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EVALUATION OF THE PHASE ASSEMBLAGE AND STRENGTH PROGRESS OF HYBRID BLENDS OF CEMENT AND FLY ASH USING KINETIC AND THERMODYNAMIC HYDRATION MODEL

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Phase assemblage and strength are essential engineering properties of hybrid blends of cement and siliceous fly ash (FA). This study presents a kinetic and thermodynamic model for evaluating reaction level, phase assemblage of reaction products and strength progress of hybrid blends of cement-fly ash with various water/binder ratios and FA/binder ratios. First, the reaction level of cement and glass phase of FA are determined using a kinetic model that considers the cement hydration, the glass-phase reaction of FA and the dilution effect of fly ash. The crystalline phase of FA is assumed to be inert. Moreover, the reaction level of binders and concrete mixtures are used as input data for a thermodynamic model. Second, the phase assemblages of hydrating binary blends are determined using GEM-Selektor (Gibbs energy minimization). The mass conservation of the reactants and products of hybrid blends with fly ash are considered in thermodynamic model. Finally, by using calculation results of calcium silicate hydrate (CSH) content from GEMS, the strength progress of composite concrete is determined. The correlation coefficient between prediction and experiments for the C–S–H-based model is 0.98. The analysis results clarified that the use of fly ash in concrete with a low water/binder ratio is a suitable option.

INTRODUCTION

Fly ash (FA) is a coal combustion product that is categorized as supplementary cementitious material. Fly ash is increasingly utilized in concrete constructions to supplement partial cement. The utilization of fly ash has many benefits, for example high slump, high long-term strength, good resistance to chloride ingress and acid attack, low CO_2 emission and good sustainability [1].

Strength is an essential engineering characteristic of hybrid blends of cement and FA. The prediction of strength progress of hybrid blends of cement and FA attracts wide interest from many researchers. These prediction models can be divided into three types: (1) the macro-regression model, (2) the hydration-based model, and (3) the thermodynamics-based model. The first of these – the macro-regression model – is built on the basis of the maturity function, Abram's law or machine learning-based regression. Han et al. [2] analyzed the strength progress of hybrid blends of cement-fly ash with various water/binder ratios and FA contents by using modified equations of apparent activation energy. Hwang et al. [3] predicted the strength of hybrid blends of cement-fly ash using a modified efficiency factor, which is a function of time, FA/binder ratio and Blaine fineness of FA. Topcu and Sarıdemir [4] analyzed the strength of hybrid blends of cement-fly ash using fuzzy logic and artificial neural networks. The second type – the hydration-based model – is built based on the degree of hydration. Wang and Park [5] evaluated the strength progress of hybrid concrete containing moderate or high-volumes of FA using a blended hydration model. Maekawa et al. [6] proposed a multi-component model for hybrid concrete and evaluated the hydration heat, strength progress and durability aspect of concrete. Baert et al. [7] analyzed the hydration heat of hybrid concrete with fly ash and calculated the reaction level of binders. Furthermore, Liu et al. [8] predicted the thermal stress of hardening concrete using a hydration-based model [7]. The third type – the thermodynamic model – is built based on the thermodynamic equilibrium between the pore solution and hydration products by using a specific database. Weerdt et al. [9] determined the phase assemblage of hybrid blends with FA and limestone and evaluated the strength of concrete using coarse porosity. Fernández et al. [10] made short- and long-term thermodynamic modeling of cement-fly ash-slag ternary blends and found that the total volume of solid phase to be the dominant factor of strength. Durdziński et al. [11] determined the phase assemblage of composite paste using the thermodynamic model and found that strength can be evaluated using a bilinear function of the gel-space ratio.

Although many previous models have been proposed for analyzing the strength of hybrid concrete with fly ash, all of these previous models show weak points. First, the macro-regression model of [2-4] is a type of phenomenon-based model and does not consider the microstructures of concrete. The physical meaning of the parameters in the macro-regression model is not clear. The second, the hydration-based model [5-8], calculates the reaction level of binders and evaluates the strength using the reaction level of the binders. However, this model has difficulty determining the phase-assemblage of hydrating blends. Thermodynamic equilibrium is not covered in the hydration-based model [5-8]. The third, the thermodynamic model [9-11], is useful for calculating the phase assemblage of composite cement, but requires the reaction level of fly ash as input data. This reaction level, in turn, relates to the physical and chemical properties of the fly ash, concrete mixtures and curing conditions [12-15]. Weerdt et al. [9] measured the hydration degree of cement in hybrid concrete with fly ash using XRD-Rietveld analysis and Durdziński et al. [11] measured the hydration degree of clinker in blended cement using the PONKCS method. These experimental measurements are time- and cost-consuming. Here, a theoretical model for evaluating the reaction level of cement and fly ash in blended concrete would be helpful for concrete researchers.

To combat the weaknesses of previous studies, this research presents a kinetic and thermodynamic model for evaluating reaction level, phase assemblage of reaction products and strength progress and development of hybrid blends with fly ash with assorted water/binder ratios and FA content. A blended hydration model can be used for determining the reaction amount of cement and FA. The dilution aftereffect of fly ash is recognized as a part of the blended hydration model. Furthermore, the phase assemblages of hydrating binary blends are determined – and the strength of hardening concrete is evaluated – in line with the items in calcium silicate hydrate or combined water. The analysis shows the use of fly ash in concrete with a low water/binder ratio is a suitable option.

THEORETICAL

Kinetic and thermodynamic model

Kinetic model of hybrid blends with fly ash

Kinetic model of cement hydration

Our previous study proposed a model for the kinetic hydration process of Portland cement [1, 5, 13]. This model takes into account the kinetic phases of hydration, for example, the initial dormant, boundary reaction and diffusion phases. The input parameters of the hydration model consist of cement compositions, concrete mix ratios and curing circumstances. The output result of the hydration model is the reaction amount of cement. Our previous studies proposed the kinetic reaction equation of rate of cement hydration $d\alpha_i/dt$ can be simplified as follows [1, 5, 13]:

$$\frac{d\alpha_i}{dt} = f\,[B(T),\, C(T),\, D_e(T),\, k_{ri}(T),\, r_0] * C_{w\text{-free}} * \frac{S_w}{S_0} \quad (1)$$

$$\alpha = \frac{\sum_{i=1}^{4} \alpha_i g_i}{\sum_{i=1}^{4} g_i} \quad (2)$$

where α_i (i = 1, 2, 3 and 4) denotes the reaction level of the mineral compound of cement C_3S, C_2S, C_3A and C_4AF, respectively; α denotes the degree of cement hydration; B and C are reaction coefficients in the initial dormant period; D_e represents the reaction coefficient in the diffusion period; k_{ri} is the reaction coefficient in the boundary reaction period; r_0 denotes the radius of anhydrates particles in the cement; S_w represents the contact area between the capillary water and hydrating cement particles [1, 5, 13] and S_0 denotes the total area for the condition of hydration products forming in an unconstrained manner. $C_{w\text{-free}}$ denotes the coefficient considering the consumption of capillary water. Based on the reaction level of compound compositions of cement, the values of coefficients at 20 °C are determined and shown in Table 1 [1, 5, 13]. The acceleration of cement hydration due to elevated temperature is described using Arrhenius's law [1, 5, 13].

