

Evaluation of carbonation depth of high calcium fly ash blended concrete

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ABSTRACT

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High calcium fly ash (FH) is the combustion residue in electric power plants burning lignite or sub-bituminous coal and can be used to produce high performance concrete. For concrete incorporating FH, hydration of Portland cement and reaction of FH will proceed simultaneously. Hence the carbonation of FH blended concrete is much more complex than that of control concrete. This paper presents a numerical procedure to evaluate carbonation depth of FH blended concrete. This numerical procedure consists of a blended cement hydration model and a carbonation reaction model. First, by using the blended cement hydration model considering cement hydration, reaction of free CaO in FH, and reaction of other phases in FH except free CaO, the properties of hardening FH blended concrete, such as calcium hydroxide contents, calcium silicate hydrate contents, reaction degree of high calcium fly ash, and porosity can be determined. Second, by using the carbonation reaction model, the diffusivity of CO₂ in FH blended concrete is calculated and the carbonation depth of FH blended concrete is predicted. The proposed numerical procedure is verified using experimental results of FH blended concrete with different water to binder ratios and high calcium fly ash replacement ratios.

Keywords: carbonation; high calcium fly ash; hydration; kinetic modeling; calcium hydroxide

Introduction

Fly ash is created in coal-burning electricity generating stations and it has been broadly employed for producing high performance concrete. Fly ashes could be split into two groups based on calcium content. The very first kind of fly ash, that contains under 10% analytical CaO, is known as low calcium fly ash (LH) and generally is a product from the combustion of anthracite and bituminous coals. The 2nd kind of fly ash, typically that contains 15 to 40% analytical CaO, is known as high calcium fly ash (FH) and generally is a product of combustion of lignite and sub-bituminous coals [1,2].

Carbonation is a fundamental durability issue of fly ash blended concrete. Many experimental investigations have been done about carbonation of Portland cement concrete or FH blended concrete. Papadakis [3,4] found that the carbonation of Portland cement concrete relates with both environmental conditions, such as CO₂ concentration and ambient relative humidity, and the compositions of cement and concrete, such as the amount of carbonatable constituents and porosity. Burden [5] studied the carbonation of FH blended concrete with different water to binder ratios (0.34 to 0.5) and FH replacement ratios (30% to 50%). The results show that FH concrete carbonate



significantly more rapidly than Portland cement concrete of the same water to binder ratios. Cwik et al [6,7] found that carbonation of high calcium fly ash has a potential for CO₂ removal in coal fired power plant. About 21% CO₂ emission can be sequestered as carbonation of high calcium fly ash blended concrete. Ashraf [8] reported carbonation of concrete has been traditionally viewed as a detrimental aspect for cement-based materials. Nonetheless, it can also be regarded as an opportunity to create a sustainable concrete industry by storing CO₂ in cement-based materials and utilizing carbonate binders with low CO₂ footprint.

Compared with abundant experimental investigations, theoretical modeling about carbonation of FH blended concrete is limited. Most of current models [9-11] considers hydration of cement clinkers, diffusion of CO₂ in porosity of concrete and reaction between CO₂ and carbonatable constituents. Due to lack of FH reaction, these models [9-11] are only valid for Portland cement concrete and can not be adopted to evaluate carbonation depth of FH blended concrete. Papadakis [12] predicted Carbonation depth of the FH blended concrete as a further result considering both environmental conditions and carbonatable constituents in concrete. But Papadakis' model is not a kinetic model and the kinetic of reactions involved in FH concrete were not reflected in his model. Ta et al [13] proposed a meta model for predicting carbonation depth of concrete considering environmental condition and material properties. However, Ta et al's model did not consider the difference of reactivity of cement and FH. Ekolu [14] evaluated natural carbonation depth of outdoor carbonation based on the statistics of 163 data of 10-years carbonation. But the fundamental mechanisms of carbonation, such as production of carbonatable substances and diffusion of CO₂, are not considered in Ekolu [14]'s study.

