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Cementing Efficiency of Fly-ash in Mortar Matrix According to Binder-Water Ratio and Fly-ash Replacement Ratio

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Abstract

This paper predicts the cementing efficiency of fly-ash(FA) based on mortar test considering binder-water ratio and FA replacement ratio as experimental variables. The cementing efficiency prediction model proposed by statistical analysis enables us to estimate the value according to the binder-water ratio and FA replacement ratio of matrix. When FA replacement ratio is the same, the lower the binder-water ratio, the higher the estimated cementing efficiency. There are significant differences in the values according to binder-water ratio at FA replacement ratios of 15% or less, but there are almost no differences when FA replacement ratio is more than 15%. As the binder-water ratio increases, the variations in the values according to FA replacement ratio are great at FA replacement ratios of 15% or less. As the FA replacement ratios increase, the values increase for FA replacement ratios of 15% or less, but decrease for more than 15%. The values range from -0.71 to 1.24 at binder-water ratio of 1.67-2.86 and FA replacement ratio of 0-70%. The RMSE of the 28-day compressive strength predicted by modified water-cement ratio is 2.2 MPa. The values can be trusted, as there is good agreement between predicted strength and experimental strength.

Keywords : fly-ash, cementing efficiency, relative strength, modified cement-water ratio, strength prediction

1. Introduction

Fly ash(FA) is economical and eco–friendly, as it is recycled material of an industrial by–product. Due to the dynamic characteristics and good durability of FA concrete, FA has gradually been used in the concrete industry. To minimize the trial mixes of concrete containing FA, improve the accuracy and efficiency of design of mix proportion [1,2] and predict compressive strength[3,4,5], it is important to understand the cementing efficiency of FA. To predict the cementing efficiency of FA, Smith[6], considering differences in strength development according to the pozzolan reaction, expressed the cementing efficiency of FA using k to convert mass of FA(F) into equivalent mass of OPC(kF). The water–binder ratio($W/(C+F)$) can be converted into modified water–cement ratio ($W/(C+kF)$) according to the cementing efficiency of FA[7]. The compressive strength is generally used to determine the cementing efficiency, and the following are the concepts that can be utilized: the strength activity index[8], the concept of relative strength[9] which expresses the ratio of compressive strength of pozzolan concrete to that of OPC concrete, and the overall efficiency[10] which combines the general efficiency incorporating the influence of age with the percentage efficiency according to the pozzolan replacement ratio.

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Cho[11] suggested a prediction model for the cementing efficiency of FA through a statistical analysis using the concept of Bolomey's strength equation and relative strength(Rs). Since the prediction model enables researchers to calculate the cementing efficiency of FA using only concrete mixture rather than experimental test results, it can be utilized in the mix design and quality control of FA concrete. However, the model was derived based on the ready-mixed concrete data, rather than by controlling the mixture factors that can affect the cementing efficiency under the same experimental conditions. For this reason, it should be verified through an experiment designed to use the variables of the suggested prediction model as experimental factors.

The cementing efficiency of FA in the prediction model is determined by factors other than aggregate in the mixture. This research aims to present a prediction model for cementing efficiency of FA, and estimate cementing efficiency(k_p) based on a mortar experiment using binder-water ratio and FA replacement ratio as experimental variables.

2. Prediction model for cementing efficiency

Cementing efficiency is affected by the physical and chemical characteristics of the binder, mix proportion, age, and curing condition. For this reason, it is almost impossible to suggest a prediction model for cementing efficiency that can consider all these factors. The various prediction models were suggested by considering binder type[8,9] and fineness[4], pozzolan replacement ratio[3,4,8,9], and age[4,10]. These were used for the design of mix proportion[1,2] and strength prediction[3,4,5]. In particular, it is revealed that as more FA is used, the cementing efficiency of FA gradually becomes lower, within the range between 0.2 and 1.3[2,3,4,10]. However, the value was reflected only by the FA replacement ratio of various mixture factors, so to reflect the optimal mixture in terms of strength and economic feasibility, we suggest an equation for predicting cementing efficiency of FA based on the contents of matrix materials and Rs, as shown in Eq. (1) from a previous study[11].

$$k = \left(\frac{C+F-0.5W}{F}\right) \times (Rs-1)+1 \quad ---(1)$$

where, Rs is relative strength(ratio of compressive strength of FA mixture to that of OPC mixture); C, F, and W are OPC, FA, and water content in the mixture, respectively; k is the cementing efficiency of FA.

