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A model to predict the amount of calcium hydroxide in concrete containing mineral admixtures

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Abstract

This study examines in detail the degree of reactivity of admixtures, such as fly ash and blast furnace slag, and their effect on the levels of calcium hydroxide in cement paste. Experimental results indicate that reactivity between calcium hydroxide and mineral admixture is dependent on the amount of calcium hydroxide and the degree of hydration of mineral admixtures.

From these results, a model was formulated to predict the reaction between calcium hydroxide and mineral admixtures, and its validity verified by comparing calculated data with the data from the tests with cement mortar specimens. The calculated values of calcium hydroxide agree well with the test results. The parameters of the prediction model are dependent on the physical and chemical characteristics of mineral admixtures.

Keywords: Hydration; Ca $(OH)_2$; Fly ash; Granulated blast-furnace slag; Modeling

1. Introduction

Mineral admixtures, such as fly ash and granulated blast furnace slag, are incorporated into concrete to improve the quality of the concrete. For example, mineral admixtures reduce heat of hydration, improve fluidity of fresh concrete, and control the alkali silica reaction. However, reducing the amount of cement by introducing admixtures decreases the level of calcium hydroxide in the mix, and, in addition, mineral admixtures will cause a pozzolanic reaction, which also consumes calcium hydroxide. Recent research has confirmed the significant role calcium hydroxide plays in the stability of concrete exposed to aggressive environments [1]. Because calcium hydroxide in concrete affects the rate of carbonation [2], the steel reinforcement will be in a passive state against corrosion as long as calcium hydroxide is present. Moreover, the density of the transition zone is also influenced by the amount of calcium hydroxide [1]. Therefore, a healthy balance must be reached whereby a concrete mix has an appropriate level of admixtures but not at levels that compromise the beneficial effects of calcium hydroxide. To evaluate the performance of these admixtures in concrete, it is necessary to predict the amount of calcium hydroxide in concrete.

The research results of an investigation to examine experimentally the reactivity between mineral admixtures and calcium hydroxide in concrete pastes are discussed below. A model for the reaction rate between mineral admixture and calcium hydroxide was formulated, and the experimental results were used to predict the amount of calcium hydroxide in mortar containing mineral admixtures. The relation between parameters in the prediction model and physical and chemical properties of admixture was also considered.

2. Experimental program

A series of two experiments were performed: Series 1 consisted of pastes containing mineral admixtures and

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Table 1
Physical properties and chemical compositions of cement, fly ash, and blast furnace slag

	Density (g/cm^3)	Blaine (cm^2/g)	Chemical composition (%)					
			SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Cement	3.15	3260	22.2	4.9	3.0	64.0	1.3	2.1
Fly ash A	2.26	2900	49.6	25.9	5.7	11.6	2.3	0.4
Fly ash B	2.34	3130	66.2	27.2	2.5	1.1	0.5	0.0
Fly ash C	2.16	2840	51.2	25.5	5.3	10.6	2.2	0.5
Slag A	2.88	4360	31.8	13.0	0.2	43.2	6.0	2.1
	2.88	6030	31.8	13.0	0.2	43.2	6.0	2.1
Slag B	2.89	4270	32.8	12.5	0.4	41.9	7.0	2.0
	2.89	5960	32.5	12.6	0.4	41.9	7.0	2.2
Slag C	2.89	4060	32.6	15.5	0.3	42.3	5.7	2.0
	2.89	6100	32.4	15.7	0.2	42.8	6.3	2.0

calcium hydroxide (in order to examine the basic reaction between the admixtures and calcium hydroxide). In Series 2, mortar samples were used as a baseline to verify the prediction method for the amount of calcium hydroxide in concrete.

2.1. Materials

ASTM Portland cement was used. Three types of fly ash and six types of blast furnace slag were used, each with different Blaine and chemical compositions. The physical and chemical properties of the cement and admixtures are shown in Table 1.

2.2. Mix proportions and test methods

2.2.1. Series 1

In order to examine the reactivity between mineral admixtures and calcium hydroxide, pastes containing fly ash or blast furnace slag were prepared and then the reagent, calcium hydroxide, was incorporated. The amount of calcium hydroxide added to the admixture was 5%–50% by mass. The paste was placed in a plastic bottle, and nitrogen was added in order to prevent carbonation. Sealed curing of paste specimens was carried out at 20 °C. Mix proportions of the pastes are shown in Table 2.