To overcome the shortcomings in current models [9-14], this paper presents a new numerical procedure to evaluate carbonation depth of FH concrete. The flowchart of numerical procedure is shown in Figure 1 This numerical procedure starts with a blended cement hydration model considering both cement hydration and FH reaction. The properties of hardening FH blended concrete, such as calcium hydroxide contents, calcium silicate hydrate contents, reaction degree of high calcium fly ash, and porosity are determined as functions of curing age. Furthermore, by using the carbonation reaction model, the diffusivity of CO₂ in FH blended concrete is calculated and the carbonation depth of FH blended concrete is predicted.

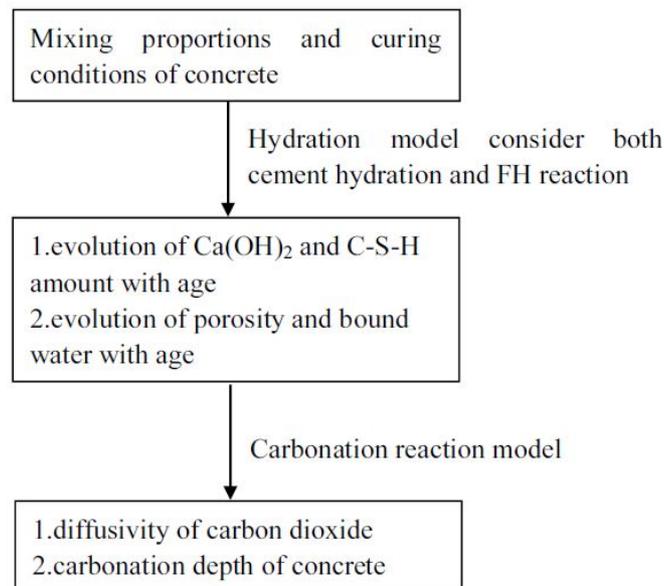


Figure 1. The flowchart of numerical procedure.

Hydration model of cement-FH blends

Introduction of FH blended cement hydration model

In our previous studies [1,2,15], a hydration model is proposed for analyzing the hydration of blended concrete containing supplementary cementitious materials, such as fly ash, slag, and silica fume. The hydration degree of cement and reaction degree of FH are adopted as fundamental indicators to evaluate properties of hardening FH blended concrete. The hydration degree of cement (α) is defined as the ratio of the mass of hydrated cement to the mass of cement in the mixing proportion. The value of the hydration degree of cement (α) ranges between 0 and 1. $\alpha=0$ means cement hydration does not start and $\alpha=1$ means all the cement has been hydrated. The hydration degree of cement can be determined using an integration method in the time domain ($\alpha = \int_0^t \left(\frac{d\alpha}{dt} \right) dt$, where t is time; $\frac{d\alpha}{dt}$ is the rate of cement hydration. The detailed equation for $\frac{d\alpha}{dt}$ is available in our former research [15]). Similarly, the reaction degree of FH (α_{FH}) is defined as the ratio of the mass of reacted FH to the mass of FH in the mixing proportion. The value of the reaction degree of FH (α_{FH}) ranges between 0 and 1. $\alpha_{FH}=0$ means the FH reaction does not start and $\alpha_{FH}=1$ means all the FH has reacted. The reaction degree of FH can also be determined using an integration method in the time domain ($\alpha_{FH} = \int_0^t \left(\frac{d\alpha_{FH}}{dt} \right) dt$, where $\frac{d\alpha_{FH}}{dt}$ is the rate of the FH reaction. The detailed equation for $\frac{d\alpha_{FH}}{dt}$ is available in our former research [15]).

Mutual interactions between cement hydration and FH reaction

High calcium fly ash contains free CaO. The reaction of free CaO in FH is first order reaction whose rate is directly proportional to the degree of reaction. Fan and Wang [15] proposed that the reaction degree of free CaO α_{CF} can be described as follows:

$$\alpha_{CF}(t) = 1 - \frac{1}{e^{kt}} \quad (1)$$

where k is reaction rate coefficient (k is 0.09/h when temperature is 20 degree [15]).

