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A simplified model for prediction of pozzolanic characteristics of fly ash, based on chemical composition

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Abstract

The correlation between type and quantity of glassy phase and chemical composition of fly ash has been reviewed. A simplified model based on above has been proposed for assessment of pozzolanic reactivity of fly ash in terms of compressive strength of fly ash cement mortar. The model is fitted for 10%, 20%, 35% and 50% of fly ash replacement and for 28, 91 and 365 days of curing period using a least squares technique. The model is found to predict well for more than 20% fly ash replacement. The correlation coefficient (R^2) between predicted and experimental values is maximum for 50% replacement. The model fit for 10% replacement of fly ash is poor.

Keywords: Fly ash; XRD; Glass content; EDX; Compressive strength

1. Introduction

Unlike high calcium fly ash, low calcium fly ash needs assessment in terms of pozzolanic reactivity before use in cement or concrete industry due to non-reactive minerals, low glass percentage and loss on ignition (LOI). Pozzolanic behavior of fly ash can be evaluated directly by means of compressive strength development with time of fly ash/hydrated lime or fly ash/cement paste, mortar or concrete. Measuring the pozzolanic behavior indirectly by means of electrical resistance of cement paste containing the pozzolan can reduce the test pezriod [1,2]. Development of prediction model can save both resource and the test period.

The pozzolanic characteristic of fly ash depends upon the type and quantity of glassy phase, fineness and LOI [3]. Various studies have been made to correlate compressive strength of fly ash/lime and fly ash/cement mortar or concrete with chemical composition and fineness of fly ash [4–7]. Though factors like LOI, fineness, and pozzolanic content affect the compressive strength but there is not a very strong relationship with only any one of the above [4]. Vincent et al. [5] have shown that the chemical composition of fly ash expressed in mole fraction correlates with strength better than chemical composition expressed in weight percent. Watt and Thorne [6] have discussed about the possibility of correlating crushing strength of fly ash/lime mortar with chemical composition, fineness and glass content. Dhir et al. [7] have shown that there is a good correlation of 28-day compressive strength of Ordinary Portland cement/fly ash concrete with LOI and fineness. However, in the above prediction models the factors are considered separately and the effect of quality and quantity of glassy phase has not been considered.

Mehta [3] and Diamond [8] observed that the amount of analytical calcium content (expressed as an oxide) in fly ash is an indicator of type of glass content. Diamond [8] suggested a chart correlating analytical calcium content (expressed as an oxide) with hump position in X-ray diffraction analysis (XRD) of fly ash as a measure of type of glass in the fly ash. The glass content in a low calcium fly ash can be determined directly by dissolving fly ash in HF acid or indirectly by deducting the glassy phase and LOI from whole fly ash and it may be difficult to conduct these tests for all the projects. Hubbard et al. [9] have defined the pozzolanic performance index (PPI) as a quantitative determination of glassy phase in low calcium fly ash. The PPI is 10 times the molar ratio of potash to alumina and given as

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Table 1
The range of parameters used for model input [4] and present study

Parameters	(K/A) * 10			CaO			LOI			Fineness		
	Min	Max	Ave.	Min	Max	Ave.	Min	Max	Ave.	Min	Max	Ave.
Brinks and Halstead [4]	0.67	1.73	1.06	1.1	11.6	4.54	1	18	7.55	2430	5355	3643
Present study	0.72	1.2	1.0	1.4	16.8	5.8	1.2	8.2	3.5	3415	4420	3913

(K/A) * 10. Sharma et al. [10] also found that there is a good correlation between the PPI and soluble silica content and they have given a semi-empirical method for assessment of lime reactivity of fly ashes based on soluble silica content and fineness. Sivapullaiah et al. [11] have also observed that there is a good correlation between compressive strength of fly ash and soluble silica content.

