



Effects of superplasticizers on carbonation resistance of concrete



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HIGHLIGHTS

- The effects of superplasticizers on concrete carbonation were researched.
- The effects of superplasticizers on carbonation of hydration products were researched.
- The effects of superplasticizers on concrete pore structure were investigated.
- The effects of superplasticizers on morphology of hydration products were investigated.
- The bonding state was researched by measuring the bond energy of calcium and oxygen.

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ABSTRACT

The effects of polycarboxylic acid (PC), naphthalene sulfonate (NS), and aliphatic (AH) superplasticizers on the carbonation of concrete were investigated. These three kinds of superplasticizers can improve anti-carbonation performance of concrete, and their order according to magnitude of effect are as follows PC > AH > NS. The mechanism behind this phenomenon was investigated using mercury intrusion porosimetry of the concrete, thermogravimetric analysis, X-ray diffraction, scanning electron microscopy, and X-ray photoelectron spectrometry of synthetic hydrated products. The effects of superplasticizers on carbonation resistance are associated not only with pore structure but also with the morphology of hydrated products.

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1. Introduction

A major concern in the deterioration of reinforced concrete is the corrosion of the steel reinforcement. The alkalinity of the concrete at the location of the steel, which can be reduced by carbonation, is the main factor causing this corrosion. A number of studies on concrete carbonation are available. Most of these studies focus on the effects of raw materials and associated environmental factors [1–4]. Carbonation is a chemical reaction between carbon dioxide (CO₂) and calcium hydroxide (CH), hydrated calcium silicate (C-S-H) or ettringite (AFt), in the presence of moisture [5,6]. The permeation and hydration characteristics of concrete are directly related to carbonation [7].

Nowadays, superplasticizers are used widely to produce flowable, strong, and durable Portland cement concretes and mortars. The hydration behaviors of Portland cement in the presence of superplasticizers have been investigated by a number of researchers [8–11]. The dispersing effect of superplasticizers on cement particles can improve the workability of cement, thereby improving the compactness, permeation resistance, and carbonation resistance of concrete.

However, other previous studies [12,13] have shown that superplasticizers affect not only the rheological behaviors of cement pastes but also their hydration characteristics. Superplasticizers can adhere to certain faces of hydrated product crystals and prevent or decelerate the addition of new growth layers on the faces [14]; as a result, superplasticizers can change the characteristics and morphologies of hydrated products. The change in the morphologies of hydrated products can affect the carbonation reaction of the concrete. However, the mechanisms underlying

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the effects of superplasticizers on the carbonation of concrete are still not understood.

In this study, an experimental investigation on the effects of polycarboxylic acid (PC), naphthalene sulfonate (NS), and aliphatic (AH) superplasticizers on the carbonation of concrete was conducted in an accelerated carbonation chamber. The porosities of different samples were measured using mercury intrusion porosimetry (MIP). The characteristics of the hydrated products that can react with CO₂ were measured by thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectrometry (XPS).

2. Experimental methods

2.1. Materials

The composition and properties of the cement used for concrete carbonation measurement are shown in Table 1. The mixture designs are listed in Table 2.

CH was prepared in CaO solution with water to solid ratio of 4:1. AFt was synthesized in Ca(OH)₂ and Al₂(SO₄)₃·18H₂O solution with a molar ratio of 6:1 and subsequently dried using a vacuum drying oven. C-S-H was synthesized with digest lime and silica through a hydrothermal method, with calcium/silicon (C/S) molar ratio of 1.5 and water to solid ratio of 5:1. Temperature was elevated to 120 °C in 2 h, maintained for 10 h, and then cooled down in 2 h. The reaction pressure was 0.198 MPa [15].

2.2. Measurements

2.2.1. Specimen preparation

The concrete specimens were 100 mm cubes cured at a temperature of 20 °C and a relative humidity (RH) of 95 ± 5% for 26 days and then dried at 60 °C for two days. The amounts of superplasticizers for the carbonation test were as follows: 0.18%, 0.27%, and 0.36% for PC; 0.21%, 0.32%, and 0.42% for NS; and 0.32%, 0.42%, and 0.52% for AH. Synthetic hydrated product specimens were prepared for XRD, SEM, and XPS tests using the following amounts of superplasticizers: 0.27% PC (0.27PC), 0.32% NS (0.32NS), and 0.42% AH (0.42AH), according to the carbonization test of concrete, the depth of carbonization is the least when these amount of superplasticizers were added.

