

## Effect of curing conditions and ionic additives on properties of fly ash–lime compacts

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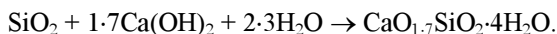
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**Abstract.** In the present work the reaction between fly ash and lime in fly ash–lime compacts under water curing and steam curing conditions was studied thoroughly in relation to the processing conditions. Fly ash from different sources were collected, characterized, mixed with lime in different ratios and compacted. The compacts were cured with water and steam separately. The reduction in the free CaO content in these compacts was measured as a function of curing time and curing process. Role of two ionic additives, FeCl<sub>3</sub> and MgCl<sub>2</sub>, on the reaction between fly ash and lime was also investigated by measuring the free CaO content. Kinetics of these reactions was studied by determining the reaction order and rate constants with respect to the free CaO content and it was observed that the curing conditions and additives affected the reaction kinetics significantly.

**Keywords.** Fly ash; free CaO; reaction kinetics; curing; additives.

### 1. Introduction

Due to its pozzolanic nature, fly ash reacts with lime in presence of moisture. The amorphous silica from the fly ash reacts with Ca(OH)<sub>2</sub> produced during hydration of the fly ash–lime compacts. This reaction produces an amorphous calcium silicate hydrate (C–S–H) as shown by Ma and Brown (1997) below



The pozzolanic reaction takes place at a slower rate and the un-reacted fly ash particles behave more or less as an inert material and serve as nuclei for precipitation of Ca(OH)<sub>2</sub> and formed C–S–H (Farry *et al* 1989; Pietersen *et al* 1990). The hydrates formed possess cementitious properties and develop strength in fly ash–lime compacts. Farry *et al* (1989) reported that the duration of the period before the onset of the pozzolanic reaction depends on the alkalinity of the pore solution. Highly alkaline solutions are more capable of solubilizing silica by breaking Si–O bonds in the glassy, silica rich portions of fly ash. Roy and Silsbee (1992) have shown that the hydroxyl ions, which can be derived from fly ash alone, are insufficient. The formation of an appropriate hydrate structure

on the surface of the fly ash particles also assist in promoting fly ash hydration. Brown (1986) showed that with the increase in pH, the silica solubility of fly ash increased. Lokken *et al* (1990) empirically demonstrated that the presence of Ca(OH)<sub>2</sub> would markedly increase the solubility of SiO<sub>2</sub> in fly ash, thereby making it available to undergo pozzolanic reaction as illustrated in the above equation. Jiang and Roy (1992) suggested that well crystallized hydrated calcium silicates may form under hydrothermal conditions and form strong networks with superior mechanical properties in fly ash–lime based compacts.

The fly ash–lime compacts are quite suitable for making building materials, like bricks and blocks. These bricks and blocks are suitable for uses in masonry applications just like common burnt clay bricks. But fly ash bricks are eco-friendly and have some techno-commercial advantages compared to burnt clay bricks. Many workers (Barbier 1986; Muntcan *et al* 1987; Tsunematsu *et al* 1987; Song *et al* 1996; Kumar 2002) studied the utilization of fly ash in building brick and block making with respect to parameters, like the nature of fly ash, processing conditions etc.

In our previous studies, we developed a relationship between residual free lime remaining in the FA–lime compacts and lime binding modulus. Lime binding

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modulus is a ratio between the amount of lime added and the total amount of lime binding constituents present in fly ash, like  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  (Basumajumdar *et al* 2005). We also observed that heat treatment also influenced the mechanical strength of the steam cured fly ash–lime compacts (Maitra *et al* 2005). We have also observed that water absorption and desorption mainly followed 1st order kinetics in case of water cured fly ash–lime compacts and followed 2nd order kinetics in the case of steam-cured fly ash lime compacts (Maitra *et al* 2005). Again, we developed an artificial neural network model for describing the interaction between fly ash and lime (Maitra *et al* 2007).

In the present investigation the interaction between fly ash and lime was studied by determining the kinetic parameters for steam curing, water curing and also in presence of two additives,  $\text{MgCl}_2$  and  $\text{FeCl}_3$ .

