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A model for predicting carbonation of high-volume fly ash concrete

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Abstract

The carbonation process and the factors affecting concrete carbonation are presented. A mathematical model based on carbonation process for predicting the carbonation depth of high-volume fly ash (HVFA) concrete was developed. An accelerated carbonation test was conducted on ordinary Portland cement (OPC) concrete and HVFA concrete. The depths of carbonation predicted from the model are compared with the test results. It is shown that the effective water/binder ratio and the cement content are the key factors affecting HVFA concrete carbonation. The increase of curing period can improve the carbonation behavior of HVFA concrete. The carbonation behavior of HVFA concrete with appropriate mix proportion can meet the requirements of structural concrete. The agreement between test results and the prediction from the model is good. The model can be used to predict the evolution of carbonation depth with time. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Carbonation; Fly ash; Concrete; Model

1. Introduction

Concrete containing fly ash has been used in many parts of the world for several decades. Various standards and codes have generally limited the use of fly ash from 10% to 25% in structural concrete. Relatively large volumes of fly ash are used only in mass concrete. The development of structural concrete utilizing high-volumes of fly ash was undertaken by CANMET commencing in 1985 [1]. The investigation by CANMET and others confirmed that high-volume fly ash (HVFA) concrete has many excellent properties [2,3].

In the design of concrete structures, carbonation is one of the many important factors that determine the service life of a concrete structure. Numerous papers have been published about concrete carbonation with and without cementitious materials [4]. There are conflicting published data concerning the carbonation of concrete containing fly ash. In general, however, the presence of fly ash does seem to result in a more rapid carbonation. It is, therefore, important to know the carbonation behavior of HVFA concrete. The HVFA concrete studied in this report is significantly different, in terms of water/binder ratio, from those reported by Malhotra [1] and Bilodeau et al. [2]. The data on carbonation reported in this study cannot be compared directly with the data reported by Malhotra [1] and Bilodeau et al. [2].

In this study, a mathematical model about HVFA concrete carbonation has been developed and experimentally validated. The model allows a quantitative prediction of the carbonation of concrete with time.

2. Factors affecting concrete carbonation

Concrete carbonation is a complicated physicochemical process. The process includes the diffusion of CO_2 in the gaseous phase into the concrete pores, its dissolution in the aqueous film of these pores, the dissolution of solid $Ca(OH)_2$ in the water of the pores, the diffusion of dissolved $Ca(OH)_2$ in pore water, its reaction with the dissolved CO_2, and the reaction of CO_2 with C-S-H and with the yet unhydrated C_3S and C_2S. In addition, there is a parallel process. This process includes the hydration of cementitious materials and the reduction of concrete porosity.

The carbonation process indicates that the factors controlling carbonation are the diffusivity of CO_2 and

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the reactivity of CO_2 with the concrete. The diffusivity of CO_2 depends upon the pore system of hardened concrete and the exposure condition. The pore system of concrete depends upon the type and the content of binder, water/binder ratio, and the degree of hydration. The main exposure conditions related to carbonation are the concentration of CO_2 and relative humidity. The reactivity of CO_2 with concrete depends mainly upon the type and the content of binder and the degree of hydration. Thus, the main factors affecting concrete carbonation are the type and the content of binder, water/binder ratio, the degree of hydration, the concentration of CO_2, and relative humidity.

3. Mathematical model

Based on the carbonation process and the factors affecting concrete carbonation, a mathematical model was reported by Jiang et al. [5], Eq. (1):

$$x = 839(1 - \mathrm{RH})^{1.1}\sqrt{\frac{\frac{W}{r_c C} - 0.34}{r_{\mathrm{HD}} r_c C}}\, C_0 \sqrt{t} \tag{1}$$

where x is the depth of carbonation (mm), RH is relative humidity, W is the content of water (kg/m^3), C is the content of cement (kg/m^3), C_0 is the concentration of CO_2 (%), r_c is the coefficient for cement type, r_{HD} is coefficient of degree of hydration, t is the time of exposure (days).

Test results show that the above model is not suitable for HVFA concrete [3]. This is because HVFA concrete is different from OPC concrete and blended cement concrete. The main difference is that the fly ash used in HVFA concrete cannot be completely hydrated. If each SiO_2, Fe_2O_3, and Al_2O_3 molecule combines with one CaO molecule after hydration, the maximum fly ash content M (%) which can be hydrated is [3], Eq. (2):

$$\begin{aligned} M = {} & (C_1 - 0.93S_1 - 0.55A_1 - 0.35F_1 - 0.70\overline{S}_1) \\ & /(0.93(S_2 - S_1) + 0.55(A_2 - A_1) + 0.35(F_2 - F_1) \\ & + 0.70(\overline{S}_2 - \overline{S}_1) - (C_2 - C_1)) \end{aligned} \tag{2}$$

where C_1, S_1, A_1, F_1 and S_1 are the content of CaO, SiO_2, Al_2O_3, Fe_2O_3 and SO_3 in cement, respectively; C_2, S_2, A_2, F_2 and S_2 are the content of CaO, SiO_2, Al_2O_3, Fe_2O_3 and SO_3 in fly ash, respectively. In HVFA concrete, the fly ash content is higher than M. Thus, some fly ash cannot be hydrated. This has been confirmed by some test results [3,6]. It is not appropriate to use water/cement ratio or water/binder ratio in the carbonation calculation of HVFA concrete. For HVFA concrete, the effective water/binder ratio defined by Eq. (3) should be used.