Since Eq. (1) is based on Bolomey's strength equation, which is expressed as a linear equation for the compressive strength based on cement-water ratio, binder-water ratio is used instead of water-binder ratio. The Rs in Eq. (1) is an experimental value. To express the cementing efficiency of FA with a function of the mixture composition, a linear function of binder-water ratio and FA replacement ratio was suggested as shown in Eq. (2). That is, the prediction model for cementing efficiency of FA can be expressed as a function of the mixture by replacing Rs in Eq. (1) with Eq. (2), the estimation equation for Rs. Therefore, the accuracy of Eq. (2) is an important factor in the reliability of the estimated cementing efficiency of FA(k_p).

$$Rs = c(C+F)/W + dF/(C+F) + e \quad ---(2)$$

where, $(C+F)/W$ is the binder-water ratio of FA mixture; $F/(C+F)$ is the FA replacement ratio of FA mixture; c, d, and e are the experimental constants.

If the concrete contains FA, k_p could be determined only by the factors in the matrix such as unit contents of cement, FA, and water, binder-water ratio, and FA replacement ratio, using Eqs.(1) and (2). The k_p was verified by comparing predicted strength using $(C+k_pF)/W$ and experimental strength and analyzing the standard error of estimation(Root Mean Squares Error, RMSE).

3. Experimental plan and results

Experimental variables are binder-water ratio and FA replacement ratio, and the other conditions of the experiment including factors related to the mixture were controlled equally.

3.1 Materials

As the binder for the mortar experiment, OPC of Company H and 2 kinds of FA(ASTM Class F) from Boryeong were used. The properties of the binder are indicated in Table 1. Standard sand prescribed in KS L ISO 679 from Jumunjin was used as a fine aggregate.

Table 1. Properties of binder

Binder	Density (g/cm^3)	Blaine (cm^2/g)	Ignition Loss (%)	Flow ratio* (%)	Compressive strength (MPa) of OPC or Activity index(%)** of FA	
					7-day	28-day
OPC	3.15	3348	1.77	-	29.0	40.9
FA	2.19	3540	3.50	100	71	90

* Flow ratio is the flow percentage of FA mortar to control mortar.
** Activity index is the ratio of compressive strength of FA mortar to control mortar.
For FA mortar, OPC and FA are mixed in the mass ratio of 3:1.

To evaluate the strength activity index(AI), which has a close relationship with the pozzolan reaction of FA, the mass ratio of binder and standard sand was 1:3 with water-binder ratio of 0.5 according to KS L 5405, and the specimen was manufactured and cured according to KS L ISO 679. The flow ratio of FA was measured as 100%, while the 7-day AI and the 28-day AI were measured as 71% and 90%, respectively.

3.2 Mix proportions

Considering the general range of concrete with specified compressive strength lower than 40 MPa, the binder-water ratio was set to three different levels: 1.67, 2.06, and 2.86. FA replacement ratio was set to nine different levels: 0, 5, 10, 15, 20, 25, 30, 50, 70% considering the generally applicable range of FA replacement ratio lower than 25% and the special range required to replace a high volume of FA[12] in order to reduce heat of hydration and secure high durability. Therefore, a total of 27 mortars were mixed by changing binder-water ratio and FA replacement ratio in order to understand the cementing efficiency of FA, as shown in Table 2.

An equal volume of binder and aggregate was put into the mortars. The mass ratio of binder and aggregate was 1:2.45 according to KS L 5105. To effectively understand the influence of water-binder ratio, the volume of OPC and FA was mixed to be equal in the FA replacement ratio. The binder-water ratio was adjusted according to the unit quantity, and FA was replaced for OPC in the control group mortar by weight.

