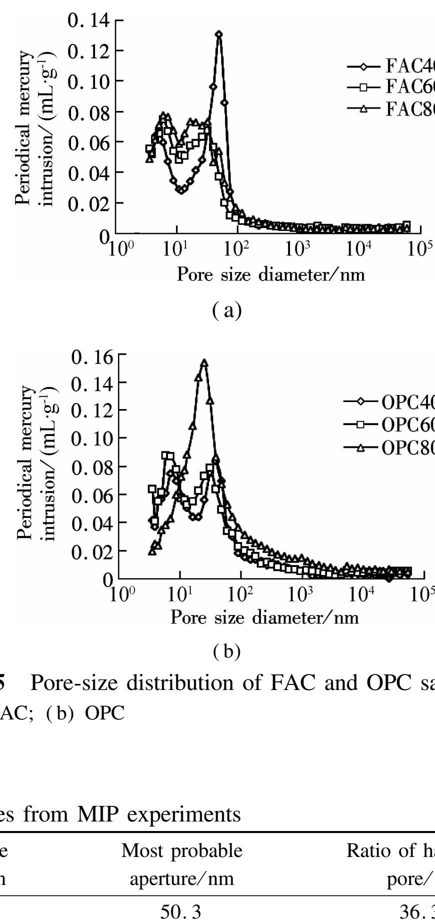

Fig. 5 Pore-size distribution of FAC and OPC samples. (a) FAC; (b) OPC

Tab. 4 Results of microscopic pore-structures from MIP experiments

Item	Curing temperature/℃	Porosity/%	Average pore diameter/nm	Most probable aperture/nm	Ratio of harmless pore/%
FAC	40	23.40	15.5	50.3	36.3
	60	17.74	13.0	6.03	50.8
	80	19.48	13.4	6.03	51.4
OPC	40	19.16	15.2	40.3	44.1
	60	21.16	14.7	6.03	45.5
	80	26.45	23.2	26.30	30.0

From Tab. 4 and Fig. 5, we can see that the initial curing temperature produces a significant effect on the microscopic pore-structures of both FAC and OPC specimens. For the OPC concrete, the concrete porosity and average pore diameter increase and the ratio of harmless pore decreases with the increase of curing temperature, which is consistent with results obtained by Kjellsen et al.[9,26]. Given the beneficial effect of increasing temperature on the activation of pozzolanic materials, corresponding 60 and 80 ℃ curing temperatures, concrete porosity, average pore diameter, and most probable aperture of FAC samples are all lower than those of OPC samples, and the ratio of harmless pores of FAC samples is higher than that of OPC samples. Therefore, the negative effect of accelerated curing on concrete microscopic pore-structures is improved to a certain degree with the use of fly ash.

3 Conclusions

1) Accelerated curing degrades the chloride resistance of ordinary concrete, whereas accelerated curing with the upper temperature limit of 60 ℃ increases the chloride resistance of mineral admixture concrete. However, surpassing this temperature also decreases the chloride resistance.

2) The incorporation of mineral admixtures, such as fly ash, slag, or silica fume, improves the concrete microscopic pore-structures and the negative effect of accelerated curing on chloride penetration resistance. Moreover, the effect of single mixing is better than that of the control, whereas the effect of binary mixing is better than that of single mixing, and the effect of ternary mixing is better than that of binary mixing.

3) Pre-curing of concrete at a normal temperature of 20 ℃ is beneficial for improving the negative effect of accelerated curing on the chloride resistance of concrete, and a higher pre-cured strength usually results in a greater improvement on the chloride resistance of concrete.

4) The negative effect of accelerated curing is alleviated with the increasing testing age as a result of the successive hydration of the binder materials in concrete. The negative effect of accelerated curing on chloride resistance for specimens at 300 d improved from 20.8% to 43.9% compared with that for specimens at 28 d.

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普通混凝土加速养护抗氯盐渗透能力的负效应改善

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摘要:为了对加速养护引起的普通混凝土抗氯盐渗透能力负效应进行改善,制作了 4 种掺矿物掺和料混凝土试件. 在达到一定的初始强度后,试件被分别放入 40, 60 和 80 ℃水槽中进行加速养护. 在 28, 100, 200 和 300 d 龄期,根据 ASTM C1202 试验标准测定了试件的电通量,同时还对部分试件进行了快速氯离子扩散系数和压汞实验. 实验结果表明,加速养护会导致普通混凝土的抗氯盐渗透能力线性劣化,而通过掺加矿物掺合料能够改善混凝土的微观孔隙结构和负效应. 对掺矿物掺合料混凝土而言,60 ℃是获得较优抗氯盐渗透能力的加速养护温度上限. 20 ℃常温条件的预养护对减轻此负效应有利,同时随着测试龄期的增长混凝土中胶凝材料的不断水化负效应也得以减轻.

关键词:负效应改善;抗氯盐渗透能力;普通混凝土;加速养护

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