At defined times, the amount of combined water and calcium hydroxide was measured. The specimen was heated at 1000 °C for 6 h, after drying at 105 °C for 24 h. The amount of combined water was considered as the weight reduction on heating from 105 °C to 1000 °C. The mass of H_2O in calcium hydroxide was calculated from the combined water weight. The amount of calcium hydroxide in paste was measured by Differential Scanning Calorimetry (DSC). The amount of combined water and the amount of calcium hydroxide are expressed as the weight per unit weight of mineral admixture in this paper.

Table 2
Mix proportions of paste

Ca $(OH)_2$/Ad. (%)	W/Ad. (%)	W/(Ad.+Ca$(OH)_2$) (%)	
5	40	38	Fly ash, Slag
10	40	36	Fly ash, Slag
25	50	40	Fly ash, Slag
35	60	44	Slag
45	60	41	Slag
50	60	40	Fly ash

Ad. (admixture): fly ash, slag.

Table 3
Mix proportions of mortar

Ad.	W/(C+Ad.)	Ad./(C+Ad.)	C	Ad.	W	S
Fly	0.45	30	454.1	194.6	291.9	1254.9–1259.7
		50	324.3	324.3	291.9	1214.4–1222.3
	0.55	30	401.5	172.1	315.5	1262.5–1266.7
		50	286.8	286.8	315.5	1226.7–1233.7
	0.65	30	359.9	154.2	334.2	1268.6–1272.3
		50	257.1	257.1	334.2	1236.5–1242.7
Slag	0.45	50	324.3	324.3	291.9	1291.4
		70	194.6	454.1	291.9	1281.7
	0.55	50	286.8	286.8	315.5	1294.8
		70	172.1	401.5	315.5	1286.2
	0.65	50	257.1	257.1	334.2	1297.5
		70	154.2	359.9	334.2	1289.8

Ad. (admixture): fly ash, slag (kg/m^3).

2.2.2. Series 2

To verify the applicability of the prediction method obtained from the paste experiment, an experiment using mortar specimens was performed (Table 3). Water-binder ratios of mortar were 0.45, 0.55, and 0.65. Cement replacement ratios of fly ash were 30% and 50%, and replacement ratios of blast furnace slag were 50% and 70%. Mortar specimens were cured in a water bath at 20 °C, and the calcium hydroxide was measured at the ages of 1, 3, 7, 14, 28, and 91 days.

3. Experimental results and discussions

3.1. Reaction between calcium hydroxide and mineral admixtures

Fig. 1(a) and (b) show the amount of combined water incorporated into the paste specimens in Series 1. The amount of combined water, i.e., the degree of hydration of mineral admixture, depended on the amount of added calcium hydroxide. The hydration rate of pastes containing blast furnace slag was faster than pastes containing fly ash. Similar results were obtained using other types of fly ashes and blast furnace slags.

The amount of calcium hydroxide that reacted with admixtures is shown in Fig. 2(a) and (b). For a given age, the amount of calcium hydroxide which had reacted with the mineral admixture in a paste containing a high amount of

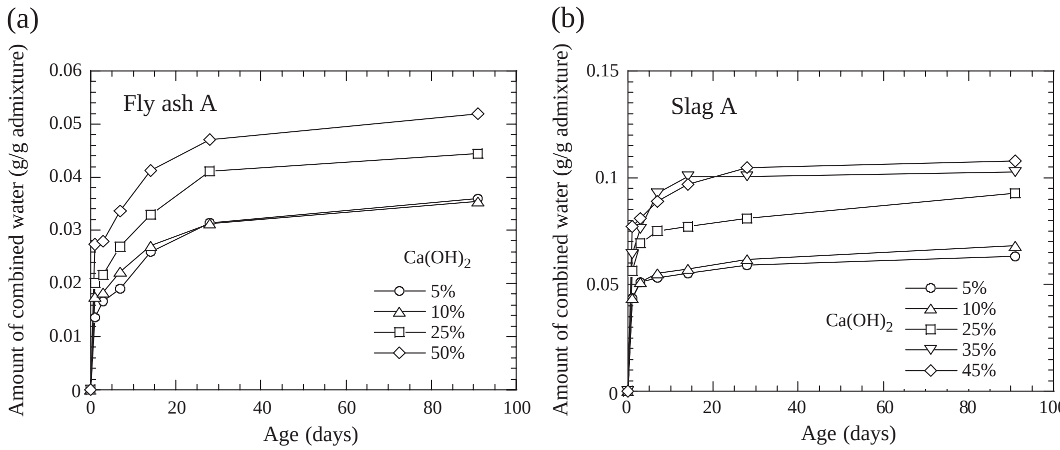

Fig. 1. Amount of combined water in paste (Series 1).

calcium hydroxide was larger than that in a paste with a low amount of calcium hydroxide.