Cement-FH blends consists of free CaO in FH, other phases except free CaO in FH, and cement. The reactions of free CaO and cement produce calcium hydroxide, and the reaction of other phases except free CaO consumes calcium hydroxide. Considering the production of calcium hydroxide from cement hydration and reaction of free CaO in FH, the consumption of calcium hydroxide from reaction of other phases in FH except free CaO [15], using the molar weights of reactants and products, the content of calcium hydroxide in FH-cement blends can be determined as follows:

$$CH(t) = C_0 RCH_{CE} \alpha + 1.321 CF(t) - \nu_{FH} \alpha_{FH} P \quad (2)$$

where $CH(t)$ is calcium hydroxide content, C_0 and P are the masses of cement and FH, respectively. RCH_{CE} and ν_{FH} are the produced CH from 1 gram cement and the consumed CH from 1 gram FH, respectively, and $CF(t)$ is the mass of reacted free CaO at time t .

Similarly, the mass of calcium silicate hydrate (C-S-H) relates with cement hydration and FH reaction. The mass of C-S-H can be determined as follows:

$$CSH(t) = 2.85(f_{s,c} \alpha C_0 + \gamma_S f_{s,p} \alpha_{FH} P) \quad (3)$$

where $f_{s,c}$ and $f_{s,p}$ are the mass fraction of silica in cement and FH respectively. γ_S is active fraction of FH. $2.85f_{s,c} \alpha C_0$ considers the production of C-S-H from cement hydration, and $2.85\gamma_S f_{s,p} \alpha_{FH} P$ considers the production of C-S-H from FH reaction.

The porosity of hydrating blends is reduced due to the Portland cement hydration, reaction of free CaO in FH, and reaction of other phases in FH except free CaO. The porosity, ϵ , can be estimated as follows:

$$\epsilon = W/\rho_W - \Delta\epsilon_c - \Delta\epsilon_{CF} - \Delta\epsilon_{FH} \quad (4)$$

where W is mass of water, ρ_W is density of water, $\Delta\epsilon_c$, $\Delta\epsilon_{CF}$, and $\Delta\epsilon_{FH}$ are the porosity reduction due to Portland cement hydration, reaction of free CaO in FH, and reaction of other phases in FH except free CaO respectively, which can be determined from the amount of chemically bound water consumed in Portland cement hydration, reaction of free CaO in FH, and reaction of other phases in FH except free CaO respectively [15].

Verification of proposed FH blended hydration model

Experimental results from Papadakis [12] are used to verify the proposed FH blended cement hydration model. Papadakis [12] studied properties development of high calcium fly ash blended paste. The physical properties and chemical compositions of cement and FH are shown in Table 1. The mixture proportions are given in Table 2. In the control specimen, the water to cement ratio (W/C) was 0.5. Two different cases were studied: FH to replace either aggregate or cement. In the former case, three contents of FH were selected: 10%, 20%, and 30% addition to the cement weight giving specimens FHA1, FHA2, and FHA3, respectively. In the latter case, 10%, 20% and 30% replacements of the control cement weight, giving specimen FHC1, FHC2, and FHC3 respectively, were selected.

The development of porosity and calcium hydroxide was measured at 3, 7, 14, 28, 49, 112, 182, and 364 days after casting [12].

Table 1. physical and chemical characteristic of cement and FH [12]

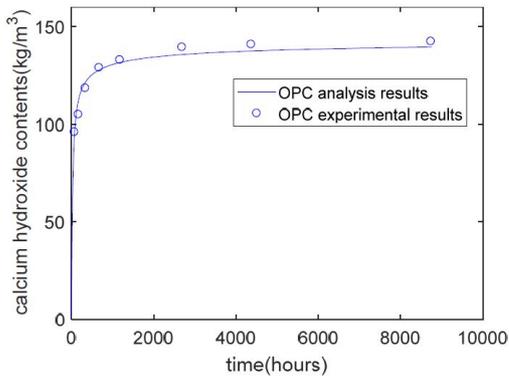
	Cement	FH
Physical properties		
BET specific surface (m^2/g)	1.3	6.2
Particle mean diameter (μm)	14.0	12.6
Density (kg/m^3)	3130	2660
Chemical analysis (%)		
SiO ₂	20.10	39.21
Al ₂ O ₃	4.25	16.22
Fe ₂ O ₃	3.49	6.58
CaO	63.20	22.78 (5.18 free)
SO ₃	2.88	4.3
LOI	0.86	2.10