Table 1. Coefficients of cement hydration model.

B_{20}	C_{20}	K_{rC3S20}	K_{rC2S20}	K_{rC3A20}	$K_{rC4AF20}$	D_{e20}
			$(cm \cdot h^{-1})$			
$8.1\cdot10^{-9}$	0.02	$9.0\cdot10^{-6}$	$2.7\cdot10^{-7}$	$1.4\cdot10^{-6}$	$6.8\cdot10^{-8}$	$8.6\cdot10^{-10}$

Compared with ordinary concrete, high-strength concrete has a lower water/binder ratio and significant capillary water-withdrawal. Capillary water withdrawal is considered using (S_w/S_0) and $C_{w\text{-free}}$ in Equation 1. (S_w/S_0) considers the reduction in the contact area between hydrating cement particles and capillary water; $C_{w\text{-free}}$ considers the reduction in the concentration of capillary water. $C_{w\text{-free}}$ can be calculated as follows:

$$C_{w-free} = \frac{W_{CAP}}{W_0} = \frac{W_0 - 0.4C_0\alpha - 0.33FA_{\text{glass}}\alpha_{\text{glass}}}{W_0} \quad (3)$$

where W_{CAP} and W_0 are the contents of capillary water in hydrating concrete and water in the concrete mixture, respectively. C_0 and FA_{glass} are the cement and glass phase contents of in mixtures, respectively, α_{glass} is the reaction level of the glass phase in fly ash. For hybrid blends with fly ash, the content of capillary water depends on reactions of cement and FA. In addition – compared with cement hydration – the consumed capillary water of the FA reaction is much lower and the value of $C_{w\text{-free}}$ of hybrid blends with fly ash is higher than in plain concrete. Consequently, the reaction level of cement in hybrid blends with fly ash is higher than in plain concrete.

Kinetic model of fly-ash reaction

Siliceous fly ash is a type of pozzolanic material that can react with calcium hydroxide, forming secondary calcium silicate hydrate [16]. Siliceous fly ash generally consists of a reactive glass phase and an inert crystalline phase. With increasing glass phase content, the reactivity of fly ash increases. Compared to cement, the reactivity of fly ash is low. The initial dormant period of the reaction of fly ash is long. In addition, the kinetic reaction process of binary composite is similar to that of plain cement [17]. At a late hydration age, the controlling stage of the pozzolanic reaction is diffusion [18]. Considering the material characteristics and reaction kinetics of fly ash from our previous study, the reaction of glass phase fly ash comprises the phases of initial dormancy, boundary reaction and diffusion. Our previous studies proposed the kinetic reaction equation process of glass phase of fly ash can be simplified as follows [1, 5, 13]:

$$\frac{\alpha_{\text{glass}}}{dt} = \frac{CH(t)}{FA_{glass}} f(B_{\text{glass}}(T), C_{\text{glass}}(T), D_{e\text{glass}}(T), k_{r\text{glass}}(T), r_{0FA}) \quad (4)$$

$$\alpha_{FA} = \alpha_{\text{glass}} P_{\text{glass}} \quad (5)$$

where α_{glass} denotes the reaction level of glass phase in siliceous fly ash; $CH(t)$ is the mass of calcium hydroxide in concrete, FA_{glass} is the mass of glass phase of fly ash in concrete, $B_{\text{glass}}(T)$ and $C_{\text{glass}}(T)$ are reaction coefficients in the initial dormant period, $k_{r\text{glass}}$ is the reaction coefficient in the boundary reaction stage and $D_{e\text{-glass}}$ is the reaction coefficient in the diffusion stage. r_{FA0} denotes the average radius of the particles of the fly ash. α_{FA} denotes the reaction level of fly ash and P_{glass} represents the mass percentage of glass phase in siliceous fly ash. As shown in Equation 5, the reaction level of fly ash equals the reaction level of the glass phase multiplied by the mass percentage of glass phase. The crystalline phase in fly ash is assumed to be inert. The fly-ash reaction is also sensitive to temperature: when the curing temperature increases, the fly-ash reaction accelerates. Similar to cement hydration, the acceleration of the fly-ash reaction at elevated temperatures is described using Arrhenius's law [1, 5, 13].

For binary composites, the calcium hydroxide content is dependent on both the hydration of cement and the reaction of fly ash. Our previous studies showed the mass of calcium hydroxide can be established as follows [1, 5, 13]:

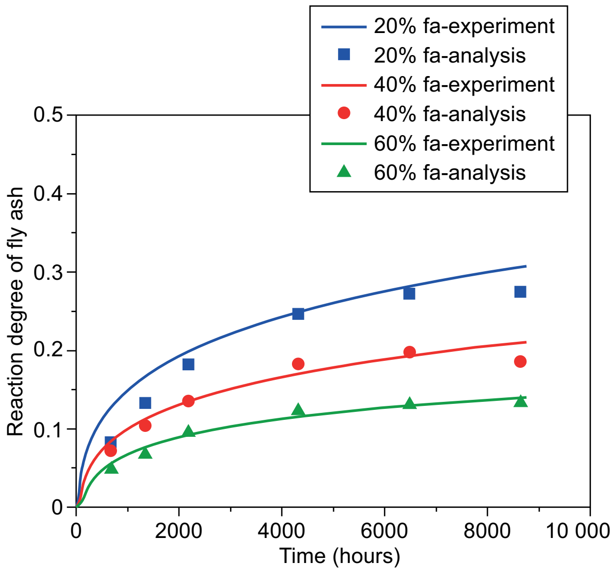
$$CH(t) = RCH_{CE}*C*\alpha - v_{FA}*\alpha_{\text{glass}}*FA_{\text{glass}} \quad (6)$$

where RCH_{CE} is the calcium hydroxide production when the unit mass of cement hydrates; α is the hydration degree of cement; and $RCH_{CE}*C*\alpha$ and $v_{FA}*\alpha_{\text{glass}}*FA_{\text{glass}}$ denote the calcium hydroxide production from the hydration of cement and from the reaction of fly ash, respectively.