3.3 Specimen preparation and curing

After mixing each mortar according to KS L ISO 679, the flow test was carried out according to KS L 5111, and specimens were manufactured using the cubic mould(50×50×50mm) according to KS L 5105. After the formation, the moulds were kept in a constant temperature and humidity chamber at 21℃ and relative humidity of 95% for 24 hours.

Then, the moulds were detached and the specimens cured in a water tank at 23±2℃ until the day of testing.

3.4 Test results

Table 2 indicates the flow, compressive strength, and *Rs* of each mortar. The difference between the flow of mortar with FA and that of the control group was shown to be lower than 10% up to the FA replacement ratio of 50%, which means there was no significant change in the flow according to FA replacement. The *Rs* was shown to be highest (more than 1) at an FA replacement ratio of 15%. When FA replacement ratio was lower than 15%, *Rs* increased in a manner proportional to the FA replacement ratio. However, when FA replacement ratio was higher than 15%, *Rs* increased in a manner inversely proportional to the FA replacement ratio.

Table 2. Mix proportions and test results

Mix proportions		Mortar flow (mm)	28-day compressive strength (MPa)	*Rs*
B/W	F/B			
2.86	0	105	39.5	-
	0.05	113	34.5	0.874
	0.10	109	36.1	0.915
	0.15	106	39.5	1.000
	0.20	107	38.6	0.978
	0.25	110	34.9	0.885
	0.30	109	31.5	0.797
	0.50	109	28.0	0.709
	0.70	110	13.4	0.340
2.06	0	138	37.4	-
	0.05	137	36.3	0.970
	0.10	132	36.8	0.983
	0.15	136	38.8	1.037
	0.20	136	35.1	0.937
	0.25	141	33.4	0.892
	0.30	141	32.4	0.866
	0.50	145	21.1	0.563
	0.70	174	6.4	0.172
1.67	0	175	33.7	-
	0.05	175	33.6	0.996
	0.10	177	34.0	1.008
	0.15	186	34.5	1.022
	0.20	188	32.2	0.954
	0.25	192	30.9	0.918
	0.30	191	26.9	0.797
	0.50	190	15.1	0.448
	0.70	218	5.3	0.157

B/W = binder-water ratio; F/B = FA replacement ratio; Rs = the ratio of strength of FA mortar to that of control mortar
The B/W of 2.86, 2.06, and 1.67 are equal to W/B of 0.35, 0.485, and 0.60, respectively.
The binder content of all mixtures is 760g.

4. Prediction of the cementing efficiency of FA

4.1 Estimation equation for Rs

It is necessary to present a model to accurately estimate *Rs* using the mix proportions in order to propose a prediction model for cementing efficiency of FA using only the mix proportions. Therefore, to present a prediction model for *Rs*, a regression analysis on experimental factors was carried out using SPSS[1]), predictive analytics software.

4.1.1 FA replacement ratio

At 28 days *Rs* according to FA replacement ratio was analyzed to be a quadratic function of FA replacement ratio as illustrated in Figure 1. The RMSE of estimated relative strength was 0.065. However, this equation cannot explain the increase in *Rs* as the binder-water ratio decreased and the FA replacement ratio increased in the FA replacement ratio of 15% or less. Thus, an estimation equation for *Rs* that reflects this phenomenon is needed in order to accurately explain the strength development.

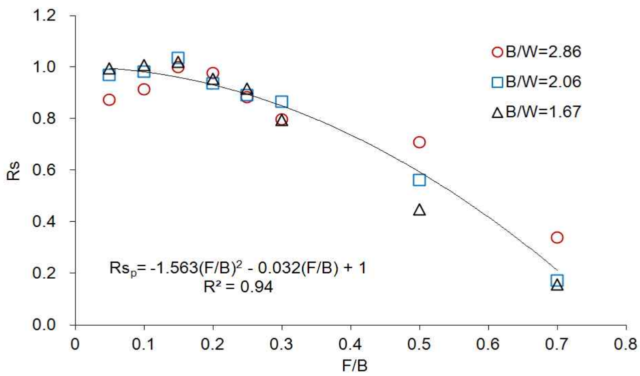


Figure 1. Rs according to FA replacement ratio by binder-water ratio

1) IBM® SPSS® Ver. 18

Table 3. Regression analysis results on Rs with binder-water ratio and FA replacement ratio (Rs = c(B/W) + d(F/B) + e)