Keeping this in mind the correlations for type of glass and analytical lime content as suggested by Diamond [8] for different fly ashes are presented. The correlation between quantity of glass and (K/A) * 10 for different fly ashes along with the data of Hubbard et al. [9] is reviewed. As the type and amount of glass can be represented by chemical composition of fly ash, a simplified method to estimate the pozzolanic characteristics of fly ash based on chemical composition and fineness will be presented.

Though in the above analysis some factors, which affect the cement/fly ash mortar strength, have been considered still there are others which may not have been quantified; the factors like cluster of particles, which may either be due to fused glass contact

Table 2
Compressive strength of cement mortar cubes for control mortar and with different percent of fly ash replacement and curing period (data from Brinks and Halstead [4])

Sl. no.	Compressive strength (N/mm^2)														
	Control mortar			Fly ash replacement											
				10% replacement			20% replacement			35% replacement			50% replacement		
	Curing period (days)			Curing period (days)			Curing period (days)			Curing period (days)			Curing period (days)		
	28	91	365	28	91	365	28	91	365	28	91	365	28	91	365
1	35.37	43.16	48.47	32.54	39.71	47.50	29.00	40.14	49.44	23.35	36.26	47.02	18.04	32.37	42.17
2	34.61	43.85	45.23	37.38	46.04	51.11	31.84	42.54	48.40	23.19	37.27	43.87	21.81	34.64	39.35
3	35.37	43.16	48.47	33.60	44.46	50.90	32.90	43.59	54.77	26.53	40.14	51.86	24.41	38.41	47.50
4	33.37	41.37	44.40	33.04	34.34	45.74	29.37	39.30	45.74	24.03	36.82	46.62	15.35	26.06	33.75
5	35.51	42.68	46.75	33.38	42.68	50.49	31.25	41.40	52.83	24.50	38.84	51.89	19.53	32.44	45.81
6	38.34	46.40	47.78	31.82	38.51	44.92	26.84	35.27	42.05	20.70	35.27	39.66	13.42	23.20	31.54
7	36.47	43.02	44.06	32.83	39.58	43.62	28.45	37.86	44.50	23.71	36.14	41.42	16.41	28.83	40.53
8	36.47	43.02	44.06	32.10	40.87	45.82	29.54	40.44	47.14	26.99	41.73	53.31	16.41	30.12	44.94
9	33.37	41.37	44.40	33.04	41.78	46.62	27.03	36.82	46.18	18.69	28.96	40.85	15.35	28.13	38.63
10	33.37	41.37	44.40	35.04	44.27	48.40	29.03	38.47	46.62	22.03	33.92	43.07	15.35	27.72	34.19
11	35.99	44.20	48.54	29.87	40.22	44.17	24.11	35.36	43.69	17.28	28.73	37.38	11.88	22.10	31.07
12	34.61	43.85	45.23	33.57	43.41	45.68	27.69	35.96	42.52	21.81	34.20	44.33	18.34	31.57	42.07
13	33.37	41.37	44.40	33.04	41.37	44.85	25.70	35.58	41.74	17.02	27.30	33.75	11.68	20.69	26.64
14	33.99	43.37	45.64	31.27	37.30	43.36	25.49	34.26	42.45	18.70	29.92	38.80	12.24	22.12	28.30
15	33.37	41.37	44.40	30.37	40.54	45.29	24.03	33.51	41.30	16.02	26.06	35.52	9.34	16.55	27.53
16	35.99	44.20	48.54	31.31	41.99	47.08	26.63	38.01	46.60	20.52	34.47	46.60	16.92	31.82	44.66
17	32.82	38.20	40.47	30.19	38.20	43.71	27.90	38.58	46.14	21.33	32.85	40.88	14.11	24.45	34.81
18	34.68	41.65	45.09	30.17	39.56	45.09	27.40	37.48	46.90	20.12	32.48	42.84	13.87	25.40	36.98
19	33.85	39.78	43.16	29.45	39.78	44.89	26.75	35.41	41.00	19.64	29.44	37.12	12.53	20.29	30.65
20	32.82	38.20	40.47	28.23	37.05	43.31	24.62	32.47	40.47	17.72	26.74	35.62	12.47	19.86	29.55
21	34.68	41.65	45.09	25.32	33.73	36.07	20.12	27.90	31.11	11.45	18.74	23.00	6.94	13.74	18.49
22	32.82	38.20	40.47	28.23	35.91	41.69	21.33	29.79	36.83	16.74	25.97	34.40	10.17	17.19	26.71
23	33.37	40.68	45.44	29.70	37.43	42.26	22.69	29.70	36.80	15.68	24.41	32.72	9.68	17.09	23.17
24	33.37	40.68	45.44	32.37	37.83	44.53	24.03	36.61	41.80	19.69	29.70	37.26	12.35	20.75	30.44
25	38.34	46.40	47.78	28.75	38.05	34.40	27.22	34.80	38.23	18.78	26.45	31.06	9.97	18.10	23.41
26	33.37	40.68	45.44	31.37	39.87	44.53	25.36	35.80	40.89	18.02	30.10	37.71	12.35	22.78	29.08
27	35.51	42.68	46.75	30.18	33.29	42.07	23.44	30.30	39.27	15.27	23.90	30.39	9.94	17.07	21.97
28	35.99	44.20	48.54	31.31	40.66	47.08	25.19	35.80	41.26	15.84	26.96	33.49	9.36	18.12	26.70
29	33.99	43.37	45.64	29.57	38.60	45.64	24.81	33.39	41.54	18.02	26.02	34.23	11.22	19.08	26.02
30	35.99	45.78	47.78	33.11	43.49	50.65	27.71	41.66	50.17	21.60	32.51	45.87	13.32	23.35	34.88
31	35.99	45.78	47.78	30.23	38.92	44.44	22.67	32.96	37.27	15.84	26.10	33.45	9.00	16.48	22.94
32	35.99	45.78	47.78	29.87	40.29	44.44	23.03	33.42	37.75	14.40	24.26	29.15	8.28	15.57	21.02
33	35.51	42.68	46.75	32.67	39.27	44.88	24.15	29.88	40.67	14.56	23.47	28.98	9.94	17.50	22.91