The increase in the amount of calcium hydroxide that reacted with admixtures was large at early ages but small over the long term. The results indicate that reactivity between calcium hydroxide and mineral admixture was dependent on the amount of calcium hydroxide and degree of hydration of the mineral admixtures. Once again, similar results were obtained using other types of fly ashes and blast furnace slags.

Although the reaction between blast furnace slag and calcium hydroxide occurred only in the initial stages of the experiment, the reaction between fly ash and calcium hydroxide continued for a long period of time. Most of the reaction between calcium hydroxide and blast furnace slag occurred within the first 7 days of the experiment, while the bulk of the reaction between the calcium hydroxide and the fly ash occurred during the first 28 days of the experiment.

Series 1 experiments examined the basic reactivity between mineral admixtures and calcium hydroxide; however, hydration of mineral admixtures in blended cement is affected by other substances such as NaOH, KOH, and gypsum [3,4]. This study measured the amount of calcium hydroxide in pastes containing NaOH or $CaSO_42H_2O$. In the paste containing NaOH, the concentration of NaOH in the mixing water was 0.5 mol/l. In the paste containing $CaSO_42H_2O$, the quantity of $CaSO_42H_2O$ was 2% of the mass of mineral admixtures. The results of these experiments are shown in Fig. 3(a) and (b). The amount of calcium hydroxide that reacted with the admixture in the early stage was greater than in the case when only calcium hydroxide was used. These figures demonstrate that the addition of NaOH or $CaSO_42H_2O$ accelerates the hydration of mineral admixtures; however, this acceleration occurs only in the first 7 days of the experiment. After this period, the additives did not affect the reaction rate between mineral admixtures and calcium hydroxide (shown by the gradient of the regression curve). Given that the purpose of this study was to estimate the long-term reaction between mineral admixtures and calcium hydroxide, and the observation that NaOH and $CaSO_42H_2O$ only have short-term effects, the influences of substances other than calcium hydroxide have not been included in our model.

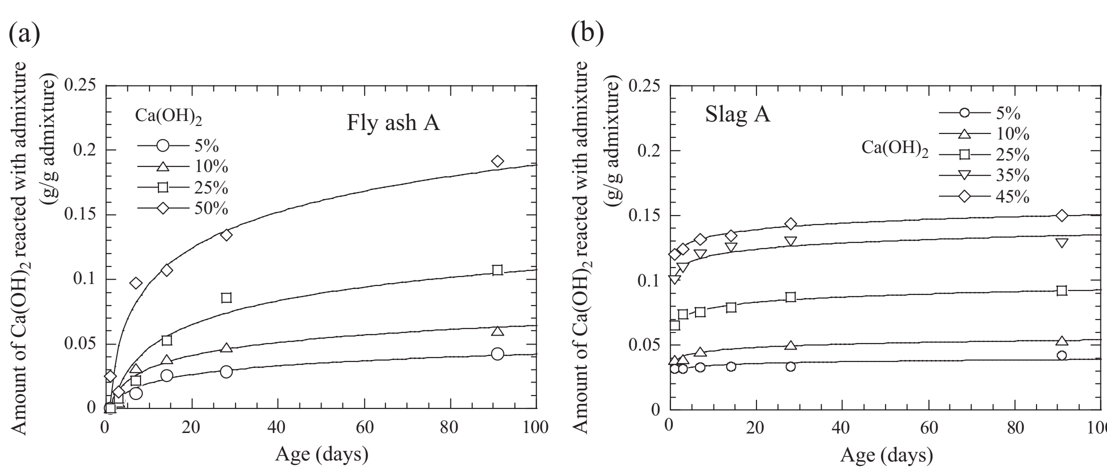

Fig. 2. Amount of calcium hydroxide reacted with admixture in paste (Series 1).