FA replacement ratio (F/B)	Regression coefficient		Standardized regression coefficient		Constant	R	R^2	RMSE
	c	d	c′	d′	e			
0 < F/B ≤ 0.15	-0.069	0.729	-0.691	0.603	1.057	0.917	0.841	0.024
0.15 < F/B ≤ 0.7	-	-1.448	-	-0.971	1.259	0.971	0.943	0.071

c and d are regression coefficients of binder-water ratio and FA replacement ratio, respectively.
Each p-value of independent variables is lower than 0.05.
R = correlation coefficient, R^2 = determination coefficient, RMSE = standard error of estimation

4.1.2 Binder-water ratio and FA replacement ratio

Figure 1 shows that Rs is highest at a FA replacement ratio of 15%, and to express a linear function of binder–water ratio and FA replacement ratio as Eq. (2), the results were divided by FA replacement ratio into two groups: one when FA replacement ratio was 15% or less and the other when FA replacement ratio was higher than 15%. Multiple linear regression analysis was performed on each group, and Table 3 provides the results of regression analysis. In particular, at an FA replacement ratio of 15% or less, the RMSE of the linear function is lower than that of the quadratic function in Figure 1, so Rs is more accurately estimated when using the linear function.

When lower than 15%, as the binder–water ratio decreased and FA replacement ratio increased, Rs went up, which is identical to the result of a previous study[11] based on the concrete data. However, when FA replacement ratio is higher than 15%, the regression coefficient of binder–water ratio was insignificant ($p>0.05$), and a linear function of FA replacement ratio was derived. The estimation equation for Rs in Table 3 had a higher coefficient of determination (R^2) and a lower RMSE than the equation presented by Cho[11] using the concrete data. Therefore, the influence of binder–water ratio and FA replacement ratio on the cementing efficiency of FA can be understood more clearly.

At the FA replacement ratio of 15%, the strength development according to the FA replacement ratio was reversed. Because the volume of binder was fixed at a certain level, the additional OPC was not supplied with the increase of FA replacement ratio. Therefore, calcium hydroxide ($Ca(OH)_2$, CH) was not yielded continually. That is, when FA replacement ratio was lower than 15%, CH that was necessary for the pozzolan reaction was supplied, but when FA replacement ratio was higher than 15%, CH was insufficient, and the pozzolan reaction decreased accordingly.

When lower than 15%, the absolute value of the standardized regression coefficient of binder–water ratio was higher than that of the FA replacement ratio; thus, not only the influence of FA replacement ratio but also binder–water ratio for Rs should be considered. However, when FA replacement ratio is higher than 15%, the absolute value of the standardized regression coefficient of FA replacement ratio was shown to be close to 1, which means Rs was absolutely affected by FA replacement ratio.

4.2 Prediction model for cementing efficiency of FA

A prediction model for cementing efficiency of FA was drawn by substituting the estimation equation for Rs with the regression coefficient shown in Table 3 for Eq. (1). The prediction model for cementing efficiency of FA can be expressed as

2) Standardized regression coefficients of independent variables indicate the relative impact on the dependent variable, and range from -1 to 1. The larger absolute value is, the greater influence.

Eqs. (3) and (4) according to FA replacement ratio.

$$k_{p1} = -0.069\frac{y}{x} + 0.092\frac{1}{x} - 0.365\frac{1}{y} - 0.029\frac{1}{xy} + 1.729 \quad -(3)$$

$$k_{p2} = 0.259\frac{1}{x} + 0.724\frac{1}{y} - 0.130\frac{1}{xy} - 0.448 \quad ------(4)$$

where, k_{p1} and k_{p2} are estimated cementing efficiency when FA replacement ratio is at 15% or less and at higher than 15%, respectively; x is FA replacement ratio(F/B); y is binder-water ratio (B/W).