or due to carbon contact [20,21]. The cluster with carbon contact may reduce the pozzolanic reactivity. Fly ash with iron cover over the cenosphere and plerosphere reduces the pozzolanic reactivity [9,21]. In certain cases fineness by air permeability correlates better to strength of cement/fly ash mortar [7,13] whereas in other cases particle size by hydrometer correlates better [4–6]. The above correlation is derived from limited data so more data and data from modern plants are required to validate the above model.

2. Fly ash data

The fly ash data from different sources were collected for analysis. Fly ash data for the study of analytical calcium content (expressed as an oxide) and hump position (2θ value) in XRD analysis were considered from [8,12,13]. The quantitative glass content data of fly ashes were taken from [9,13–17]. In the present study four Indian fly ashes (Parichha, Panki, Angul and Neyveli) of both low calcium and high calcium varieties were also considered for the above analysis. Low calcium fly ashes Parichha, Panki and Angul are characterized by 60–65% of SiO_2, 18–28% of alumina, 4–8% of iron oxide, 1–2% of CaO, and 1–8% of LOI whereas high calcium Neyveli fly ash is characterized by 25–28% of SiO_2, 27–29% of alumina, 24–28% of iron oxide, 16–18% of CaO and 1.5% of LOI. The minimum, maximum and average values for (K/A) * 10, CaO, LOI and fineness of the above fly ashes are shown in Table 1. The compressive strength of fly ash cement mortar cube as described in Brink and Halstead [4] is considered for correlation between compressive strength and chemical composition. Table 2 shows the variation of (K/A) * 10, CaO, LOI and fineness of the above fly ashes. The test specimen of 5 cm cube was made in different cement sand ratios of 1:2, 1:2.75 and 1:3 by weight with Ottawa sand. The cement is replaced with fly ash in the proportion of 10%, 20%, 35% and 50%. In the present study the compressive strength of the cube with 1:2.75 cement sand ratio is considered. The compressive strength of the cube as per ASTM standard of C-109-49 (ASTM 1949) of control mortar (with no fly ash) and mortar with fly ash replacement of different proportions at 28, 90 and 365 days of curing are shown in Table 2. The statistical analysis of least squares is used with a minimization algorithm for model fitting. The model is studied in terms of correlation coefficient (R^2) between predicted and observed compressive strength values.