The coefficients of the fly-ash reaction model are determined using experimental data from [19]. Sakai et al. [19] measured the reaction level of siliceous fly ash using the selective dissolution method. The water/binder ratio was 0.4; the replacement levels of fly ash were 20 %, 40 % and 60 %. The glass phase of siliceous fly ash was 76 %. The curing temperature was 20 °C. The reaction level was measured from early ages to long-term ages of 360 days. Using the experimental data of the reaction level of fly ash [19], the coefficients of the fly-ash reaction model are calibrated and shown in Table 2. Figure 1a shows the analysis results versus experimental results. With increasing fly ash content, the reaction level of fly ash decreased due to insufficient calcium hydroxide content. Figure 1b shows that the reaction level of the glass phase is much higher than that of fly ash. This is due to the mass fraction of glass phase in siliceous fly ash being less than unity. In addition, because the interactions between reactions of fly ash and cement are considered through capillary water and calcium hydroxide, the coefficients of the hybrid hydration model do not vary with concrete mixtures. For concrete with different mixtures such as various water/binder ratios and FA/binder ratio, the coefficients of the hydration model are the same.

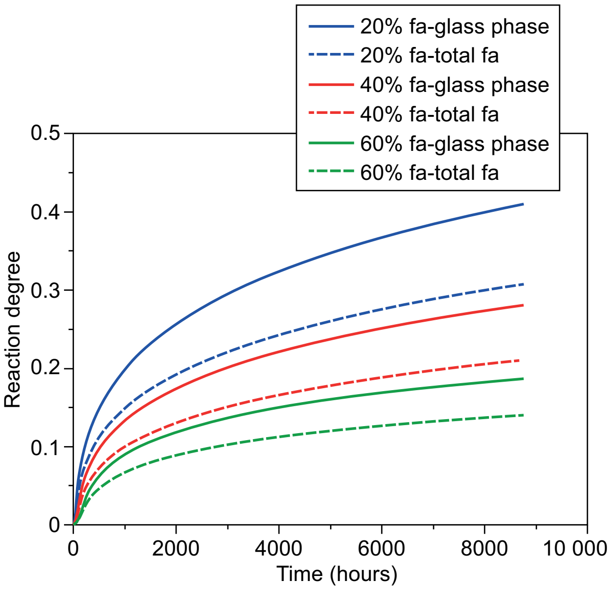
Table 2. Coefficients of the fly-ash reaction model.

B_{FA20}	C_{FA20}	K_{rFA20}	D_{eFA20}
	(cm·h^{-1})		
$8.9 \cdot 10^{-9}$	0.1	$1 \cdot 10^{-5}$	$1.9 \cdot 10^{-9}$



a)

Figure 1. Reaction level of fly ash (a) and glass phase in fly ash (b). *(Continue on next page)*



b)

Figure 1. Reaction level of fly ash (a) and glass phase in fly ash (b).

Thermodynamic model

The hydration Equations 1 to 6 consider the cement hydration, the dilution effect of fly ash and the fly-ash reaction, respectively. Based on Equations 1 and 4, the reaction level of cement and glass phase of FA in composite concrete can be calculated. Moreover, the reaction level of binders and concrete mixtures are used as input parameters of thermodynamic models, such as the GEM-Selektor (GEM, Gibbs energy minimization). The GEM algorithm is a thermodynamic modeling algorithm that can provide the molar weights (molecules and ions) of dependent components, their activities and the chemical potential of the system. The output includes all stable solid- water- and gas-phase information. Based on the GEM algorithm, the open source platform GEM-Selektor can use the thermodynamic database [20] to model the equilibrium reaction of cementitious materials and their hydration/reaction products. The C–S–H–Q model is used for evaluation of the formation of calcium silicate hydrate. As shown in Figure 2, the input data used for thermodynamic modeling include compositions for binder materials, mixture ratio data and kinetic information (hydration) and reactivity of binders. The output data are the phase assemblages of hydrating binary blends. Moreover, the strength of hardening concrete is evaluated based on calcium silicate hydrate or combined water content in phase assemblages.

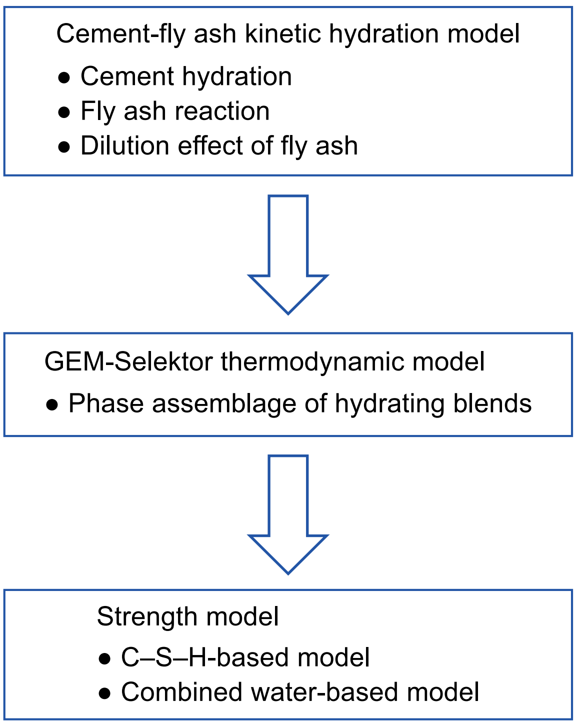


Figure 2. Flowchart of modeling.