Figure 2 illustrates the estimated cementing efficiency(k_p) of FA calculated using Eqs. (3) and (4). Eq. (3) was used when the binder-water ratio was between 1.67 and 2.86, and FA replacement ratio was 15% or less, while Eq. (4) was used when FA replacement ratio was higher than 15%. The k_p ranged from −0.71 to 1.24 when calculated using the two equations.

Eqs. (3) and (4) can be utilized for designing mix proportion, because users can understand the range of FA replacement ratio(16~17%, 12~18%, and 8~18% at B/W of 2.86, 2.06, and 1.67, respectively) at which k_p is higher than 1, and the highest FA replacement ratio at which the strength of the FA mixture is higher than that of control group, as illustrated in Figure 2.

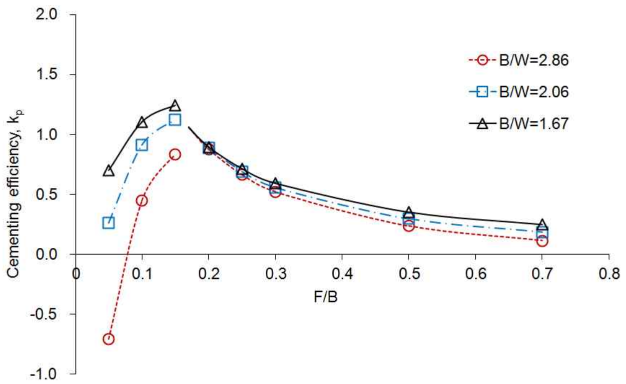


Figure 2. k_p determined by Eqs. (3) and (4) according to FA replacement ratio and binder-water ratio

The higher B/W was, the lower k_p became at the same F/B, because the decrease in CH from OPC caused the pozzolan reaction to be reduced[14]. It is difficult to expect a higher strength than the control group through FA replacement at 28 days because k_p is less than 1 at all FA replacement ratios when B/W is higher than 2.86. In particular, k_p was shown to be negative at B/W of 2.86 and F/B of 5%. That is, when FA replacement ratio is more than 7%, the effect on strength development of FA can be expected. A negative value is shown when Rs is less than 1 in Eq. (1). The Rs was shown to be less than 1, when FA replacement ratio was low and binder-water ratio was high[11]. The negative value turned positive as pozzolan reaction proceeded over time.

When FA replacement ratio was 15% or less, the higher B/W, the more variation of k_p according to F/B. However, when FA replacement ratio was higher than 15%, there was no significant difference found, and k_p gradually decreased as F/B increased.

4.3 Verification of the prediction model

The experimental cementing efficiency(k_e) calculated using Eq. (1) with Rs based on the test results and the predicted cementing efficiency(k_p) calculated using Eqs. (3) and (4) were compared. The reliability of the prediction model was evaluated by RMSE of predicted strength based on the cementing efficiency of each.

4.3.1 Strength prediction by $(C+k_eF)/W$

The Rs in Table 2 was applied to Eq. (1) to calculate k_e. The correlations between $(C+k_eF)/W$ that reflects the k_e between −1.07 and 1.19 and 28-day compressive strength($f_{(28)}$) are shown in Figure 3. The $f_{(28)}$ is expressed as the linear function of $(C+k_eF)/W$, $f_{(28)} = a\{(C+k_eF)/W - 0.5\}$, RMSE was 0.24 MPa and the coefficient of determination was close to 1. The coefficient a can be expressed as the function of water content [$a = 0.064\,W$, R^2=0.99]. This value is an index showing water sensitivity of compressive strength, which can be affected by age, strength, and cement type[13]. As the binder–water ratio gradually became lower, the yield of CH increased[14]. Therefore, the cementing efficiency of FA increased because the pozzolan reaction that formed the calcium silicate hydrate(CSH) from CH became more active with FA replacement, so that the coefficient a increased.

