

Some studies on the reaction between fly ash and lime

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Abstract. The reaction between fly ash (FA) and lime is extensively exploited for the manufacture of building bricks, blocks and aggregates. To get a better idea of this reaction, FA from different sources were mixed in different ratios with lime and compacted. The compacts were treated both by ordinary water and hydrothermal curing to promote lime bearing hydrate bond formation e.g. $\text{CaO-SiO}_2\text{-H}_2\text{O}$ (C-S-H), $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ (C-A-H) etc. The decrease in free lime content in these compacts was measured as a function of curing time and curing process. This drop in this content was correlated to the chemical composition of the fly ashes. The mathematical relationships between free lime remaining in the compacts after its maximum decrease in concentration and lime binding modulus (a ratio between the amount of added lime and the total amount of lime binding constituents present in FA) for both types of curing were developed. Further, the rate of decrease in free CaO content under both types of curing conditions was compared from kinetic study. From this study the orders of the reactions and rate constants were found out.

Keywords. Fly ash; lime; compacts; curing; kinetics.

1. Introduction

In the presence of moisture, fly ash reacts with lime at ordinary temperature and forms a compound possessing cementitious properties. The reaction between lime and fly ash produces calcium silicate hydrates, which are responsible for development of strength in fly ash–lime in the form of bricks and blocks. These bricks/blocks are suitable for use in masonry just like common burnt clay bricks at lower cost with added advantages.

Barbier (1986) studied on the possible uses of coal fly ash in the brick industry with respect to the availability and characteristics of the fly ash. Song *et al* (1996) studied the manufacture and properties of coal fly ash–clay bodies. Tsunematsu *et al* (1987) studied on the hydrothermal reactivity of fly ash with lime and gypsum with respect to the mineral composition. Kumar (2002) made a perspective study on fly ash–lime–gypsum bricks and hollow blocks for low cost housing development. Ma and Brown (1997) also studied the hydrothermal reaction of fly ash with Ca(OH)_2 and $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$. Muntcan *et al* (1987) studied on the autoclaved limestone materials with addition of fly ash. The physico-mechanical properties of the resulting siliceous limestone with 10–30% fly ash were found to be superior compared to the limestone obtained from lime and sand only. Wang *et al* (1996) studied on the reaction mechanism of fly ash–lime–water system. A model of the reaction was established.

In the present investigation the reaction between fly ash and lime in compacted form was studied by measuring the free CaO remaining in the mix after different periods of curing. The mix compositions were varied and different curing conditions were employed. The relationships between free CaO remained in the mixes after optimum curing periods and chemical composition of fly ashes were developed and the kinetic parameters of these reactions were also studied.

2. Experimental

In the present investigation twelve fly ash samples from different power plants of West Bengal (India) were collected. The ash samples were collected from the same number of ash collection hopper for all these units following procedures as laid in IS: 1528-1974, Part-VII. Particle size distributions of the ash samples were measured by sieve analyses following specifications as laid in IS: 1528-1974, Part-XIV. For the measurement of bulk density of the ash samples a fixed volume of the sample was taken in a measuring cylinder, which was tapped for sufficient number of times for thorough packing and its weight was measured. Blain's air permeability apparatus was used for measuring the surface area of the ash sample. Specific gravity of the ash samples was measured by pycnometer following specifications as laid in IS: 1528-1974, Part-IX. Chemical analyses of the ash samples were carried out following conventional technique of sodium carbonate fusion. Pulverized lime with high percentage of CaO (> 80 wt%) and considerable surface area

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(10,800 cm²/g) was used in the present investigation. The test compacts were prepared by mixing fly ash and lime in different requisite proportions in a laboratory mixer. The mixing time was 6 h for all the cases as it was found to be optimum for homogeneous mixing. The optimality was tested analysing different random proportion of the mix for SiO₂ and lime content. The homogeneous mix thus obtained was compacted with 5% moisture using a laboratory hydraulic press at different levels of compaction pressure (from 200 kg/cm² to 325 kg/cm²). The test compacts were cured under two different conditions. In water curing the test specimens were immersed in water at ambient temperature. For steam curing the samples were kept in a low-pressure autoclave at an average steam pressure and temperature of 2.5 kg/cm² and 120°C, respectively. The free lime content in the test specimens was measured chemically using the procedure described by Hanna *et al* (1938, 1939). Free lime was determined utilizing the solubility of lime in a solvent containing 1 part by volume of pure glycerol to 5 volumes of absolute alcohol. The glycerol used was anhydrous containing 99.5% glycerol with a specific gravity of 1.251 at 25°C. The alcohol used was 99% ethyl alcohol. The indicator used was 0.18 g phenolphthalein in 2160 ml of the mixed solvent. The solution used for titrating the lime was prepared by dissolving 16 g dry crystalline ammonium acetate in 1 litre of alcohol. It was standardized as follows: About 0.1 g of freshly ignited CaO was placed in a 200 ml Erlenmeyer flask and 60 ml of glycerol-ethyl alcohol solvent was added to it and the CaO was dispersed by shaking. A reflux condenser was fitted and the mixture was boiled for 5–20 min and the mix was titrated again. This process was continued until the free CaO content did not increase by more than 0.05% after 2 h of boiling.