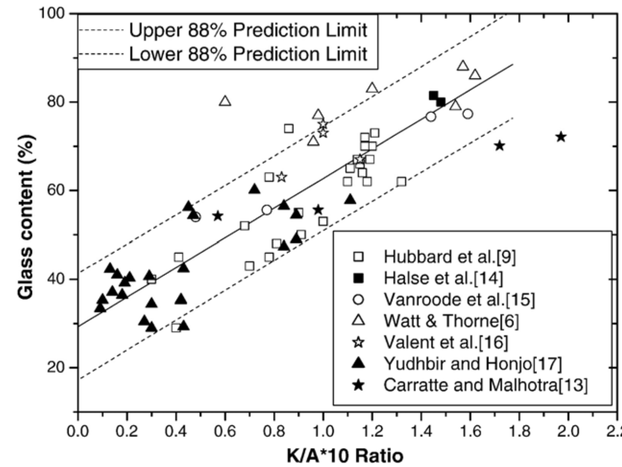

Fig. 2. Relationship between (K/A) * 10 and glass content.

3. Results and discussion

3.1. Correlation for glass type: XRD pattern for identifying amorphous phase

The location of the hump in XRD analysis depends upon the amount of analytical calcium content (expressed as an oxide) in fly ash [8]. Fig. 1 depicts the variation of hump position (2θ) values of XRD analysis of the four fly ashes used in this study along with data for other fly ashes. The increases in 2θ values indicate the change in glass type and the quantity of quartz is also reduced. High calcium Neyveli fly ash which has 16% analytical calcium content (expressed as an oxide) gives 2θ value of 28° for whole fly ash, but finer size fraction (<45 μm) indicates 2θ value

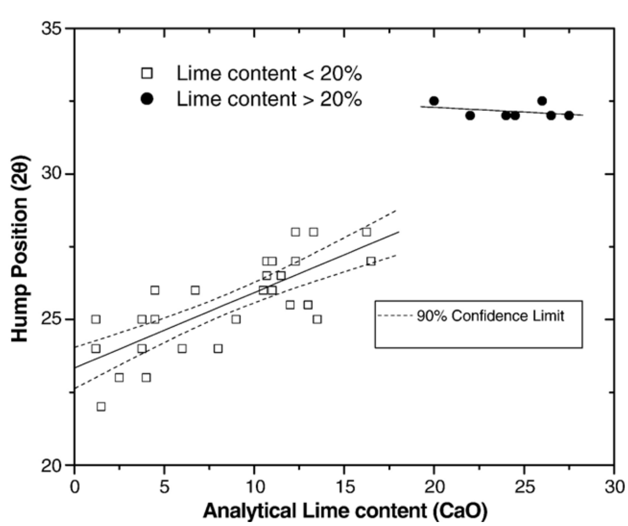

Fig. 1. Relationship between analytical lime content (expressed as an oxide) and hump position.

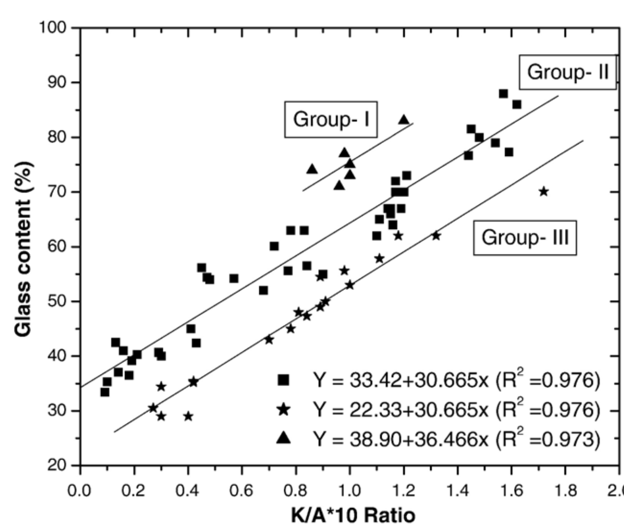

Fig. 3. Correlation between glass content and (K/A) * 10 divided into three groups.