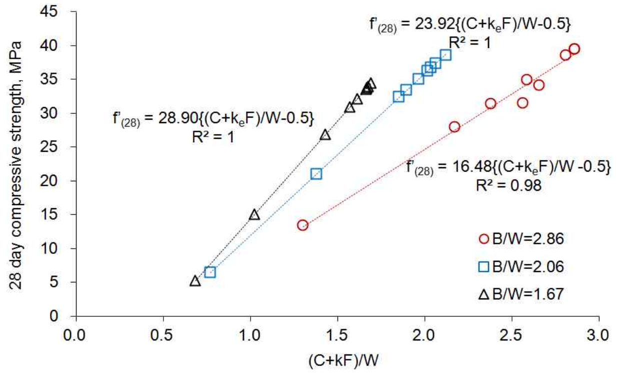


Figure 3. Relationship between modified cement-water ratio and 28-day compressive strength based on mortar test

The k_e was derived based on the FA concrete data of Han[15] and Mathews[16], and Figure 4 shows the correlations between $(C+k_eF)/W$ and compressive strength. The k_e calculated using data of Han was 0.19~1.43 within the range of B/W of 1.67~3.70 and F/B of 0~30%, while k_e calculated using data of Mathews was 0.69~1.55 within the range of B/W of 1.75~2.33 and F/B of 0~20%.

Figure 5 (a) shows the comparison between experimental strength and predicted strength by $(C+k_eF)/W$. The RMSE was 1 MPa, and the compressive strength is predicted within the error range of ±4%. Figure 5 (b) is the results of a comparison between experimental strength and predicted strength by $(C+F)/W$ without considering k_e, and the RMSE was 4.4 MPa.

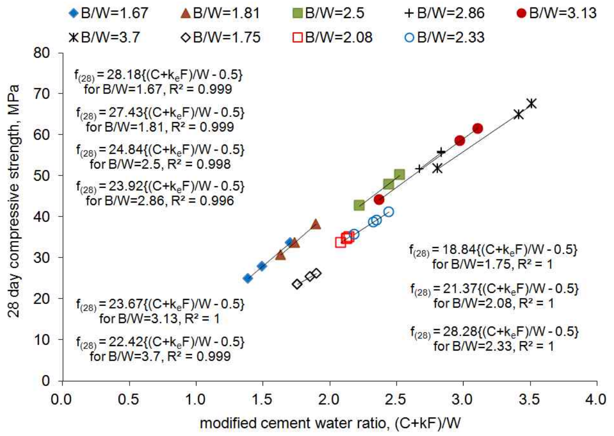
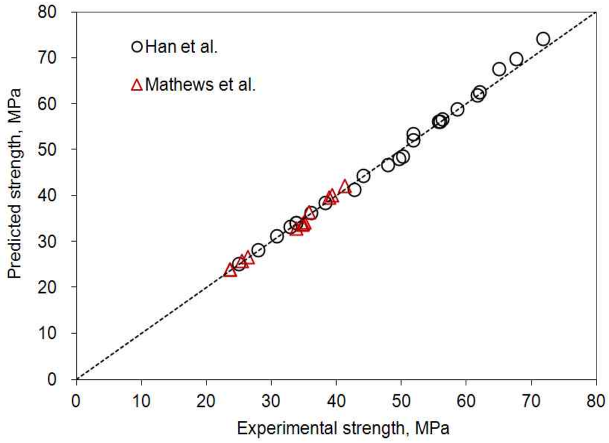
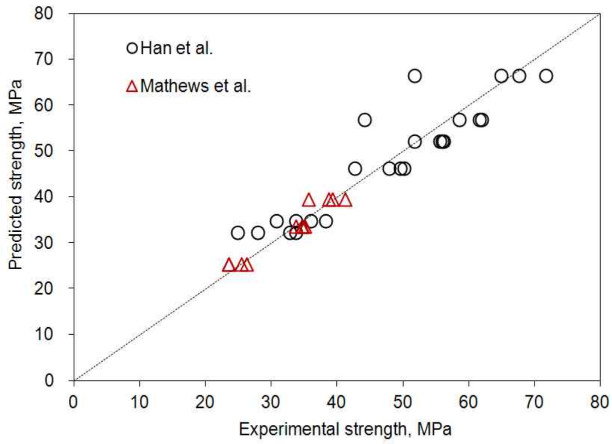