Properties evaluation of hybrid blends with fly ash

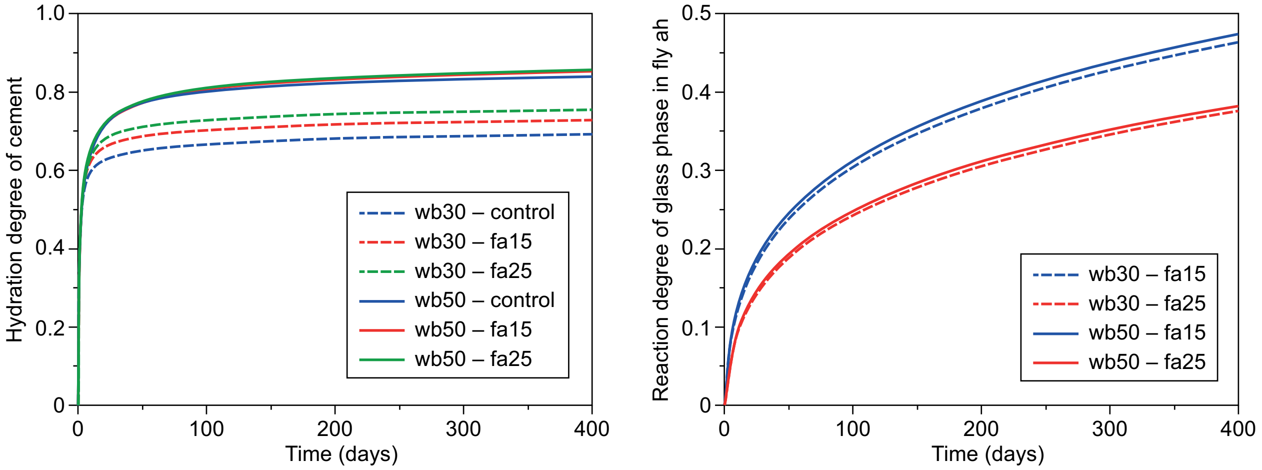
Analysis of reaction level of binders

Experimental data from [21] were used to validate the proposed hydration-strength integrated model. Lam et al. [21] measured the strength development of fly ash hybrid concrete with various water/binder ratios and FA/binder ratios. The water/binder ratios ranged from 0.3 to 0.5, and the FA/binder ratios ranged from 0 to 0.25. The compound compositions of cement and FA are shown in Table 3. Cement belongs to ASTM type I Portland cement, and fly ash belongs to siliceous fly ash. Based on Bogue's equation, the contents of C_3S, C_2S, C_3A and C_4AF of cement are determined as. 51.88 %, 21.06 %, 9.88 % and 10.34 %, respectively. The strengths of concrete were measured from early ages (3 days) to late ages (180 days).

Table 3. Compound compositions of cement and FA (%).

	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
Cement	21.23	3.44	5.97	65.42	0.91	2.63	0.14	0.26
Fly ash	57.18	5.34	28.39	3.02	5.23	0.7	0.05	0.09

The reaction level of cement component and fly ash was determined using the kinetic hydration model. Figure 3a shows the calculated reaction level of Portland cement. For plain paste – due to the decrease in the water/cement ratio – the information of capillary water decreases, and the amount of hydration also decreases [22]. However, for hybrid blends with fly ash, because of the dilution effect, the response degree of cement is greater than that in plain cement. In particular – for specimens with a low water/binder ratio of 0.3 – the



a) b)

Figure 3. Reaction level of binders: a) cement; b) fly ash.

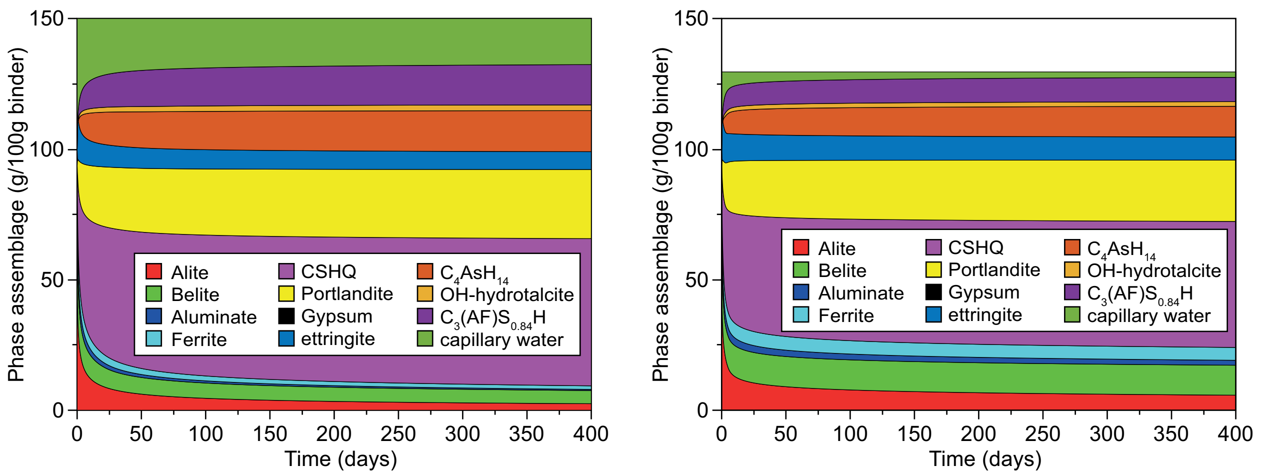
increase in the reaction level of cement is far greater than a specimen with a water/binder ratio 0.5 [5]. The case study outcomes of the reaction level of glass phase in fly ash are shown in Figure 3b. The case study results can reflect the end result water/binder ratio and FA/binder ratio on the reaction amount of fly ash. With a decreasing FA/binder ratio, the yield of glass phase in fly ash increases.

Phase assemblage of hybrid blends with fly ash

Figure 4 shows the calculated phase assemblage of hybrid blends with fly ash based on the rection level of binders and GEMS,

First, as shown in Figure 4a, b, at late ages, for plain concrete with a high water/cement ratio (0.5), the remaining cement is minimal, while for plain concrete with a low water/cement ratio (0.3), much cement remains. This is because capillary water is not enough to achieve full hydration of cement with a low water/cement ratio.

Second, as shown in Figure 4c, d, the information of Portlandite initially increases at early ages, in specimens with moderate fly ash content (15 % hybrid paste with fly ash). This is due to the dominance of producing calcium hydroxide from cement hydration. At late ages, calcium hydroxide content decreases. This is because the intake of calcium hydroxide from fly-ash reaction is dominant. Moreover, the glass phase reacts as the curing progresses, while the crystalline phase is inert and remains constant with age. In addition, compared with plain specimen, the ettringite content in fly ash hybrid specimen is much lower. This is because the reaction of aluminum phase in fly ash consumes gypsum: the ettringite is unstable after the depletion of gypsum, and transforms into monosulfate.



a) b)

Figure 4. Phase assemblage of cement – fly ash blends: a) water/binder ratio 0.5, no fly ash; b) water/binder ratio 0.3, no fly ash. *(Continue on next page)*