Table 2. mixing proportions of specimens [12]

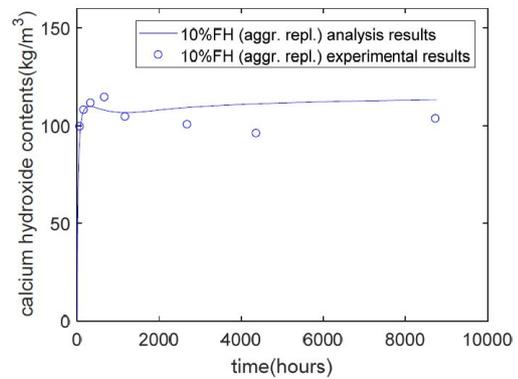
specimens	Cement	FH	Binder (cement + FH)	Water	Water to binder ratio	FH to binder ratio
control	1	0	1	0.5	0.5	0
FHA1	1	0.1	1.1	0.5	0.45	0.09
FHA2	1	0.2	1.2	0.5	0.42	0.16
FHA3	1	0.3	1.3	0.5	0.38	0.23
FHC1	0.9	0.1	1	0.5	0.5	0.1
FHC2	0.8	0.2	1	0.5	0.5	0.2
FHC3	0.7	0.3	1	0.5	0.5	0.3

Calcium hydroxide contents

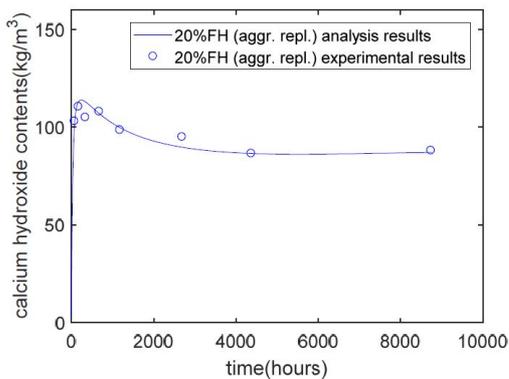
The evaluation results of calcium hydroxide contents are shown in Figure 2. It can be seen that the CH content of the control specimen increases with time until a steady state is attained (Figure 2(a)). The CH content of FHA specimens presents a rather complicated picture due to the simultaneous CH production from reaction of cement and free CaO and CH consumption from other phases of the FH. In the first week, due to the rapid free CaO hydration, CH contents are slightly higher in fly ash specimens (Figure 2(b)-(d)) than that of control specimen (Figure 2(a)) [12,15]. These CH contents pass through a maximum, due to higher CH production, but afterwards decrease, as the FH-CH reaction proceeds at higher rates. At late age, with the FH replacing ratio increasing from 10% to 30%, the CH contents decrease correspondingly. For concrete with 10% FH (Figure 2(c)) and 20% FH (Figure 2(b)), at the age of 1 year, the calcium hydroxide will slightly increase. This may be because the depletion of active part of FH. Because the proposed model has modeled the rapid production of calcium hydroxide from free CaO reaction in FH, the production of calcium hydroxide from cement hydration, and the consumption of calcium hydroxide from other phases reaction in FH, the proposed model can describe the complicate evolution process of cement-FH blends.



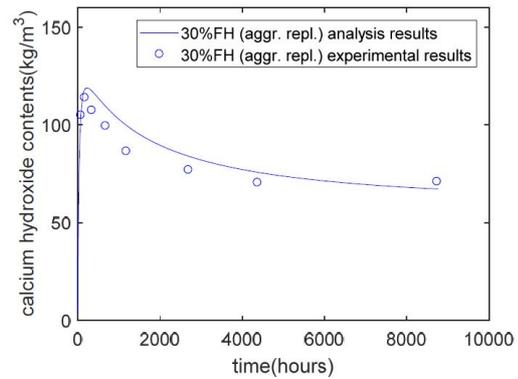
(a) OPC concrete



(b) FHA1 concrete: FH replaces aggregate by 10% weight of cement



(c) FHA2 concrete: FH replaces aggregate by 20% weight of cement



(d) FHA3 concrete: FH replaces aggregate by 30% weight of cement

Figure 2. Development of calcium hydroxide contents.