## 2. Experimental

In the present investigation twelve fly ash samples from different power plants of West Bengal (India) were collected. Collection of the ash samples was carried out 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 apparatus was used for measuring the surface areas of the ash samples. 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 (>80wt%) and considerable surface area ( $10,800 \text{ cm}^2/\text{g}$ ) 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 proportions of the mix for  $\text{SiO}_2$  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  $200 \text{ kg/cm}^2$  to  $325 \text{ kg/cm}^2$ ). 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  $2.5 \text{ kg/cm}^2$  and  $120^\circ\text{C}$ , respectively. The free lime content in the test specimens was measured following the procedure described by Swenson and Thorvaldson (1951).

## 3. Results and discussion

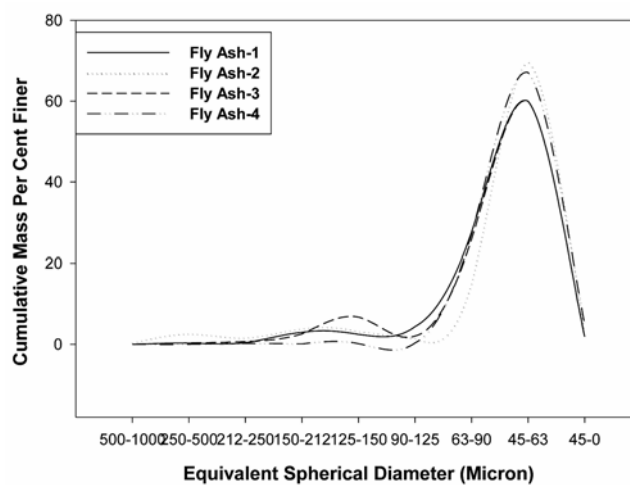
### 3.1 Selection of ash samples

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). 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. 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: 9 : 1, 4 : 1 and 7 : 3, respectively.

### 3.2 Free lime content in FA–lime compacts under different curing conditions

The reaction of lime with fly ash in the compacted masses were studied by measuring the remaining free lime concentration of the cured samples both naturally and under accelerated conditions after different curing periods. The drop in free lime concentration was observed to occur at comparatively rapid rate initially after the onset of curing process. But after a definite period the rate of drop in free lime concentration decreases and no significant change in free lime concentration took place.

Under ambient condition of curing (figure 2), it was observed that the concentration of free CaO reduced maximum between a period of 50 and 55 days and beyond this period the reduction in free CaO content in the samples was not significant. In the case of hydro-thermal curing, this period was observed to be 10 h (figure 3). It was also observed that within this period, the



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

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

	A (Wt%)	B (Wt%)	C (Wt%)	D (Wt%)	E (Wt%)	F (Wt%)	G (Wt%)	H (Wt%)
A. Chemical composition of the ash samples (A–H)								
SiO <sub>2</sub>	53.20	62.20	54.30	61.11	57.48	60.11	60.20	64.31
Al <sub>2</sub> O <sub>3</sub>	24.50	22.50	23.30	23.80	32.60	26.55	23.90	25.60
Fe <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	0.30	0.21	1.43	0.30	0.28	0.22	0.51	0.60
K <sub>2</sub> O	2.15	0.92	1.38	1.10	0.46	0.75	0.73	1.02
SO <sub>3</sub>	0.20	0.11	0.23	0.25	0.19	0.35	1.97	0.16
TiO <sub>2</sub>	1.03	1.40	1.45	2.10	0.94	0.78	0.42	–
Cl	0.01	–	0.02	–	0.01	–	–	–
P <sub>2</sub> O <sub>5</sub>	0.86	–	–	–	0.24	–	–	–
B. Physical properties								
Bulk density (g/cm <sup>3</sup> )	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 <sup>2</sup> /g)	5515	3960	3775	3358	6280	3025	4120	5210