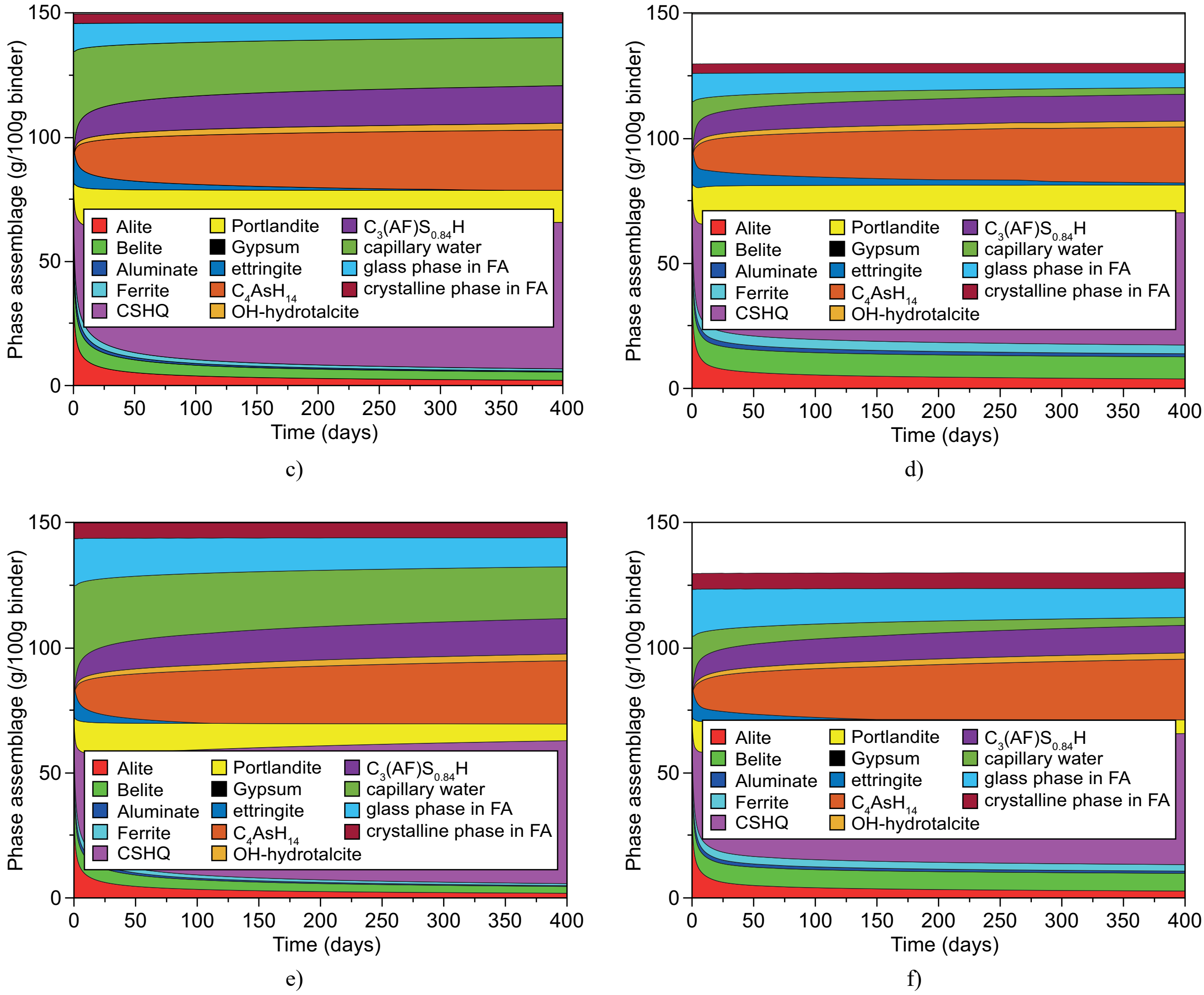


Figure 4. Phase assemblage of cement – fly ash blends: c) water/binder ratio 0.5, 15 % fly ash; d) water/binder ratio 0.3, 15 % fly ash; e) water/binder ratio 0.5, 25 % fly ash; f) water/binder ratio 0.3, 25 % fly ash.

Third, for specimens with high fly ash content (25 % hybrid paste with fly ash as shown in Figure 4e, f), the content of calcium hydroxide is much lower than that of lower fly ash specimens. This agrees with the experimental results of Papadakis [23]. In addition, for plain paste with a water/binder ratio 0.3 (Figure 4b), at late ages, much of the alite remains unreacted. While for hybrid paste with water/binder ratio 0.3 and 25 % fly ash (Figure 4f), at late ages, the unreacted alite is marginal. This is because for concrete with a low water/binder ratio, the dilution aftereffect of fly ash plays a substantial role in cement hydration. Consequently, the level of cement hydration is clearly improved.

Fourth, as shown in Figure 5, for concretes with a higher water/binder ratio 0.5 (Figure 5a), at early ages, the C–S–H content of hybrid concrete with fly ash is less than that of plain concrete. At the same time, at late ages, the C–S–H content of hybrid concrete with fly ash can exceed that of plain concrete. With increasing fly ash content, the time corresponding to C–S–H content crossover is increased. In addition, for concrete with a low water/binder ratio of 0.3, the time at which C–S–H content crossover occurs is much earlier than that of concrete with a high water/binder ratio of 0.5 (Figure 5b). It is because compared with high water/binder ratio, the dilution effect is pronounced for the low water/binder ratio concrete (shown in Figure 3a).

Strength evaluation of hybrid blends with fly ash

Evaluation strength using C–S–H content

Papadakis [24, 25] suggested that the strength progress of concrete carefully pertains to the C–S–H content. Figure 6 shows the relation between C–S–H content and strength. The x axis indicates C–S–H content and the *y* axis, the compressive strength. As demonstrated in Figure 6a, b, generally, for paste with assorted fly ash contents, there is a linear relationship between strength and C–S–H content. However, the linear regression slope changes using the variations water/binder ratios

[26–28]. For concrete with water/binder ratios 0.5 and 0.3, the slopes are 1.732 and 2.708, respectively.

As suggested by Neville [26], Thomas [27] and Mehta [28], for concrete with various water/cement ratios, the strength could be roughly expressed as a straight-line proportional to the cement/water ratio. Considering concepts similar to the cement/water ratio, the C–S–H/water ratio was used to judge the strength progress of hybrid concrete with fly ash. Figure 7 shows the relation between strength and C–S–H/water ratio for composite paste with assorted water/binder ratios and fly ash content. The *x* axis is the C–S–H(t)/water ratio and the y axis is the strength. We are able to see if there is a uniform linear relationship between strength and C–S–H(t)/water ratio. The linear equation could be written the following:

$$fc(t) = 78.65 \frac{C\text{–}S\text{–}H(t)}{W_0} - 26.39 \qquad (7)$$

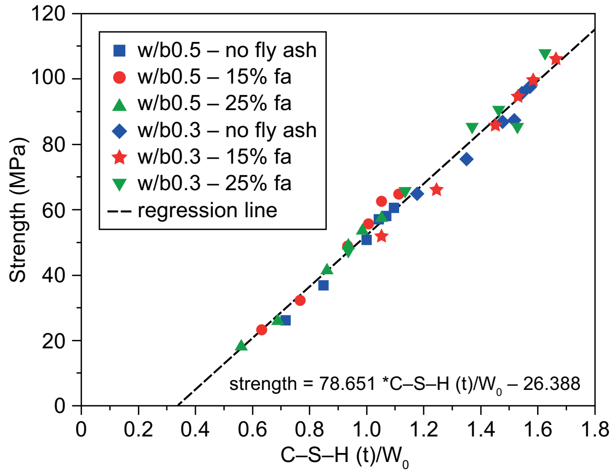


Figure 7. Strength evaluation using CSH/water ratios.