Reaction degree of FH

The evaluation of reaction degree of fly ash is shown in Figure 3. As shown in this figure, given a certain water to binder ratio, with an increasing of the replacement level of fly ash, the alkaline activating effect of the cement

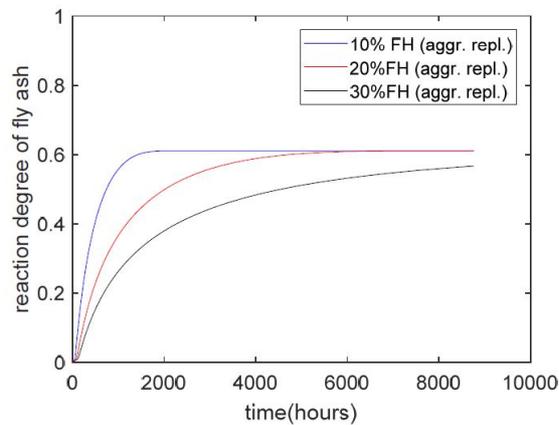


Figure 3. Reaction degree of high calcium fly ash with different FH contents: FH replaces aggregate by 10%, 20% and 30% weight of cement (water to binder ratio 0.5).

would be weaker, so that the reactivity of fly ash decreases [16-18]. On the other hand, at late age, for concrete with 10% and 20% FH, the active part of FH has totally reacted. For concrete with 30%FH, until the age of 1 year, part of FH is still un-reacted. FH consists of reactive fractions and inert fractions. The maximum value of reaction degree (about 60%) in Figure 3 corresponds to the mass percentage of reactive fraction in FH.

Porosity

The evaluation results of porosity contents are shown in Figure 4. A lower porosity is observed for all FHA specimens compared to the corresponding control values, from the initiation of the cement hydration. This decrease in porosity values is almost proportional to the fly ash content in the specimen. This behavior can be partly explained as due to the presence of free CaO in the FH and the hydration of the tricalcium aluminate present in FH. The early formation of water-rich and pore filling ettringite and its subsequent transformation to monosulfate hydrate contribute significantly to the increased hydration and decreased porosity [12].