The free lime estimation was carried out by weighing 1 g of finely ground sample into a flask, adding 60 ml of the solvent and proceeding as in the standardization of the ammonium acetate solution. The free lime content of cement was calculated as follows

$$\% \text{ CaO} = \frac{100EV}{W},$$

where, E is the equivalent of standard ammonium acetate solution in g CaO per ml, V the ml of ammonium acetate solution required and W the weight of the sample taken.

3. Results

Lime reacts with oxide components like silica, alumina and iron oxide of FA to develop different types of lime bearing phases like calcium silicate, calcium aluminate, calcium aluminosilicate etc and these phases are subsequently hydrated in the presence of water to form different hydrates. These hydrates are responsible for the development of strength in the fly ash-lime compacts (Watt and Throne 1996).

From the chemical analysis of FA samples it was observed that the total amount of silica, alumina and iron oxides varied from 70–90% in the compositions (table 1). Glassy phase content of the samples also varied between 75 and 85%. Therefore, four different FA samples were selected from the lot for carrying out experiment with total pozzolanic oxide contents of 70%, 80%, 85% and 90%, respectively (table 2). Particle size distribution of these four samples is shown in figure 1. These were likely to represent the trend in compositional variation that would affect the degree of interaction with lime. These different fly ash samples were mixed with lime in different ratios: 90 : 10, 80 : 20, 70 : 30 and 60 : 40, respectively.

3.1 Effect of compaction pressure

Compaction pressure has a distinct effect on the reaction between lime and fly ash. To study this effect fly ash and lime mixes were compacted at different pressures and the compacts were subjected to hydrothermal curing for a period of 10 h. It was observed that a sharp reduction in free CaO content took place at a compaction pressure of 200 kg/cm² and after 300 kg/cm² of compaction pressure, no significant change in free lime concentration was observed. Compaction pressure enhanced the inter-granular contacts, thus facilitating the progress of reaction by increasing the formation of more interfacial contact areas between the reactants. But a critical inter-particle gap or space is required for the formation of different interfaces and migration of the lime bearing hydrated phases formed from its origin to other places. Perhaps at higher pressures this gap is reduced which decreases the rate of reaction. Therefore, in the present investigation all the compacts were prepared with a compaction pressure of 200 kg/cm².

The depletion in free lime concentrations in the compacts was observed to occur at comparatively rapid rate initially after the onset of curing process. But after a definite curing period, lime reaction rate slowed down and no significant change in free lime concentration took place.

3.2 Curing conditions and lime binding modulus of fly ashes

Curing under ambient condition (figure 2) revealed that the maximum reduction in the concentration of free CaO takes place between 50 and 55 days and beyond this period the drop in free CaO content in the samples was not significant. In case of hydrothermal curing condition this period was observed to be 10 h (figure 3). It was also observed that within this period, the extent of reduction in free CaO content varied from 87–96% for different fly ash-lime compacts. In samples with higher proportion of fly ash, the extent of reduction in free CaO content was observed to be more. It indicates that the rate of pozzo-

Table 1. Physico-chemical properties of the ash samples.