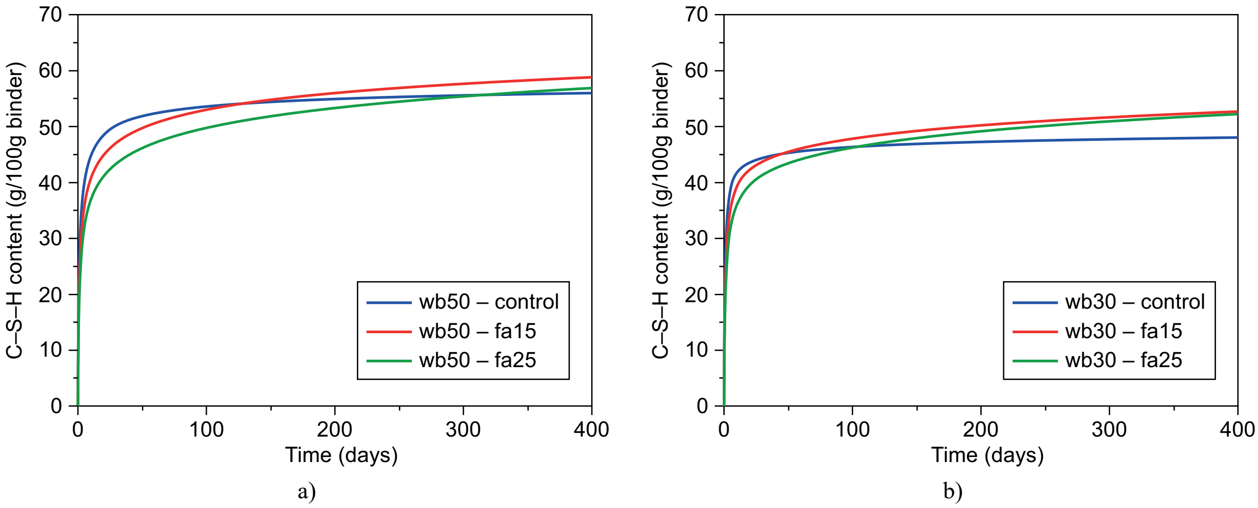


Figure 5. C–S–H contents of specimen with water/binder ratios of: a) 0.5; b) 0.3.

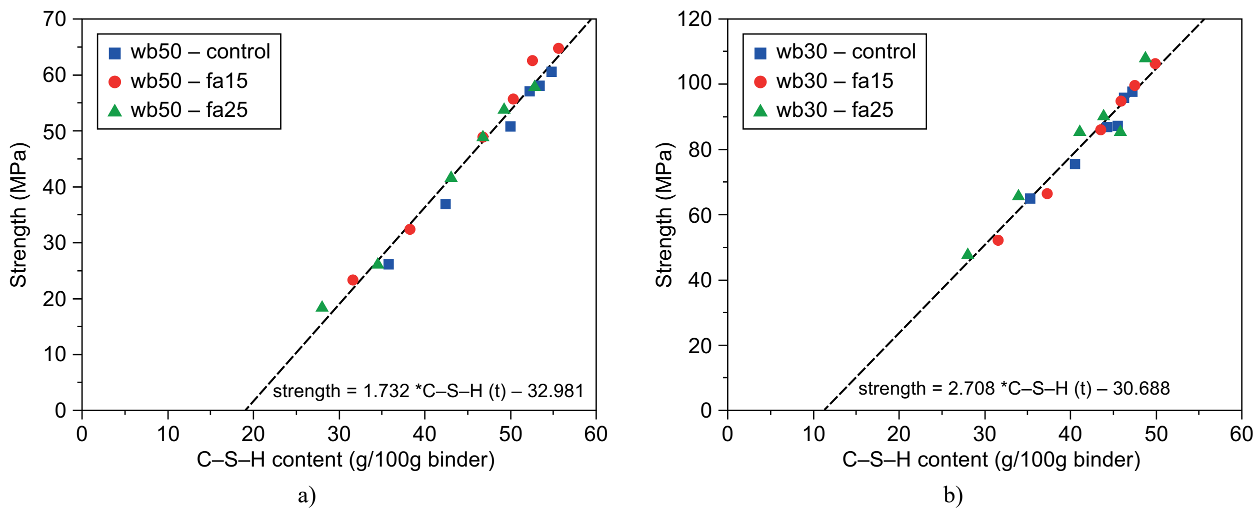


Figure 6. Strength – C–S–H relations of specimens with water/binder ratios of: a) 0.5; b) 0.3.

The correlation coefficient between prediction and experiments is 0.98. The high correlation coefficient proves the validity of proposed model.

Figure 8 shows the verifications of the strength progress model. Figure 8a, b shows that the strength progress does not start at time zero (mixing time) and that strength progress begins after a certain age. This is similar with the idea of final setting. Because of the increasing water/binder ratio, the solid phase of hydrating concrete decreases and concrete needs additional time to achieve final setting. Additionally, as the fly ash content increases, the time at which of strength progress begins increases. This is because the reactivity of fly ash is lower than that of cement, the ultimate setting and time at which strength progress begins is retarded due to the addition of fly ash.

Figure 9 shows the relative strength of hybrid concrete with fly ash. The relative strength is decided by the strength of blended concrete compared to that of plain concrete. At early ages, since the reactivity of fly ash is lower than cement, the relative strength is less than unity. In contrast, at late ages, due to the strength progress fly ash, the relative strength becomes much greater and may exceed that of plain paste. Particularly, for concrete with a low water/cement ratio of 0.3, the relative strength is greater than concrete with a water/cement ratio of 0.5. To sum, using fly ash in concrete with a low water/binder ratio is a logical option.