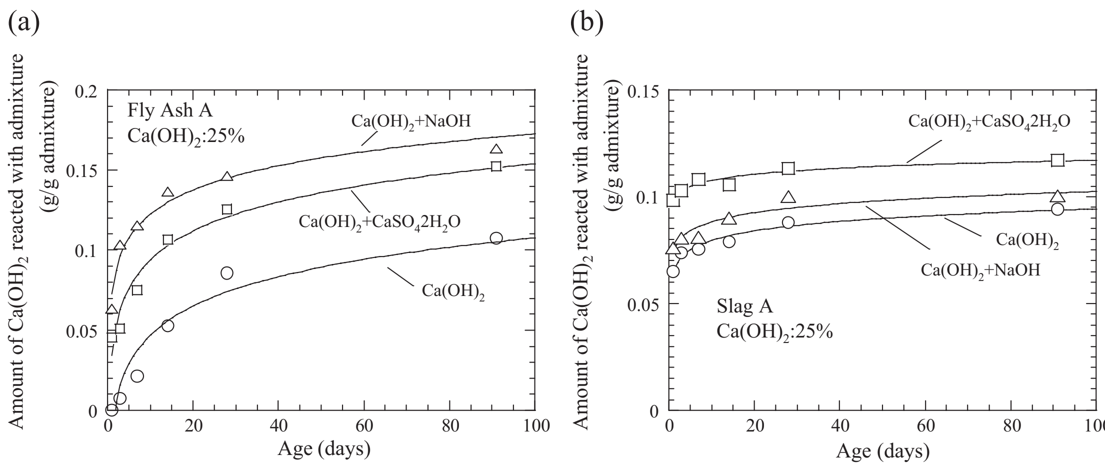

Fig. 3. Effect of NaOH and $CaSO_42H_2O$ on hydration of mineral admixture.

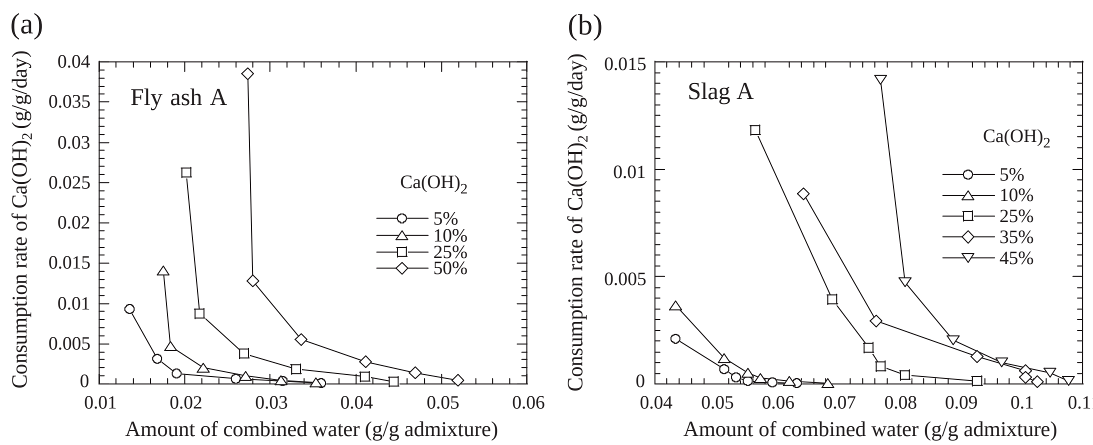

Fig. 4. Relation between combined water and $Ca(OH)_2$ consumption rate.

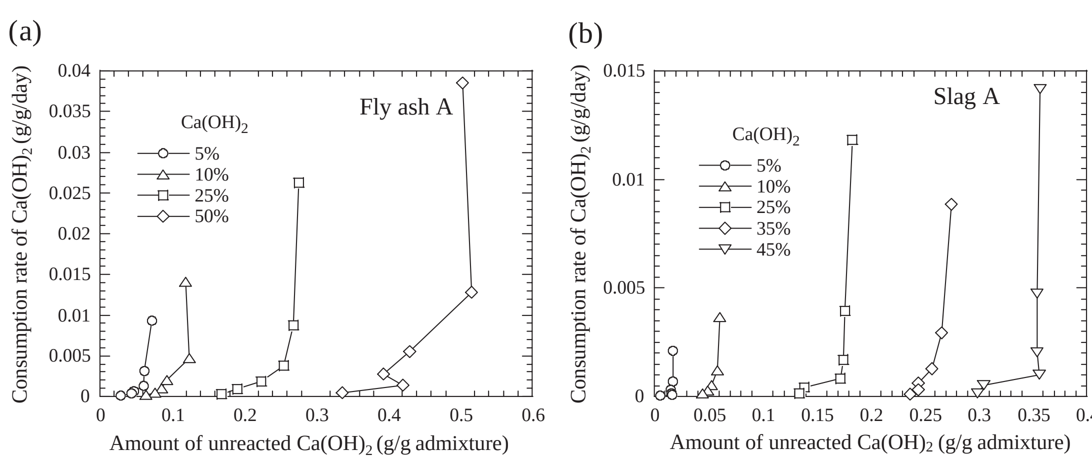

Fig. 5. Relation between unreacted $Ca(OH)_2$ and $Ca(OH)_2$ consumption rate.

3.2. Model for reaction between calcium hydroxide and mineral admixtures

The relation between the age and the amount of calcium hydroxide reacted with admixture can be formulated from Fig. 1 using regression analysis;

$$C_a = \alpha + \beta \log_{10} t \tag{1}$$

where, C_a: amount of calcium hydroxide reacted with admixture per unit weight of mineral admixture (g/g); t: age (days); α, β: experimental constants obtained from regression analysis.