A. Chemical composition of the ash samples (A–H)								
	A	B	C	D	E	F	G	H
	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%
SiO ₂	53.20	62.20	54.30	61.11	57.48	60.11	60.20	64.31
Al ₂ O ₃	24.50	22.50	23.30	23.80	32.60	26.55	23.90	25.60
Fe ₂ O ₃	6.20	7.60	8.30	7.20	3.48	5.84	7.80	4.45
CaO	1.70	1.56	1.42	1.35	1.98	4.83	2.06	1.03
MgO	1.30	1.01	0.68	1.35	1.06	1.25	0.70	0.97
LOI	8.40	2.40	5.80	1.14	1.22	0.63	0.35	0.58
Na ₂ O	0.30	0.21	1.43	0.30	0.28	0.22	0.51	0.60
K ₂ O	2.15	0.92	1.38	1.10	0.46	0.75	0.73	1.02
SO ₃	0.20	0.11	0.23	0.25	0.19	0.35	1.97	0.16
TiO ₂	1.03	1.40	1.45	2.10	0.94	0.78	0.42	–
Cl	0.01	–	0.02	–	0.01	–	–	–
P ₂ O ₅	0.86	–	–	–	0.24	–	–	–
B. Physical properties								
Bulk density (g/cm ³)	0.97	0.70	0.91	0.79	0.86	0.90	0.82	0.72
Specific gravity	2.50	1.98	2.21	2.11	2.14	2.43	2.12	1.98
Surface area (Blain's, cm ² /g)	5515	3960	3775	3358	6280	3025	4120	5210
A. Chemical composition of the ash samples (I–L)								
	I	J	K	L				
	Wt%	Wt%	Wt%	Wt%				
SiO ₂	62.72	61.57	52.00	56.37				
Al ₂ O ₃	29.93	26.33	23.00	26.80				
Fe ₂ O ₃	2.13	6.35	2.30	6.10				
CaO	2.33	0.94	10.50	2.65				
MgO	0.72	0.84	3.25	1.15				
LOI	0.52	1.40	2.50	2.14				
Na ₂ O	0.19	0.15	1.33	0.36				
K ₂ O	0.25	0.70	1.88	1.17				
SO ₃	0.19	0.30	0.63	0.35				
TiO ₂	0.75	2.09	1.95	1.10				
Cl	–	–	0.02	–				
P ₂ O ₅	–	0.13	–	0.31				
B. Physical properties								
Bulk density (g/cm ³)	0.77	0.82	0.84	0.91				
Specific gravity	2.10	2.12	2.12	2.41				
Surface area (Blain's, cm ² /g)	4510	2990	5172	3635				

lanic reaction between fly ash and CaO is the maximum up to a critical curing period. The anomalies observed in the intermediate regions might be due to the difference in reactivity of the FA samples, which depends on the particle size, chemical constituents, phase compositions, and the nature of the glassy phases present. Therefore, it may be inferred that the rate of formation of lime bearing hydrated phases such as C–S–H, C–A–H was maximum up to this period.

The reaction between fly ash and lime can be considered mostly as interface controlled. In presence of water vapour the lime is converted to calcium hydroxide and the formed calcium hydroxide reacts with components like silica, alumina, iron oxide and titania constituents of

Table 2. Pozzolanicity of the fly ash samples.

Fly ash	Pozzolanicity [total per cent of (SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃) constituents]
A	83.90
B	92.30
C	85.90 (FA2)
D	92.11
E	93.56
F	92.50
G	91.90 (FA3)
H	94.36
I	94.78 (FA4)
J	94.25
K	77.30 (FA1)
L	89.27

FA to form calcium silicate, calcium aluminate, calcium ferrate and calcium titanate. Formation of complex phases like calcium aluminosilicate, calcium iron aluminium silicate cannot be ruled out. These lime-bearing phases are ultimately converted into their hydrates in presence of water vapour.

As lime only reacts with the neutral and acidic components of FA for the development of lime bearing hydrated phases on curing, major constituents like silica, alumina and iron oxide may be considered responsible for binding of lime. The ratio of concentration of initial added lime and the sum total of silica, alumina and iron oxide, i.e. $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$, was designated as the lime binding modulus of fly ash.

The concentration of free CaO remaining after ~ 55 days for ordinary curing and after ~ 10 h for hydrothermal curing may be taken as more or less constant as the rate of decrease in free CaO beyond these periods was found to be practically insignificant. Therefore, a rela-

tionship between lime binding modulus and free lime remaining at these mentioned periods was attempted to develop. Such relationship may be useful in formulating lime-fly ash mix for optimum performances. The relationship between lime binding modulus and free lime content for hydrothermal curing follows an exponential fit and the equation takes the following formula,

$$y = ae^{(bx)}, \quad (1)$$

where, y is the free CaO remaining in the compacts after 10 h and x the lime binding modulus of fly ash. The values of the coefficient are $a = 0.19$ and $b = 7.36$, respectively. Standard error is 0.11 and correlation coefficient is 0.9937.

The relationship between lime binding modulus and free lime content for water curing follows 4th degree polynomial fit

$$y = a + bx + cx^2, \quad (2)$$

y = free CaO remaining in the compacts after 55 days and x the lime binding modulus of fly ash. The values of the coefficient are $a = 1.28$, $b = -13.90$, $c = 54.29$, standard error is 0.24 and correlation coefficient is 0.9848, respectively.