	I (Wt%)	J (Wt%)	K (Wt%)	L (Wt%)
A. Chemical composition of ash samples (I–L)				
SiO <sub>2</sub>	62.72	61.57	52.00	56.37
Al <sub>2</sub> O <sub>3</sub>	29.93	26.33	23.00	26.80
Fe <sub>2</sub> O <sub>3</sub>	2.13	6.35	2.30	6.10
CaO	2.33	0.94	4.50	2.65
MgO	0.72	0.84	3.25	1.15
LOI	0.52	1.40	2.50	2.14
Na <sub>2</sub> O	0.19	0.15	1.33	0.36
K <sub>2</sub> O	0.25	0.70	1.88	1.17
SO <sub>3</sub>	0.19	0.30	0.63	0.35
TiO <sub>2</sub>	0.75	2.09	1.95	1.10
Cl	–	–	0.02	–
P <sub>2</sub> O <sub>5</sub>	–	0.13	–	0.31
B. Physical properties				
Bulk density (g/cm <sup>3</sup> )	0.77	0.82	0.84	0.91
Specific gravity	2.10	2.12	2.12	2.41
Surface area (Blain's, cm <sup>2</sup> /g)	4510	2990	5172	3635

reduction in free CaO content varied from 87–96% for different fly ash–lime compacts. In samples with higher proportion of fly ash, the reduction in free CaO content was observed to be more. It indicates that the rate of pozzolanic reaction between fly ash and CaO is the maximum up to a critical curing period. The anomalies observed in the intermediate regions can be related to the difference in reactivity of the FA samples. The reactivity of FA samples depends on the particle size, chemical constituents, phase compositions, and the nature of the glassy phases present in the samples. 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 the components like silica, alumina, iron oxide and titania constituents of FA to form calcium silicate, calcium aluminates, calcium ferrate and calcium titanate. Formation of complex phases like calcium aluminosilicate, calcium iron aluminium silicate is also possible. These lime-bearing phases are ultimately converted into their hydrates in presence of

water vapour. These hydrates are responsible for the development of bonding and the subsequent strength in the fly ash–lime compacts.

The reduction in free lime content was the maximum in case of 9 : 1 and was the minimum for 7 : 3 fly ash–lime compacts with different fly ashes. Therefore, free lime concentration decreased more with the increase in fly ash proportion in the lime–fly ash compacts.

3.3 Role of  $FeCl_3$  and  $MgCl_2$  on free lime content in steam cured FA–lime compacts

Reducing the energy barrier for the formation of different lime bearing phases the rate of reaction between FA and lime can be improved. It will result in further reduction in the free lime content in the FA–lime compacts. Different lime bearing phases in FA–lime compacts are generated

by the interaction of cationic calcium ion and anionic silicate–aluminate framework of the fly ash. Ions with higher ionic potential (i.e. charge/size ratio) are expected to exert more pull on the anionic framework of fly ash and to cause more activation of fly ash by making the anionic framework more polarizable. Again these additives are expected to cause more ionization of lime thereby resulting in the generation of more and more  $Ca^{2+}$  in the fly ash–lime mixture.  $MgCl_2$  and  $FeCl_3$  were used as additives in the present experimental work due to the higher ionic potential value than calcium ion (as both  $Mg^{2+}$  and  $Fe^{3+}$  have lower cationic sizes than calcium ion, the cationic sizes are 114 pm for  $Ca^{2+}$ , 86 pm for  $Mg^{2+}$  and 69 pm for  $Fe^{3+}$ ). Both these additives were added in different proportions (0.25wt% to 1wt%) in the 9 : 1 fly ash–lime composition with different fly ashes. From the results it was observed that a reduction in free CaO content in all the compositions take place after hydrothermal curing. Up to a curing period of 4 h the additives did not impart any significant influence (figure 4). But after-

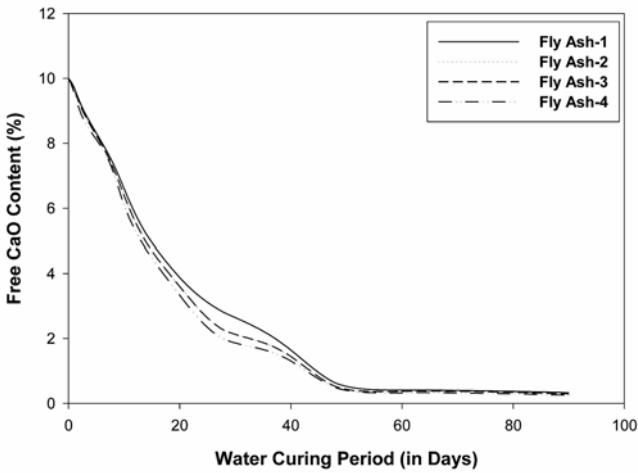


Figure 2. Variation in free CaO content in fly ash–lime (9 : 1) compacts with water curing.