Table 3
Regression coefficients and correlation coefficient (R^2) for different percent of fly ash replacements and testing periods

Coefficients	10% replacement			20% replacement			35% replacement			50% replacement		
	28 days	91 days	365 days	28 days	91 days	365 days	28 days	91 days	365 days	28 days	91 days	365 days
c_1	4.40	2.67	0.19	1.04	0.13	0.20	1.60	1.60	1.68	0.64	0.38	0.66
c_2	0.00	0.00	6.50	1.30	6.95	7.05	1.89	2.18	3.32	3.28	4.66	4.97
c_3	4.42	1.87	8.13	4.01	5.69	5.85	0.00	11.72	12.33	9.23	2.64	2.00
c_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00
c_5	−7.10	−3.96	−4.13	−5.84	−4.41	−5.54	−1.87	−3.34	−2.18	−7.96	−9.75	−2.36
c_6	0.21	0.32	0.37	0.34	0.47	0.47	0.69	0.65	0.85	0.35	0.42	0.89
c_7	27.39	33.45	36.67	24.35	30.00	36.78	16.62	16.39	20.35	10.41	25.99	23.63
c_8	0.14	0.19	0.15	0.22	0.23	0.24	0.31	0.44	0.44	0.45	0.37	0.45
Correlation coefficient (R^2)	0.714	0.641	0.693	0.885	0.882	0.877	0.861	0.894	0.876	0.919	0.932	0.900

of 32°. Evidence of the presence of calcium aluminate in finer fraction and alumino-silicate glass in coarser fraction was found from EDX microanalysis [18]. Thus it may be concluded that there is a variation in the type of glass content of fly ash with analytical calcium content (expressed as an oxide).

3.2. Correlation for glass quantity

Based on the relationship given by Hubbard et al. [9] Fig. 2 presents data from other low calcium fly ashes. Fig. 2 presents the correlation between the (K/A) * 10 vs. glass content for different