The calcium hydroxide consumption rate can be obtained by differentiating Eq. (1) with respect to time. The following is obtained;

$$\frac{dC_a}{dt} = \frac{\beta}{t \ln 10} \tag{2}$$

By substituting values for t, the consumption rates of calcium hydroxide at each age were calculated. As discussed in Section 3.1, the reaction rate of calcium hydroxide and admixtures depends on the degree of the hydration of the admixture and the amount of calcium hydroxide. Fig. 4 shows the relation between the consumption rate of calcium hydroxide and the amount of combined water at each age. Fig. 5 shows the relation between the consumption rate of calcium hydroxide and the amount of the calcium hydroxide that has not reacted with mineral admixture. These figures demonstrate that the calcium hydroxide consumption rate depends on both of the amount of the calcium hydroxide that has not reacted with mineral admixture and the combined water.

From these results, a model for reaction between calcium hydroxide and mineral admixtures was formulated by regression analysis, as shown in Eq. (3). Fig. 6 shows a schematic of Eq. (3).

$$\frac{dC_a}{dt} = ax\exp(-by) \tag{3}$$

where x is the amount of calcium hydroxide that has not reacted with mineral admixture per unit weight of mineral admixture (g/g); y is the degree of hydration of mineral admixture (the amount of combined water when the amount of combined water at the age of 91 days is assumed to be 1.0); and a and b are experimental constants depending on the characteristics of the mineral admixture.

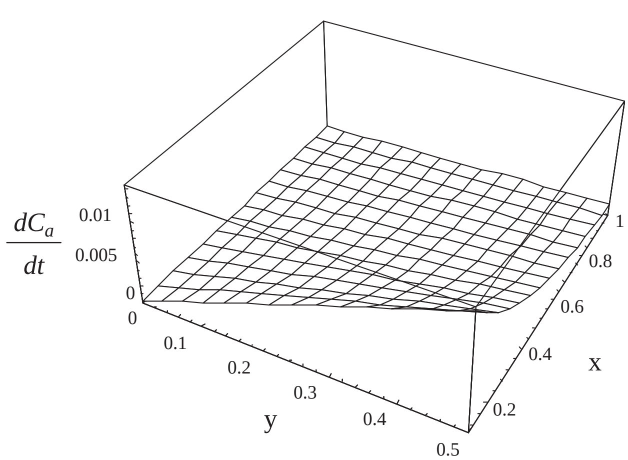

Fig. 6. Schematic of Eq. (3).

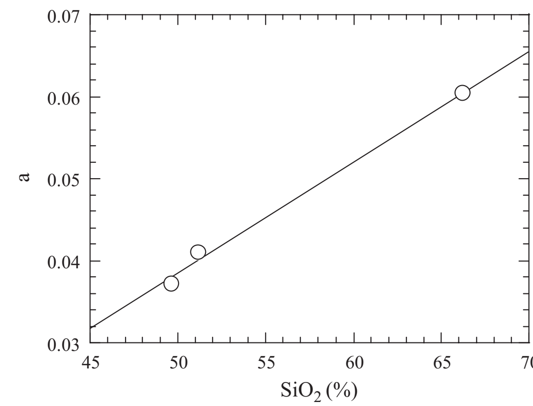

Fig. 7. Relation between "a" and chemical composition of fly ash.

3.3. Relation between characteristics of mineral admixtures and reactivity with calcium hydroxide

Below we consider the relation between the chemical characteristics of mineral admixtures and their reactivity with calcium hydroxide, such as a and b in Eq. (3). The relationship between the chemical compositions of mineral admixtures and a is shown in Figs. 7 and 8. A high correlation exists between SiO_2 content and a in fly ashes. The reaction rate between fly ash and calcium hydroxide increases the higher the SiO_2 content. With blast furnace slag, a high correlation exists between the value of $2CaO + SiO_2 + Al_2O_3$ and a. Moreover, it was observed that the value of a increases with increasing Blaine values.

Fig. 9 shows that the value of b decreases as a increases. This means that a mineral admixture with high reactivity with respect to calcium hydroxide (a is large) has small attenuation on the reaction rate due to the hydration process. The Blaine of blast furnace slag affects only the value of a

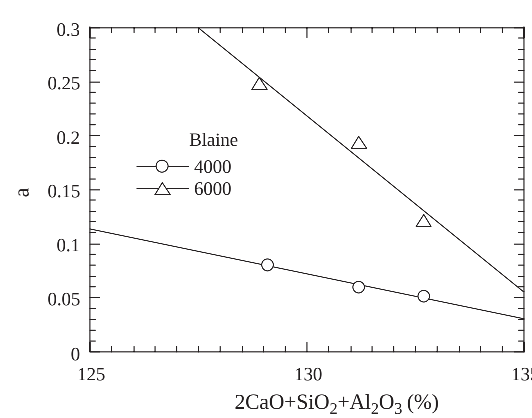

Fig. 8. Relation between "a" and chemical composition of blast furnace slag.