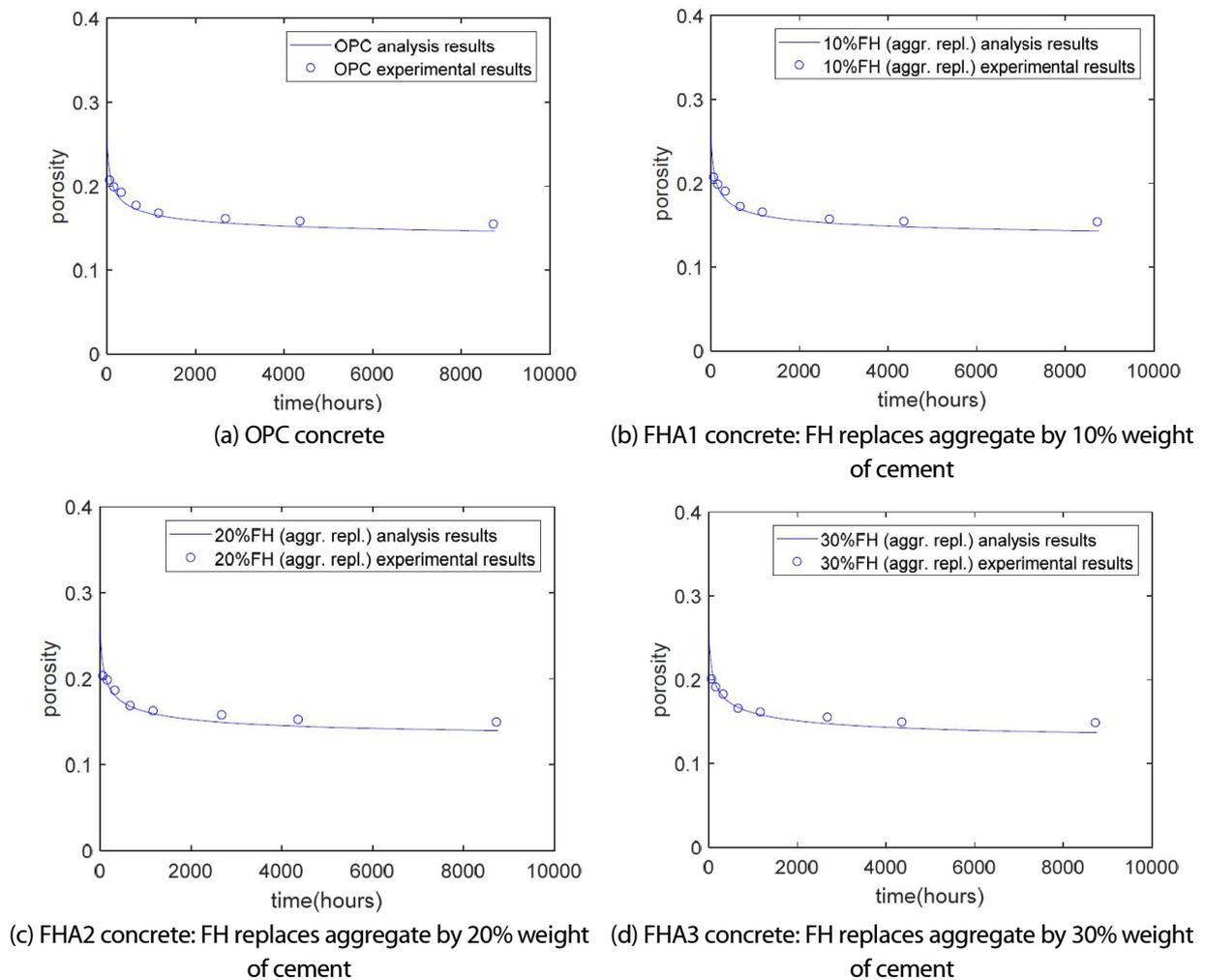


Figure 4. Development of porosity contents.

C-S-H content

The evaluation results of C-S-H are shown in Figure 5 as shown in Figure 5(a), as aggregate is partial replaced by FH, the C-S-H content is initially higher than that of control specimen. While as shown in Figure 5(a), as cement is partial replaced by FH, at early ages, C-S-H content of FHC specimens is lower than that of control specimens. At late ages, C-S-H content of FHC specimens can surpass the control specimens. This is because the silicate content of FH is higher than that of cement while the reaction rate of FH is lower than that of cement.