2.2.2. Measurement methods

Carbonation was measured in concrete specimens and synthetic hydrated product specimens. Concrete specimens were kept inside a carbonation chamber (Model SJ-2, China) for 3, 28, 56, and 100 days under the following conditions: CO₂ concentration = 20% ± 5%, RH = 70% ± 5%, and T = 20 ± 1 °C. The imposed RH ≈ 70% was selected to ensure that the carbonation rate was at a maximum. Concrete carbonation depths were measured by phenolphthalein sprayed on split discs sections after carbonizing. Around the four sides of the section every 10 mm was chosen as a measuring point and the carbonization depth was measured with a vernier caliper, and then calculated the average value. If the carbonization dividing line at the measuring point is located coarse aggregate, the average value of the carbonization depth at both side of the coarse aggregate can be used as the depth value of the measuring point. The synthesized products, including CH, AFt, and C-S-H were analyzed by TGA (Model TGA/DSC 1 STAR System; Switzerland Mettler Toledo Company) after three days of carbonation; the weight changes were determined as the sample was heated at a uniform rate of 10 °C/min from 25 °C to 1150 °C in a gas flow of nitrogen (N₂).

Pore size distribution was determined by MIP in the cement pastes of the concrete specimens aged for 28 days by using an Hg-porosimetry (Autopore, IV 9510, USA). The microstructure characteristics of the hydrated products were examined using XRD (Model D/max-2400; Japan Rigaku Corporation) and SEM (Model FEI Quanta 200; Holland FEI Company, operated at 20 kV). The bonding state was investigated via XPS (Model XSAM800; England Kratos Company) with a MgKα (hν = 1253.6 eV) X-ray source operating at 260 W (13 kV, 20 mA). The samples for microstructure analysis were sawn from each uncarbonated specimen after drying.

Table 1
Composition and properties of cement.

Type	Composition (%)							Properties		
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	LOI	Specific gravity	Setting time (hour: min)	
									Initial	Final
OPC	22.32	5.84	3.15	61.23	2.02	2.27	1.66	3.19	2:20	3:40

Table 2
Mixture proportions of concrete.

W/C ratio	Cement (kg/m ³)	Water (kg/m ³)	Fine (kg/m ³)	Coarse (kg/m ³)
0.42	350	147	735	1098

3. Result and discussion

3.1. Effects on concrete carbonation

3.1.1. Carbonation tests

Fig. 1 shows the concrete carbonation results with and without superplasticizer. The PC superplasticizer can significantly improve the carbonation resistance of concrete, but this effect does not increase with the increase in dosage of the superplasticizer. When the dosage of the PC superplasticizer is small, the carbonation resistance of concrete increased with the superplasticizer content; but when the dosage of PC superplasticizer is large, the carbonation resistance of concrete decreased with increasing dosage of PC superplasticizer. This result may be ascribed to the following mechanism: the large amount of superplasticizer reduces the actual requirement for concrete mixing water and the surplus water will enhance the formation of concrete pores, which are beneficial to the diffusion of CO₂, thereby increasing the early carbonation rate.

The NS superplasticizer can also improve the anti-carbonation performance of concrete. Variations in carbonation depths of concrete samples with different dosages of the NS superplasticizer are not obvious, but when the carbonation age is increased to 100 days, the carbonation depth decreases with an increase in the amount of superplasticizer. The effect of the AH superplasticizer on the early concrete anti-carbonation performance did not change significantly, the later change law is similar to the sample with PC superplasticizer, but the overall carbonation depth is larger than the sample with PC superplasticizer.

Although all three kinds of superplasticizer can improve the anti-carbonation performance of concrete, the magnitudes of their effects differ. PC has the most obvious effect, followed by AH. NS has the least effect.

3.1.2. Mercury intrusion porosimetry

The main influencing factor on concrete strength and durability is pore structure, which includes average pore size, pore size distribution, and total porosity. The results presented in Figs. 2 and 3 show the effects of different superplasticizers on concrete pore structure.

Cumulative pore volume is related to total porosity. The samples with superplasticizers have lower cumulative pore volume than the sample without superplasticizer. Thus, superplasticizers can improve the carbonation resistance of concrete. Fig. 3 shows the distribution of pore volumes of the samples with and without superplasticizer. The volume of large pores with a size of ≥ 100 nm in the sample Blank and sample with NS superplasticizer are higher than the volume of the sample with PC or AH superplasticizer; thus, NS contributes less to the improvement of carbonation

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