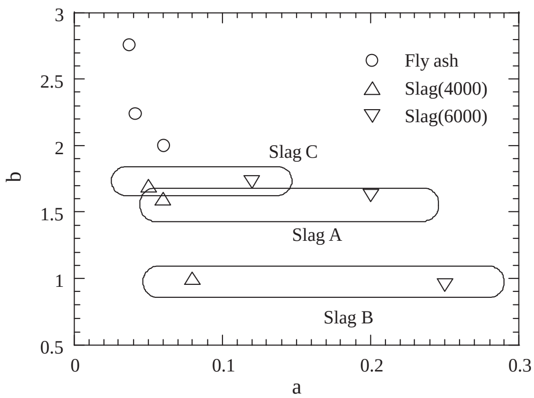

Fig. 9. Relation between “a” and “b”.

when the chemical compositions are the same. Because this experiment studied only three kinds of fly ashes and six kinds of blast furnace slag fine powder, it is necessary to examine other fly ashes and blast furnace slags in order to confirm the applicability of Eq. (3) to other types of admixtures.

3.4. Predicting the amount of calcium hydroxide in mortar

In the Series 1 experiments, large amounts of calcium hydroxide exist in the paste immediately after mixing. In two-component systems, however, which consist of Portland cement and mineral admixtures, calcium hydroxide is gradually generated by the process of cement hydration. In order to verify the applicability of Eq. (3) obtained from Series 1 results to Series 2, the amount of calcium hydroxide in the mortar using mineral admixture was predicted. Although the amount of combined water of mineral admixture in mortar was needed for the model, direct measurement could not be carried out. The amount of combined water of the binder (cement and mineral admixture) was measured, and the amount of combined water of mortar, which does not use mineral admixture, was measured. The amount of combined water of admixture was calculated by subtracting the combined water of the cement

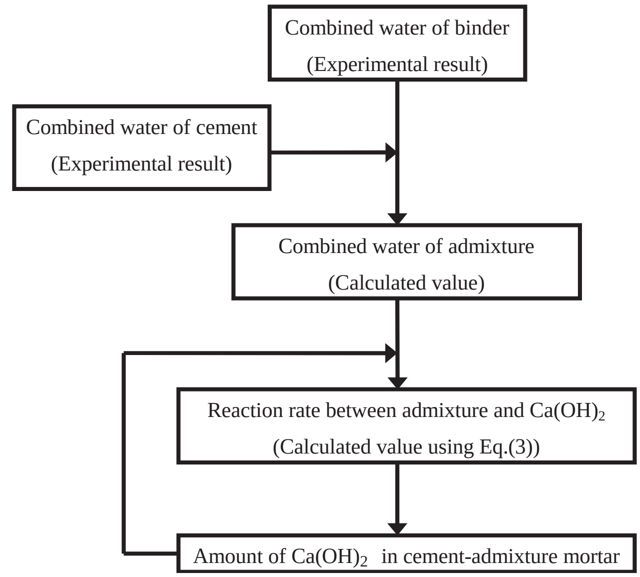

Fig. 11. Flowchart of prediction method.

from the combined water of the binder. The amount of calcium hydroxide that has not reacted with mineral admixture in mortar was calculated by subtracting the consumption amount due to hydration of mineral admixtures from the amount of calcium hydroxide generated by cement hydration. The relation between the amount of combined water of cement and the amount of calcium hydroxide in mortar, which does not use mineral admixture, is shown in Fig. 10. The flowchart of prediction is shown in Fig. 11.

From Fig. 1, it can be seen that the 91 days combined water of mineral admixture depends on the amount of calcium hydroxide. The values of y in Eq. (3) are calculated from 91 days combined water (a denominator of y is 91 days combined water). Since the amount of calcium hydroxide in mortar changes with time, the value of y changes with time. However, it is impossible to keep the ratio of the amount of mineral admixture and the amount of calcium hydroxide constant during the Series 1 experiment. Fig. 12 shows that relation between the 91 days combined

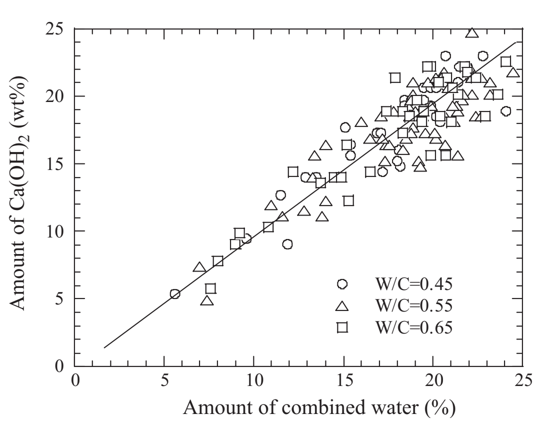

Fig. 10. Relation between the amount of calcium hydroxide and combined water in OPC mortar.