Figure 4. Relationship between modified cement-water ratio and 28-day compressive strength based on FA concrete data of ref. [15] & [16]



(a) Strength prediction by (C+keF)/W



(b) Strength prediction by (C+F)/W

Figure 5. Comparison between experimental strength and strength predicted by modified cement water ratio and binder-water ratio in ref. [15] & [16]

The Rs was drawn based on the experimental results of mortar and concrete, and then applied to Eq. (1) to obtain k_e. The RMSE of the predicted strength obtained by $(C+k_eF)/W$ was less than 1 MPa, which is very similar to the experimental strength. Therefore, Eq. (1), the ground equation for the prediction model, is reliable and thus applicable to mortar and concrete as well.

4.3.2 Strength prediction by (C+k$_p$F)/W

The 28-day compressive strength was predicted using $f_{(28)} = a\{(C+k_pF)/W-0.5\}$ where the k_p obtained from Eqs. (3) and (4) is applied. Here, the a value was calculated by the function of water content mentioned earlier. Figure 6 is derived by comparing predicted strength and experimental strength, and RMSE was 2.2 MPa.

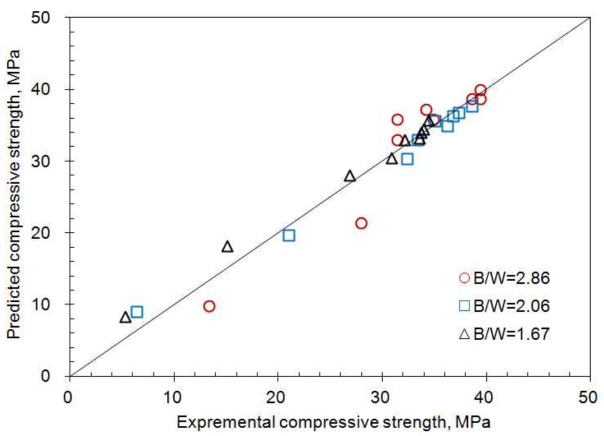


Figure 6. Comparision between experimental strength and strength predicted by (C+k$_p$F)/W

From the test results, it was found that the maximum difference between k_e and k_p was 0.36, and RMSE was 0.15. The difference was not significant, so the predicted strength obtained by $(C+k_pF)/W$ was very similar to the experimental strength. Therefore, the prediction model for cementing efficiency of FA, Eqs. (3) and (4) using B/W and F/B, is believed to have high reliability.

5. Conclusions

A prediction model for 28-day cementing efficiency of FA and estimated cementing efficiency(k_p) was presented, where the binder-water ratio and FA replacement ratio were considered. In addition, the estimated strength obtained using the modified cement-water ratio($(C+k_pF)/W$) was evaluated to determine the reliability and applicability of the prediction model for cementing efficiency of FA.

In the range of binder-water ratio of 1.67~2.86 and FA replacement ratio of 0~70%, k_p obtained from the prediction model ranged from -0.71 to 1.24. The lower the binder-water ratio, the higher k_p at the same FA replacement ratio. Up to an FA replacement ratio of 15%, as the binder-water ratio went up, the increase of k_p according to FA replacement ratio was also shown to be high. However, In FA replacement ratio of more than 15%, there were no significant differences in k_p according to binder-water ratio, but k_p gradually decreased as FA replacement ratio went up.

This is conducive to understanding the range of FA replacement ratio (16~17% at B/W of 2.86, 12~18% at B/W of 2.06 and 8~18% at B/W of 1.67) at which k_p is higher than 1 when calculated using the prediction model, which can be utilized for the mix design.

The standard error of the estimated 28-day compressive strength using $f_{(28)} = a\{(C+k_pF)/W-0.5\}$ was 2.2 MPa, which means that the predicted strength is in good agreement with the experimental strength. Therefore, the prediction model for cementing efficiency of FA and k_p can be significant and reliable.

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