$$\mathrm{W/B}^* = \frac{W}{C + F'} \tag{3}$$

where W/B* is effective water/binder ratio, F' is the fly ash content which can be hydrated. W/B* can be calculated by Eq. (4):

$$\mathrm{W/B}^* = \frac{1 - M}{1 - m} \cdot \frac{W}{(C + F)} \tag{4}$$

where m is the fly ash content (%). The carbonation reactions of OPC concrete are Eqs. (5–7):

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{5}$$

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O \tag{6}$$

$$C_3S_2H_2 + 3H_2CO_3 \rightarrow 3CaCO_3 + 2SiO_2 + 6H_2O. \tag{7}$$

In addition, the carbonation reactions of the yet unhydrated C_3S and C_2S can also take place. Based on the above reactions, the following relationship of molarity exists.

$$m_0 = [Ca(OH)_2]^0 + 3[C_3S_2H_3]^0 + 3[C_3S]^0 + 2[C_2S]^0 \tag{8}$$

where m_0 is the reactivity of CO_2 with concrete. For completely hydrated OPC concrete [Eqs. (9–12)]:

$$\begin{aligned} [Ca(OH)_2]^0 = {} & \frac{3}{2}[C_3S]_0 - 4[C_4AF]_0 + \frac{1}{2}[C_2S]_0 - [C_3A]_0 \\ & + [C\overline{S}H_2]_0 \end{aligned} \tag{9}$$

$$[C_3S_2H_3]^0 = \frac{1}{2}[C_3S]_0 + \frac{1}{2}[C_2S]_0 \tag{10}$$

$$[C_3S]^0 = 0 \tag{11}$$

$$[C_2S]^0 = 0. \tag{12}$$

For HVFA concrete, the hydration reactions of fly ash are Eqs. (13–14):

$$x\,Ca(OH)_2 + SiO_2 + m_1H_2O \rightarrow x\,CaO \cdot SiO_2 \cdot n_1H_2O \tag{13}$$

$$y\,Ca(OH)_2 + Al_2O_3 + m_2H_2O \rightarrow y\,CaO \cdot Al_2O_3 \cdot n_2H_2O. \tag{14}$$

Table 1
Composition (mass %) and physical properties of Portland cement and fly ash

	Portland cement	Fly ash
SiO_2	21.42	44.98
Al_2O_3	4.68	30.08
Fe_2O_3	6.15	13.92
CaO	63.78	3.69
MgO	1.88	1.41
SO_3	1.08	0.15
Na_2O	0.19	–
K_2O	0.53	–
Loss on ignition	1.55	4.34
Specific gravity	3.16	2.38
Fineness, retained on a 45 μm sieve (%)	8.5	2.3

Table 2
Mix proportions and results of tests on the fresh concrete

Mix no.	Cement (kg/m^3)	Fly ash (kg/m^3)	$F/(C+F)$ (%)	$W/(C+F)$	WR (%)	Air (%)	Slump (mm)
C1	222	0	0	0.60	M, 0.2	–	55
F1-55	100	122	55	0.46	SA, 1.7	3.5	50
F1-70	67	155	70	0.50	SA, 1.7	3.0	60
C2	333	0	0	0.45	M, 0.2	–	75
F2-55	150	183	55	0.38	SA, 1.7	3.5	70
F2-70	100	233	70	0.37	SA, 1.7	2.0	70

So

$$[\mathrm{Ca(OH)_2}]_1^0 = [\mathrm{Ca(OH)_2}]^0 - x[\mathrm{C}_x\mathrm{SH}_{n1}]^0 - y[\mathrm{C}_y\mathrm{AH}_{n2}]^0 \tag{15}$$

$$m_0' = [\mathrm{Ca(OH)2}]_1^0 + 3[\mathrm{C_3S_2H_3}]^0 + x[\mathrm{C}_x\mathrm{SH}_{n1}]^0 + 3[\mathrm{C_3S}]^0 + 2[\mathrm{C_2S}]^0. \tag{16}$$

Taking into account Eq. (15) and Eq. (16)

$$m_0' = [\mathrm{Ca(OH)_2}]^0 + 3[\mathrm{C_3S_2H_3}]^0 - y[\mathrm{C}_y\mathrm{AH}_{n2}]^0 + 3[\mathrm{C_3S}]^0 + 2[\mathrm{C_2S}]^0. \tag{17}$$