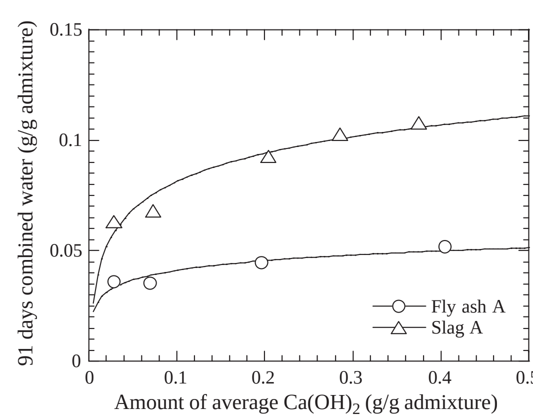

Fig. 12. Relation between the 91 days combined water and the average amount of calcium hydroxide.

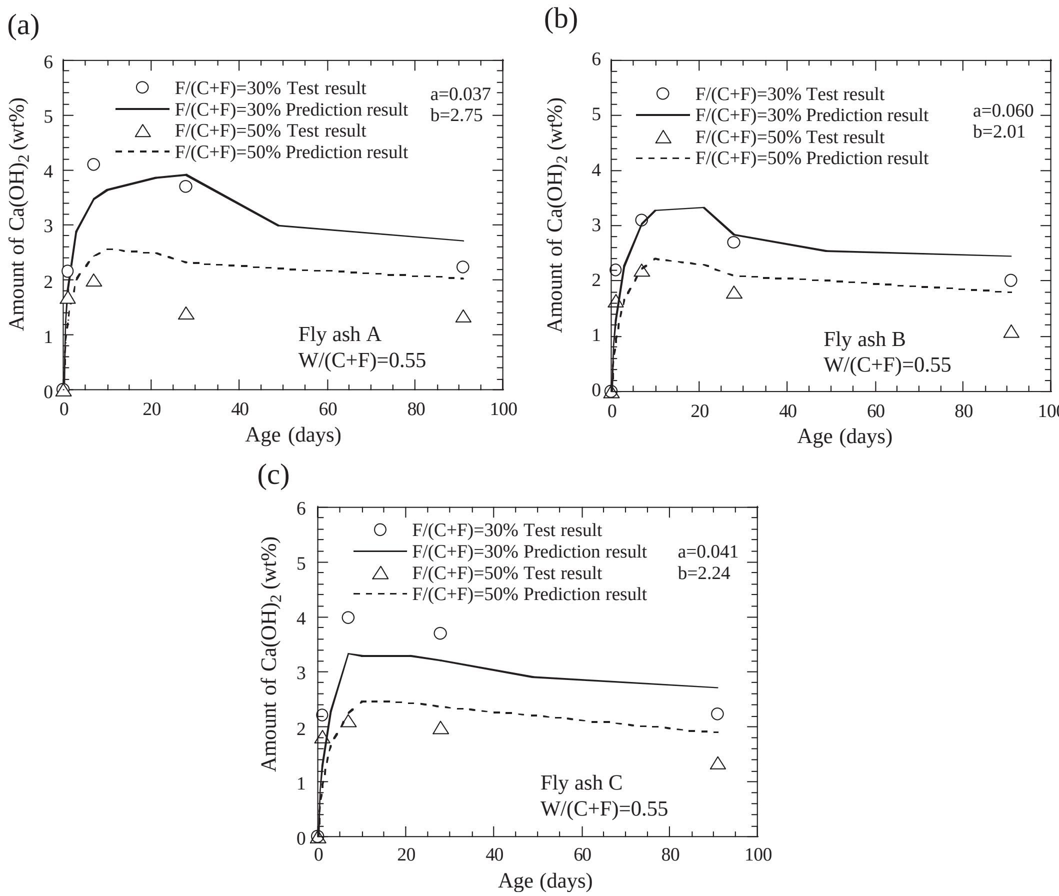

Fig. 13. Prediction result of fly ash (Series 2).

water and the average amount of calcium hydroxide. The average amount of calcium hydroxide is the mean value of the initial amount of calcium hydroxide and the amount of calcium hydroxide at the age of 91 days. Good correlation is seen between the average amount of calcium hydroxide and 91 days combined water. Therefore, in this study, the relations between the amount of calcium hydroxide and the amount of 91 days combined water for each admixture were obtained from experimental results by regression analysis. These relations were assumed to be applicable to Series 2. Using these relations: the amount of 9l days combined water was recalculated, depending on the amount of calcium hydroxide for each age; and the degree of hydration y was calculated.