Evaluation strength using combined water

As demonstrated in Figure 4, as cement hydration proceeds, the capillary water content decreases, and the combined water in hydration products increases. The combined water is calculated according to mixing water minus capillary water. The calculation outcomes of combined water are demonstrated in Figures 10a and 10b. Given a particular FA/binder ratio 0.25, once the water/binder ratio is 0.5, the information of combined

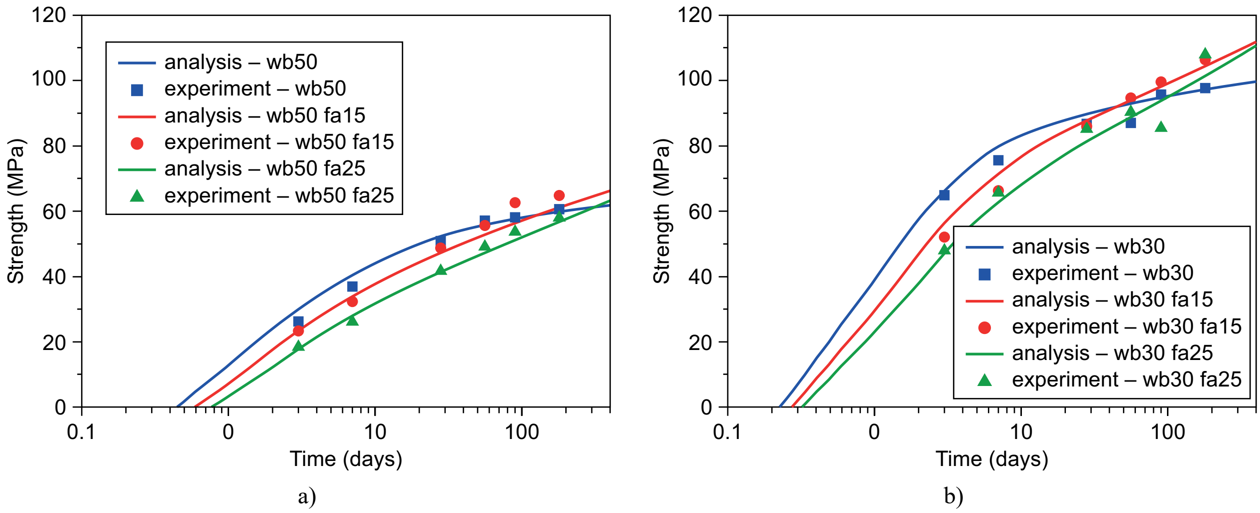


Figure 8. Strength evaluation with water/binder ratios of: a) 0.5; b) 0.3.

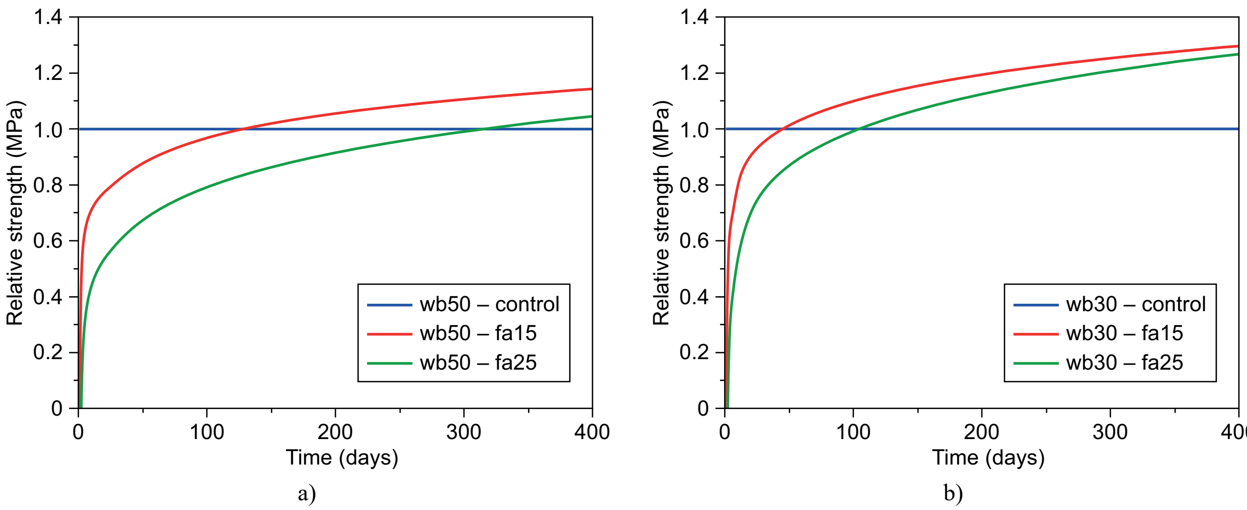
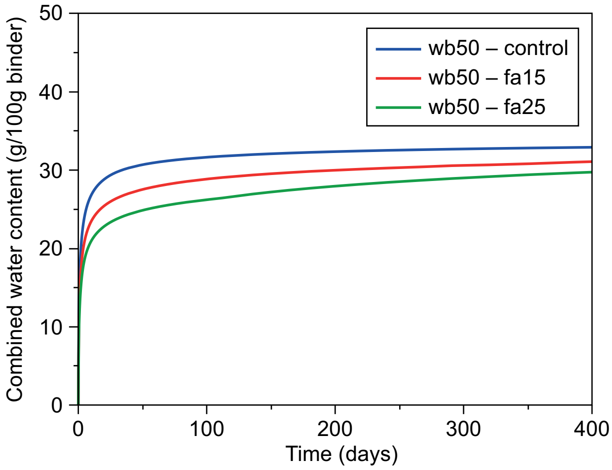


Figure 9. Evaluation of relative strength of cement-fly ash hybrids with water/binder ratios of: a) 0.5; b) 0.3.

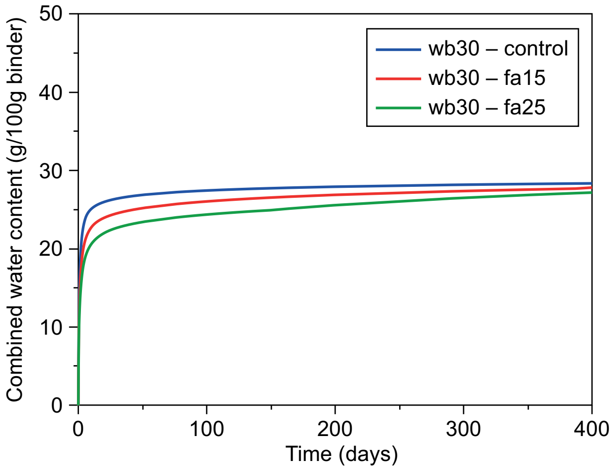
water is less than that of plain concrete (demonstrated in Figure 10a), while when the water/binder ratio is 0.3, the information of combined water resembles that of plain concrete (demonstrated in Figure 10b). This is because the dilution aftereffect of fly ash is apparent in concrete with a low water/binder ratio. Lin et al. [29, 30] suggested that the strength of concrete could be written as linear relationship proportional to the ratio of combined water to initial water. In line with the experimental outcomes of strength and calculated outcomes of combined water (demonstrated in Figure 10c), the relationship between strength and combined water can be established as the following:

$$f_c\ (t) = 140.73\ \frac{\text{Combined water } (t)}{W_0} - 27.11 \qquad (8)$$

As demonstrated in Figure 10c, case study results generally accept experimental results. The correlation coefficient between analysis and experiments is 0.92. Contrastively, when strength is evaluated using C–S–H content, the correlation coefficient between analysis and experiments is 0.98. For the fly-ash reaction, the secondary C–S–H mainly originates from the response of SiO_2 in fly ash. As well as for the fly-ash reaction, the combined



a)