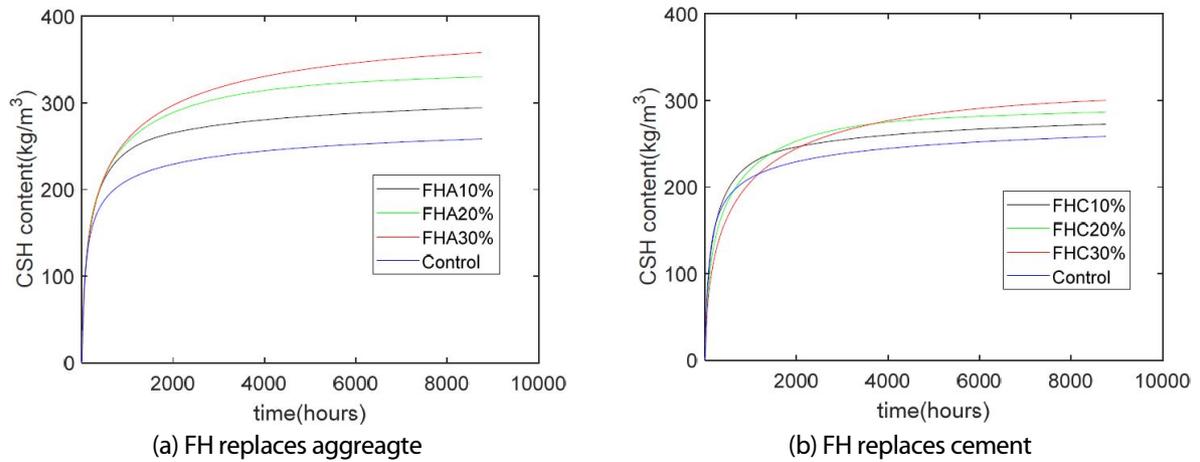


Figure 5. Compressive strength of mortars as a function of calculated C-S-H content.

Evaluation of carbonation depth of FH blended concrete

Carbonation model of FH blended concrete

Concrete carbonation is a complicated physicochemical process. For the usual range of parameters (especially for relative humidity higher than 55%, CO₂ diffusion controls carbonation process [16-18]), a carbonation front will form which divides concrete into two different regions: a fully carbonated region and one in which the carbonation has not started at all. The distance between this front and the outer concrete surface is called carbonation depth, and for the most common one-dimensional cases, its evolution with time is given by a simple analytical expression, in terms of the composition and of the environmental conditions. The evolution of the carbonation depth x_c (m) with time t (s), is given by the analytical expression as following equations [16-18]:

$$x_c = \sqrt{\frac{2D_C([CO_2]_0/100)t}{0.33CH + 0.214CSH}} \tag{5}$$

$$D_C = A \left(\frac{\epsilon - \Delta\epsilon}{\frac{C_0}{\rho_c} + \frac{P + CF_0}{\rho_{FH}} + \frac{W_0}{\rho_w}} \right)^a \left(1 - \frac{RH}{100} \right)^{2.2} \tag{6}$$

where $[CO_2]_0$ is the CO_2 content in the ambient air at the concrete surface; $\Delta\epsilon$ is the porosity reduction due to carbonation (the porosity reduction is determined based on the variations of molar volume of reactants and products of concrete carbonation [18]. Carbonation of cement-based composites is very complicated physico-chemical process. Carbonation of C-S-H can even cause the shrinkage of the paste matrix which could increase porosity. The porosity variations due to C-S-H carbonation needs more studies in the future work); RH is the ambient relative humidity. A and a are parameters which will be regressed from measured carbonation depths. Based on the proposed hydration model, the amount of CH, C-S-H and porosity can be obtained as associated results during the hydration period of cement – FH blended concrete. Furthermore, the carbonation depth can be predicted by using equations 5-6.

Verification of FH blended carbonation model

Experimental results from Papadakis [18] are used to verify the proposed model. The mixing proportions of FH specimen are similar with those shown in Table 2 but containing fine aggregate. the sand to binder ratio is 3. After one year moist curing at $20^\circ C$, the test specimens were kept for 1 month in a laboratory environment to stabilize internal humidity. They were then placed in a chamber with a controlled 3% concentration of CO_2 , temperature $25^\circ C$, and relative humidity 61% for 100 days. After carbonation, the specimens were cut normal to the exposed surfaces and the carbonation depth was determined by mean of a phenolphthalein indicator. The comparison between the prediction results and the experiment results is shown in Figure 6 ($A=0.000166$, $\alpha=6.981$). As shown in