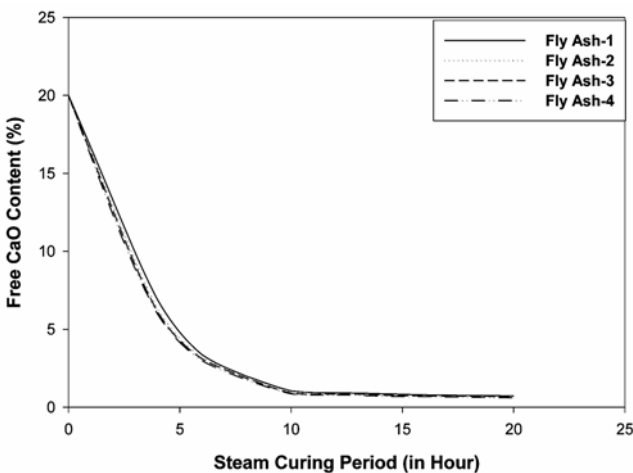


Figure 3. Variation in free CaO content of fly ash–lime compacts (4 : 1) with steam curing.

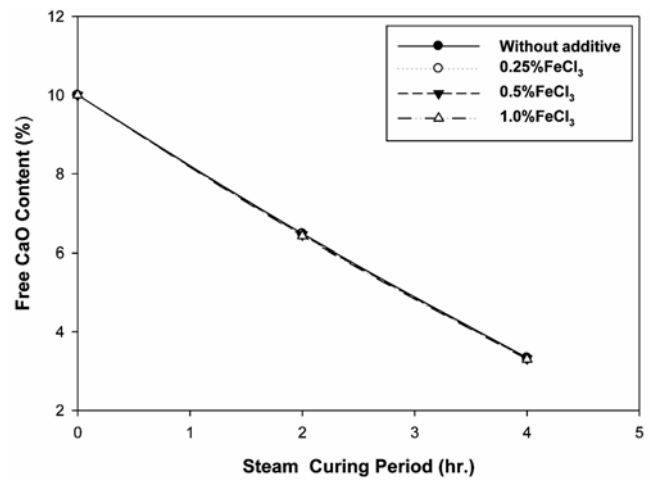


Figure 4. Variation in free CaO content with steam curing period (at the earlier stage).

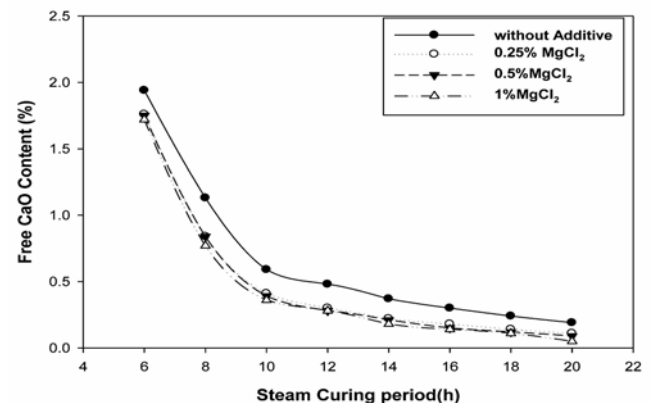


Figure 5. Variation of free CaO with steam curing period (with  $MgCl_2$  additive).

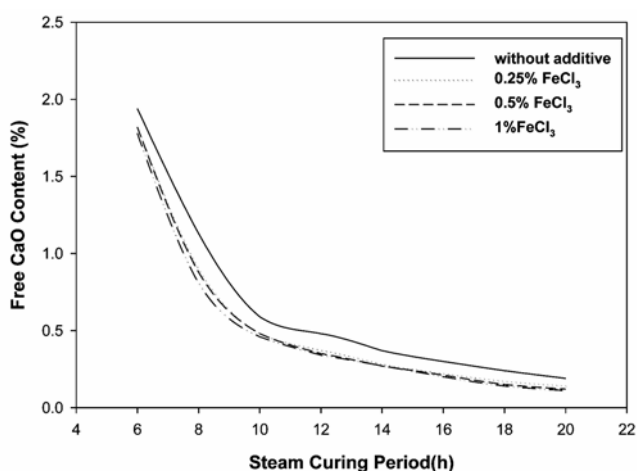
wards, the additives exhibited a significant influence (figures 5 and 6).  $MgCl_2$  produced a better result in this regard compared to  $FeCl_3$  in the reduction in free lime content as it caused about 35% more reduction in the free lime content compared to  $FeCl_3$  when added in equal proportion. This can be correlated to the more covalency in  $FeCl_3$  due to the less cationic size and higher ionic charge of  $Fe^{3+}$  compared to  $Mg^{2+}$ . From the results it was further observed that beyond a level of 0.25%, the effect of  $MgCl_2$  in reducing the free lime content was not very much significant.