Figs. 13 and 14 show examples of predicted results for mortars using fly ash and blast furnace slag, respectively. The agreement between the prediction model and the experimental results is very good, and Fig. 15 compares

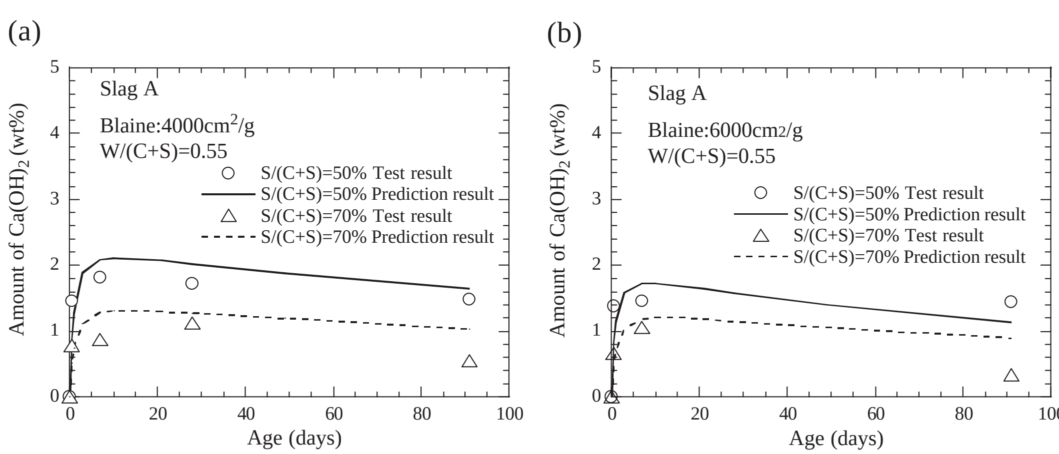

Fig. 14. Prediction result of blast furnace slag (Series 2).

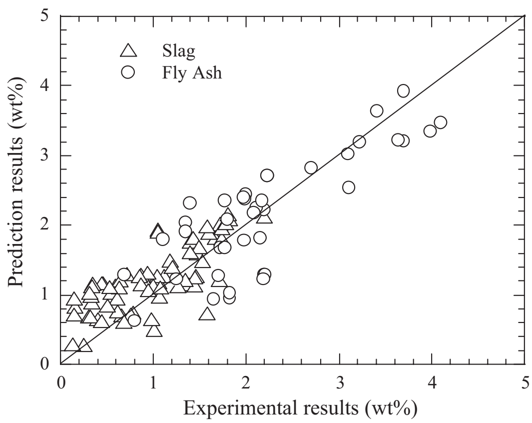

Fig. 15. Prediction result of all specimen (Series 2).

the experimental results with the calculated results for all mortars. Based on this comparison, the proposed model is believed to be sufficiently accurate. However, if the replacement ratio of mineral admixture becomes large, for example, if the cement is replaced by as much as 50% fly ash or 70% blast furnace slag, the differences between experimental results and calculated results will be large, as shown in Figs. 13 and 14.

As demonstrated above, this research calculated the amount of combined water of mineral admixture by subtracting the combined water of cement from the combined water of binder. This procedure disregarded any cement and mineral admixture interaction in the hydration process. However, Diamon [3] and Uchikawa [4] have demonstrated the influence of the interaction between cement and mineral admixture, and this experiment has underscored that this interaction effect cannot be ignored when the replacement ratio is large. To establish an accurate model applicable to all potential mixes, it will be necessary to quantitatively determine the interaction effects on hydration.

4. Conclusions

The following conclusions can be obtained from this study:

(1) The consumption rate of calcium hydroxide by mineral admixtures is greater when the degree of hydration of mineral admixture is lower, and the amount of the calcium hydroxide that has not reacted with mineral admixture is large.
(2) Eq. (3) can predict the amount of calcium hydroxide in the mortar using fly ash or blast furnace slag. Therefore, it is possible to evaluate the performance of admixtures in concrete.
(3) The parameters a and b in Eq. (3) are dependent on the physical and chemical characteristics of mineral admixtures.

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