If the OPC concrete and HVFA concrete have the same cement content, comparing Eq. (17) with Eq. (8), the result of $m_0 > m_0'$ can be obtained. That is, the reactivity of OPC concrete with CO_2 is greater than HVFA concrete, but this does not mean that the carbonation of HVFA concrete must be more rapid than OPC concrete. This is because there is another main factor affecting concrete carbonation or pore system of hardened concrete. Under ordinary condition, the y and $n2$ in Eq. (17) can take the values of 1 and 6, respectively. For the completely hydrated HVFA concrete [Eqs. (18–19)]

$$m_0' = m_0 - [\mathrm{CAH_6}]^0 \tag{18}$$

$$[\mathrm{CAH_6}]^0 = \frac{M}{1-M} \cdot C \cdot m_{\mathrm{fa}} \frac{1}{102 \times 10^{-3}} \tag{19}$$

where m_{fa} is the content of Al_2O_3 in fly ash (%), 102×10^{-3} is the molar mass of Al_2O_3 (kg/mol). From reference [5], Eq. (20):

$$m_0 = 8.03 \cdot C. \tag{20}$$

Thus [Eqs. (21–22)]:

$$m_0' = (1-k)m_0 \tag{21}$$

$$k = \frac{M}{1-M} \cdot m_{\mathrm{fa}} \cdot \frac{1}{102 \times 10^{-3}} \cdot \frac{1}{8.03}. \tag{22}$$

The model for predicting carbonation depth of HVFA concrete is Eq. (23):

$$x = 839(1-\mathrm{RH})^{1.1} \sqrt{\frac{\mathrm{W/B^*} - 0.34}{\alpha k' C} C_0} \sqrt[n]{t} \tag{23}$$

where α is the degree of hydration of cement, k' is a coefficient related to carbonation reactivity, which can be calculated by Eq. (24), n is a parameter related to the pore system of concrete, the value of n is between about 2.0 and 2.1.

$$k' = 1 - \beta k \tag{24}$$

where β is the degree of hydration of fly ash.

For HVFA concrete itself, the model shows that the key factors affecting carbonation are W/B* and C. The model also shows that, provided the mix proportions are appro-

Table 3
Experiments' results of carbonation of concrete specimens

			Depth of carbonation (mm)					
	Compressive strength (MPa)		Duration of exposure[a]			Duration of exposure[b]		
Mix no.	28 days	90 days	7 days	14 days	28 days	7 days	14 days	28 days
C1	25.6	30.1	14	15	17	11	13	16
F1-55	24.9	28.3	20	22	25	16	18	22
F1-70	16.8	25.2	48	50	50	45	50	50
C2	30.2	38.3	10	11	12	7	10	12
F2-55	32.3	41.0	13	16	18	9	12	14
F2-70	25.7	35.7	17	25	42	15	22	40

[a] Curing period of 28 days.

[b] Curing period of 90 days.

priate, the carbonation behavior of HVFA concrete can meet the requirements of structural concrete.

Table 4
Predicted and observed depth of carbonation (mm)

Mix no.	Exposure time (days)	Predicted[a]	Tested[a]	Predicted[b]	Tested[b]
F1-55	7	16	20	14	16
	14	21	22	20	18
	28	29	25	27	22
F2-55	7	10	13	9	9
	14	14	16	13	12
	28	18	18	17	14
F2-70	7	19	17	18	15
	14	27	25	25	22
	28	37	42	36	40

[a] Curing period of 28 days.
[b] Curing period of 90 days.

4. Outline of experiments

Analyses of the cement and fly ash employed are given in Table 1. The mix proportions of the concrete tested are given in Table 2. Test specimens for accelerated test were cured at 20°C (±3°C) until the time of testing. According to GBJ 82–85 (Chinese standard), the accelerated carbonation test was conducted in a test chamber kept at a temperature of 20°C, a relative humidity of 70% and a concentration of CO_2 of 20%. Test specimens were 100 × 100 × 200 mm. Depth of carbonation was determined by removing a slice about 50-mm thick from the end of the specimen, spraying the freshly broken samples with phenolphthalein indicator, and measuring the depth to the colour change. The depth of carbonation was measured at eight points each side, using a scale which enabled a single measurement of depth of carbonation to be made to within ±1 mm.

5. Test results and comparison with model prediction

Test results are given in Table 3. Table 3 shows that at a given binder content, the depth of carbonation of HVFA concrete is greater than OPC concrete. The more the concrete contains fly ash, the greater the depth of carbonation becomes. In addition, the depth of carbonation decreased with the increase of curing period. Carbonation depths of some HVFA concrete at the curing period of 90 days are close to the OPC concrete.

Values of carbonation depth predicted from the model are compared with some of the experimental data in Table 4. It can be seen that the agreement between test results and the predications of the model is good. The correlation coefficient between them is 0.90.

6. Conclusions

The model for predicting HVFA concrete carbonation is in good agreement with the test results obtained in an accelerated carbonation apparatus. It can be used to predict the evolution of carbonation depth with time. However, more tests are required to confirm these preliminary observations.

From this study, it can also be seen that at a given binder content, the carbonation depth of HVFA concrete is greater than OPC concrete. The increase of curing period can improve the carbonation behavior of HVFA concrete. The carbonation depth of HVFA concrete of appropriate mix proportion can approach that of OPC concrete, and meet the requirements of structural concrete.

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