The equations thus developed were tested on different fly ash-lime compacts with different lime binding modulus (appendix 1). The variations in all the cases were observed within $\pm 5-6\%$. This might be related to the difference in mineralogical compositions, particularly the glassy phases in the fly ash samples.

From the relationship it is evident that the drop in free lime concentration under steam curing takes place at a faster rate compared to the natural curing process. This might be ascribed to the relatively more activation of the fly ash framework at elevated temperature and steam pressure.

To understand the nature of reaction of fly ash with lime, the order of the reaction was found out from the

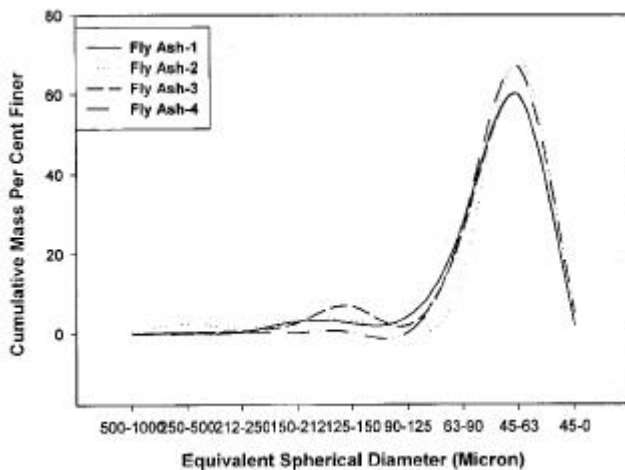


Figure 1. Particle size distribution of different fly ash samples.

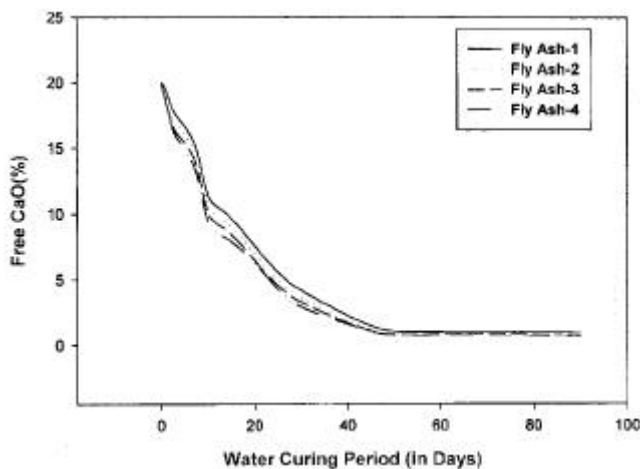


Figure 2. Variation in free CaO of fly ash-lime compacts (80 : 20) with water curing.

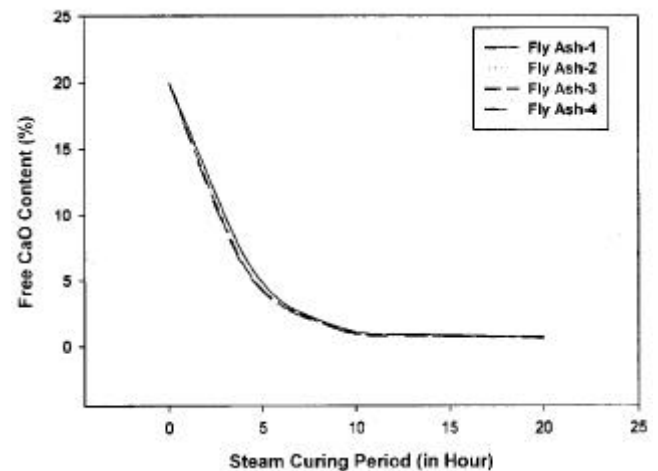


Figure 3. Variation in free CaO content of fly ash-lime compacts (80 : 20) with steam curing.

previous experiment. For the sake of simplicity in the experimental procedures here only the fly ash with the maximum lime binding modulus was taken with four different compositions of fly ash and lime, ca., 90 : 10, 80 : 20, 70 : 30 and 60 : 40.

From the standard error and correlation coefficient of linearity of all the plots for different orders it might be concluded that for the water curing process the rate of reaction between fly ash and lime is most likely to follow first order kinetics with respect to the lime concentration while in steam curing the reaction between lime and fly ash in the compacted form is most likely to follow second order reaction kinetics with respect to the lime concentration. Probably steam pressure aids in the formation of more interfaces between fly ash and lime and the thermal energy associated with the steam helps in overcoming the energy barrier of the reaction. It was also observed that with the increase in lime concentration the values of the rate constants increased.