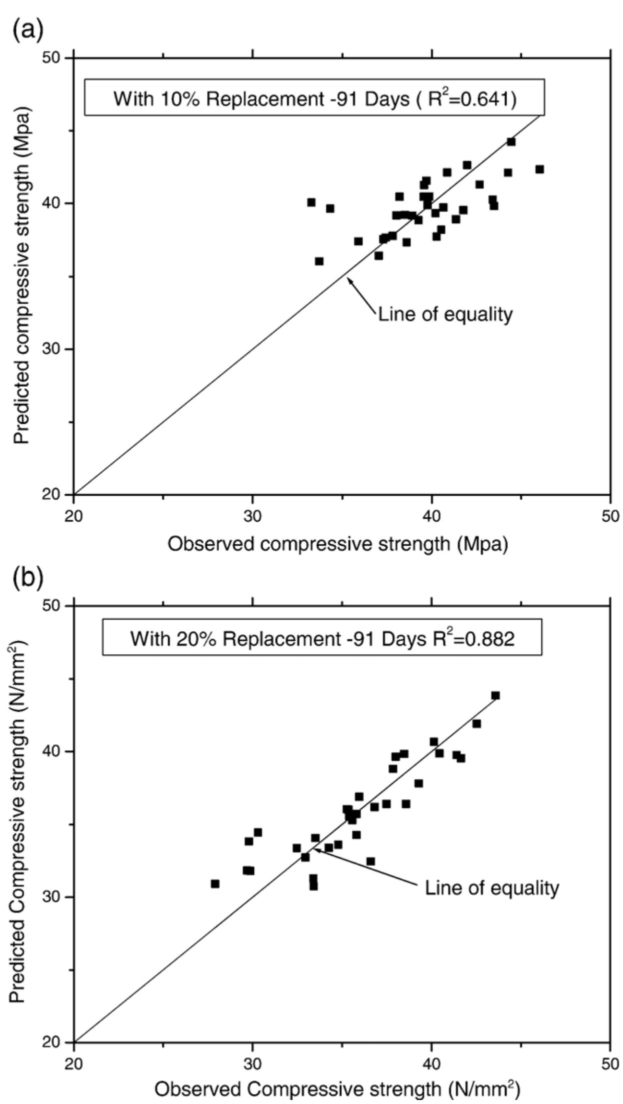

Fig. 4. Observed and predicted compressive strength at 91 days for (a) 10% fly ash replacement and (b) 20% fly ash replacement.

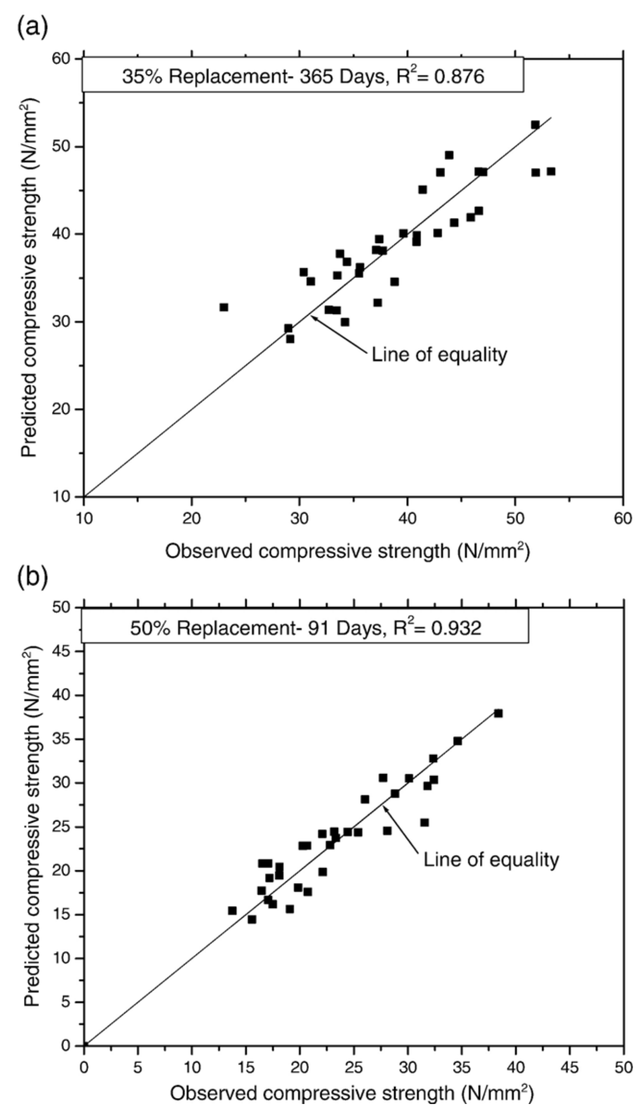

Fig. 5. Observed and predicted compressive strength at 91 days for (a) 35% fly ash replacement and (b) 50% fly ash replacement.

fly ashes. The data points include the data of Hubbard et al. [9], and other fly ashes [13–17]. As the variation of the Al_2O_3 in the fly ash ranges from 15% to 30%, the value of (K/A) * 10 mostly depends upon the percent of K_2O in fly ash, so higher K_2O value may indicate higher percent of glass content in a fly ash. Das and Yudhbir [18] observed that EDX analysis of floaters of low calcium fly ashes showed higher K value compared to whole fly ash and as the floaters in fly ash contains mostly glass phase, the above relationship seems acceptable. Fig. 2 suggests that a good correlation exists between glass content and (K/A) * 10. It has also been reported that glass content in fly ash varies up to 5% even due to fluctuation in power generation for the same coal and from same plant [19], so it appears that the above relationship may be acceptable to estimate glass content with ± 12.5% tolerance. Fig. 3 shows the above correlation in which the fly ashes may be divided into three categories; it was observed that the fly ashes having low loss on ignition (LOI) (< 1.5%) value and high specific surface (air permeability) belong to Group I and Group III represents fly ash with high LOI value (> 6.7%) for the fly ash data considered here.