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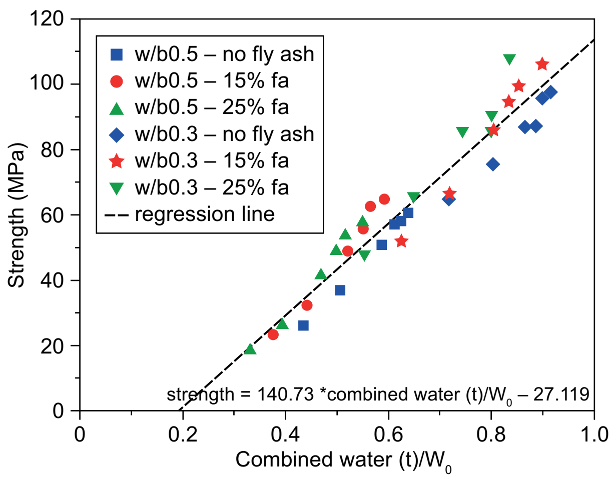

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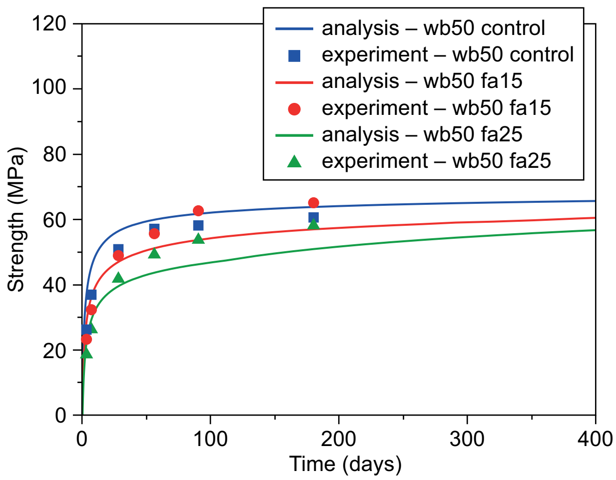
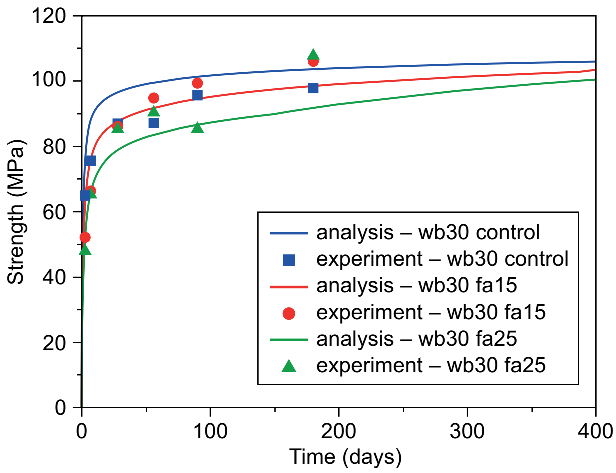


d)



e)

Figure 10. Combined water contents of specimen with water/binder ratios of: a) 0.5; b) 0.3; c) evaluation strength using combined water/water ratio; evaluation results with water/binder ratios of: d) 0.5; e) 0.3.

water mainly results in Al_2O_3. In contrast to Al_2O_3, the response of SiO_2 could have a greater contribution to the strength. In addition, as shown in Figure 10d and Figure 10e, the combined water-based strength model cannot reflect the strength crossover between plain concrete and fly ash hybrid concrete. In other words, the combined water-based strength model is not suitable for strength evaluation of fly ash hybrid concrete.

DISCUSSION

The proposed hydration–strength integrated model shows advantages over previous models. The main advantages of the proposed integrated model are summarized as follows:

- In past studies [10, 22, 31], the Portland cement hydration type of Parrot and Killoh [32] was used for analyzing the response degree of cement. Parrot and Killoh's model [32] is usually valid for a number of Portland cement types. However, for hybrid concrete with fly ash, Parrot and Killoh's model is not valid because it does not consider the fly-ash reaction and the dilution aftereffect of fly ash. In particular, for concrete with low water/binder ratios, the dilution aftereffect of fly ash will be significant. In contrast, our model considers the dilution aftereffect of fly ash by utilizing a capillary water-concentration coefficient (equation (3)). Moreover, the reaction of fly ash is considered using equation (4).
- This research presents a kinetic and thermodynamic hydration model for evaluating the strength progress of fly ash-cement composites. The suggested model shows some advantages in contrast to previous models. In contrast to hydration-based model in previous studies, the suggested model can evaluate phase assemblage. And in contrast to thermodynamic model in previous studies, the suggested model has thought about the dilution effect because of fly ash addition. Moreover, the results of phase assemblage can be used for evaluation of durability of fly ash hybrid concrete.

CONCLUSION

This research presents a kinetic and thermodynamic model for evaluating reaction-level phase assemblage of reaction products and strength progress of hybrid blends with fly ash.

- The response degree of cement and FA are determined utilizing a kinetic model that considers cement hydration, fly-ash reaction and the dilution aftereffect of fly ash. A case study shows that for hybrid blends with fly ash – because of the dilution effect – the response degree of cement is greater than that of plain cement. In particular, for specimens with a low water/binder ratio, the increase in strength is far greater than a specimen with a high water/binder ratio
- The response degree of binders and concrete mixtures are utilized as input data of thermodynamic model. The phase assemblages of hydrating binary blends are determined using GEM-Selektor. For plain paste with a water/binder ratio of 0.3, at late ages, much of the alite remains unreacted. In contrast, for hybrid paste with a water/binder ratio 0.3 and 25 % fly ash, at late ages, the unreacted alite is marginal. C–S–H crossover occurs between fly ash hybrid concrete and plain concrete. Moreover, for concrete with a low water/binder ratio of 0.3, the time at which the C–S–H content crossover occurs is much earlier than that of concrete with a high water/binder ratio of 0.5.
- There is a uniform linear relationship between strength and C–S–H(t)/water ratio. For the C–S–H -based model, the correlation coefficient between analysis and experiments is 0.98. For concrete with a low water/cement ratio of 0.3, the relative strength is much greater than concrete with a high water/cement ratio of 0.5. Case study results that were clarified using fly ash in concrete with a low water/binder ratio provide a rational option. In addition, the combined water-based strength model cannot reflect the strength crossover between plain concrete and fly ash hybrid concrete. The combined water-based strength model is not suitable for strength evaluation of fly ash hybrid concrete.

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