The rate of the reaction between fly ash and lime progressively decreased with curing time. This might be related to the formation of different lime bearing hydrated phases, such as calcium silicate hydrate, calcium aluminate hydrate etc on the surface of the ash particles. These hydrated phases cover the surface of the ash particles and reduce the contact of lime and particles further, thereby reducing the rate of reaction.

4. Conclusions

From the present investigation, it appeared that

(I) The optimum compaction pressure for making class F fly ash–lime compacts by water/steam curing process is 200–250 kg/cm².

(II) For water curing process the maximum reduction in free CaO content takes place after 50–55 days, whereas, for steam curing process the same takes place after 10 h.

(III) The relationship between lime binding modulus of fly ash (CaO/SiO₂ + Al₂O₃ + Fe₂O₃) and free lime remaining after 10 h of steam curing is $y = ae^{bx}$, where y is the free CaO content and x the lime binding modulus of fly ash. The values of the coefficients are $a = 0.19$ and $b = 7.36$, respectively. Standard error is 0.11 and correlation coefficient is 0.9937.

(IV) The relationship between lime binding modulus of fly ash and free lime remaining after 55 days of water curing is $y = a + bx + cx^2$, where y = free CaO remaining in the compacts after 55 days and x the lime binding modulus of fly ash. The values of the coefficient are $a = 1.28$, $b = -13.90$, $c = 54.29$, standard error is 0.24 and correlation coefficient is 0.9848, respectively.

(V) The decrease in lime concentration with fly ash with curing time follows mostly first order kinetics and in case of steam curing it follows mostly second order kinetics with respect to the lime concentration in the mix.

Appendix:

Table A. Theoretical and experimental free lime content in samples after 10 hours of steam curing.

Lime binding modulus	Predicted free lime after 10 h of steam curing	Determined free lime after 10 h of steam curing	Variation (%)
0.217	0.938	0.987	5.3 (+)
0.32	2.00	1.932	3.4 (–)
0.224	0.987	1.05	6.4 (+)
0.357	2.64	2.79	5.9 (+)
0.212	0.903	0.927	2.7 (+)
0.424	4.3	4.08	4.9 (+)
0.112	0.43	0.447	4.1 (+)

Table B. Theoretical and experimental free CaO content in samples after 55 days of water curing.

Lime binding modulus	Predicted free lime after 55 days of water curing	Determined free lime after 55 days of water curing	Variation (%)
0.326	2.51	2.66	6.1 (+)
0.448	5.95	6.27	5.5 (+)
0.214	0.79	0.83	4.7 (+)
0.238	1.05	1.02	2.8 (–)
0.119	0.39	0.38	1.9 (–)
0.163	0.45	0.479	6.5 (+)
0.265	1.416	1.474	4.1 (+)

Table C. Standard error (S), correlation coefficient values (R) of linearity for plots of free lime concentration against curing period of different fly ash and lime ratios for different assumed orders and reaction rate constants (k) from the order.

A: Water curing				
Fly ash: lime	Order	S	R	k
9 : 1	1	0.2530	0.9607	$3.22 \times 10^{-2} \text{ day}^{-1}$
	2	1.6352	0.9059	
4 : 1	1	0.2530	0.9611	$2.6 \times 10^{-2} \text{ day}^{-1}$
	2	0.5332	0.8903	
7 : 3	1	0.1957	0.9833	$2.19 \times 10^{-2} \text{ day}^{-1}$
	2	0.1225	0.9616	
3 : 2	1	0.2148	0.9778	$2.5 \times 10^{-2} \text{ day}^{-1}$
	2	0.0774	0.9638	
B: Steam curing				
Fly ash: lime	Order	S	R	k
9 : 1	1	0.6279	0.9511	$1.0076 \text{ per cent}^{-1} \text{ hour}^{-1}$
	2	1.9093	0.9700	
	3	0.9093	0.9134	
4 : 1	1	0.9093	0.9134	$20.29 \times 10^{-2} \text{ per cent}^{-1} \text{ hour}^{-1}$
	2	0.3006	0.9783	
	3	0.7031	0.9418	
7 : 3	1	0.5029	0.9427	$9.68 \times 10^{-2} \text{ per cent}^{-1} \text{ hour}^{-1}$
	2	0.1619	0.9726	
	3	0.3183	0.9613	
3 : 2	1	0.4802	0.9471	$7.52 \times 10^{-2} \text{ per cent}^{-1} \text{ hour}^{-1}$
	2	0.1153	0.9768	
	3	0.1991	0.9586	

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