3.3. Correlation for compressive strength

Dhir et al. [7] observed a good correlation of 28 days strength of fly ash concrete with LOI and fineness. Based on the relationship given by Hubbard et al. [9] and subsequent studies by Sharma et al. [10] and Sivapullaiah et al. [11], (K/A) * 10 may be an indicator of strength of fly ash concrete. However, it is difficult to predict the strength of fly ash concrete with any single property of fly ash [7]. Thus a simplified model has been proposed for prediction of compressive strength incorporating (K/A) * 10 ratio, analytical calcium content (expressed as an oxide), LOI and fineness. The model is developed for 28, 91 and 365 days compressive strength of 1:2.75 cement mortars with different percent of fly ash replacement based on data as presented in Table 2. To keep the values of model input parameters comparable the fineness is normalized by dividing with 1000. Different models were tried with combinations of the above four model input parameters using a least squares technique. It is found that Eq. (1) fits well for the above model. The coefficients of Eq. (1) are given in Table 3.

$$CS = c_1((K/A)*10)^{c_2} + c_3(CaO)^{c_4} + c_5(LOI)^{c_6} + c_7\left(\frac{\text{Fineness}}{1000}\right)^{c_8} \quad (1)$$

where CS is the compressive strength and c_1–c_8 are the coefficients determined by least squares technique.

The values of coefficients vary with percentage of fly ash replacement and curing period. It can be observed that the coefficients $c_4 \approx 0.0$ for all percent of replacement and for different curing periods. The values of analytical lime content (expressed as an oxide) in this study varies from 1.1% to 11.6%, so there may be very less variation in type of glass to effect the compressive strength. The negative values of c_5 agree with the inverse relationship between LOI and strength of fly ash cement mortar [7]. Figs. 4 and 5 show typical results of the variation between predicted and observed compressive strength of fly ash as determined from the above analysis. The predicted and observed values are compared in terms of correlation coefficient (R^2) and the results are presented in Table 3. It can be seen that R^2 is more than 0.85 for 20%, 35% and 50% fly ash replacement. It was also observed that the variation in R^2 value for different curing periods was negligible (e.g. 0.877 to 0.885 for 20% replacement). However, the R^2 value for a particular curing period (e.g. 91 days) varies from 0.641 to 0.932 as the percent replacement varies from 10% to 50%. The R^2 for 10% replacement varies from 0.64 to 0.714 depending upon the curing time period. As it can been seen from Table 3 coefficient c_2 is 0.0 for the above case and in all other cases it is more than one. So in the model effect of quantity of glassy phase (i.e. (K/A) * 10) is not considered. The other parameters are comparable with other percent of replacement. This may be the reason for poor fit with 10% replacement. So the above correlation should only be used for cement mortar with 20%–50% of fly ash replacement.

4. Conclusion

From the above study following conclusions may be drawn:

1. The relationship between compressive strength of cement fly ash mortar and chemical composition ((K/A) * 10, CaO, LOI) and fineness of fly ash was modeled by a linear power equation. The coefficients of the models as determined by least squares techniques vary with percent replacement of fly ash and curing time period.
2. A good correlation ($R^2 > 0.85$) between predicted and observed values was observed for more than 20% of fly ash replacement. There is better correlation as the percent of fly ash replacement increases. The variation of R^2 at different curing periods for a particular percent of fly ash replacement is negligible.
3. The model prediction for 10% fly ash replacement was poor.

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