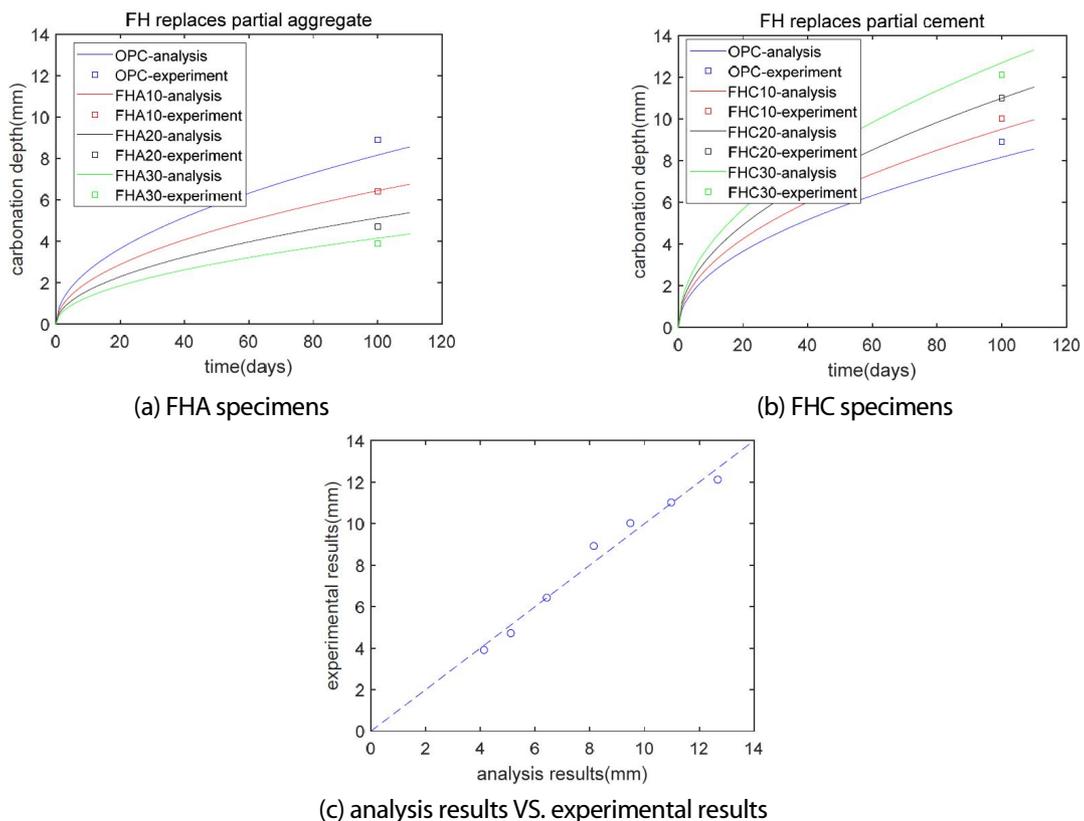


Figure 6. Carbonation depth of FH blended concrete.

the prediction results agree well with the experiment results. For concrete incorporating FH replacing cement (FHC10, FHC20, and FHC30), compared with control Portland cement concrete, with the increasing of FH contents, the carbonation depth will increase. While for concrete incorporating FH replace aggregate (FHA10, FHA20, and FHA30), the carbonation depth will decrease.

The carbonation of concrete depends on both environmental conditions, such as CO₂ concentration and ambient relative humidity, and the compositions of cement and concrete, such as the amount of carbonatable constituents and porosity. The proposed hydration model considers the influence of water to cement ratio, FH to cement ratio, degree of hydration, curing methods on the amount of CH, C-S-H and porosity. The diffusivity of CO₂ in carbonated concrete was expressed as a function of ambient relative humidity, porosity and the mix proportion. The proposed model considers both external and internal conditions of carbonation and can be used to evaluate the carbonation depth of concrete containing FH.

Conclusions

This paper presents a numerical procedure to evaluate carbonation depth of FH blended concrete. This numerical procedure consists of a hydration model and a carbonation reaction model. First, by using the blended cement hydration model, the properties of hardening FH blended concrete, such as the amount of carbonatable constituents and porosity, are determined. Second, by using the carbonation reaction model, the diffusivity of CO₂ in FH blended concrete is calculated and the carbonation depth of FH blended concrete is predicted.

The proposed numerical procedure is verified using experimental results of FH blended concrete with different water to binder ratios and high calcium fly ash replacement ratios. For concrete containing FH replacing cement, compared with control Portland cement concrete, the carbonation depth will increase. While for concrete incorporating FH replace aggregate the carbonation depth will decrease. Given a same FH to binder ratio, as water to binder ratio decreases, carbonation depth decreases. Summarily, the proposed model considers both external and internal conditions of carbonation and can be used to evaluate the carbonation depth of concrete containing FH.

Acknowledgement

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