### 3.4 Kinetics of reaction between FA and lime

Assuming that the decrease in lime content in FA–lime compacts with curing time follows an order based reaction kinetics where the rate of decrease in free lime concentration is proportional to any power of the initial lime concentration, the rate equation can be presented by the following equation

**Table 2.** Reaction order and reaction rate constants for reactions under various conditions.

Process	Composition (fly ash: lime)	Reaction order	Reaction rate constants ( $\times 10^{-2}$ )
Water curing	9 : 1	0.88	3.08
	8 : 2	0.94	3.72
Steam curing	9 : 1	1.69	13.17
	8 : 2	1.77	16.48
	9 : 1		
	0.25% $MgCl_2$	1.96	19.29
	0.5% $MgCl_2$	2.04	21.31
	1% $MgCl_2$	2.16	21.87
	0.25% $FeCl_3$	1.84	17.37
	0.5% $FeCl_3$	1.90	19.78
1% $FeCl_3$	1.93	20.24	



**Figure 6.** Variation in free CaO content with steam curing period (with  $FeCl_3$  additive).

$$-d[(CaO)/dt] = k [CaO]^n, \quad (1)$$

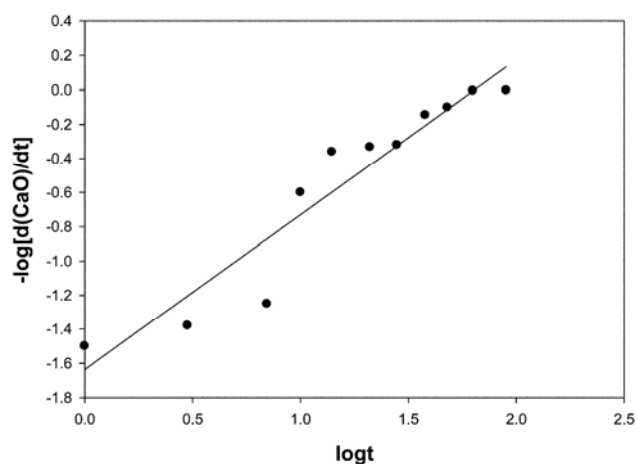
where  $k$  is the reaction rate constant and  $n$  the order of the reaction. The order of the reaction represents the relationship between the initial concentration of lime and the rate of decrease in free lime concentration with time. The reaction rate values are an indication of the speed of reaction.

Taking log of both sides

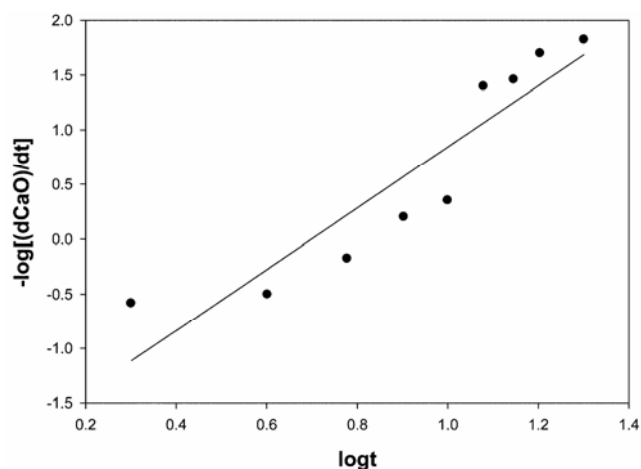
$$-\log[d(CaO)/dt] = \log k + n \log [CaO]. \quad (2)$$

So from a linear plot of the  $\log[d(CaO)/dt]$  against  $\log [CaO]$  (figures 7–10), order of the reaction and the reaction rate constant were determined from the slope and intercept of the plot. The values are given in table 2.

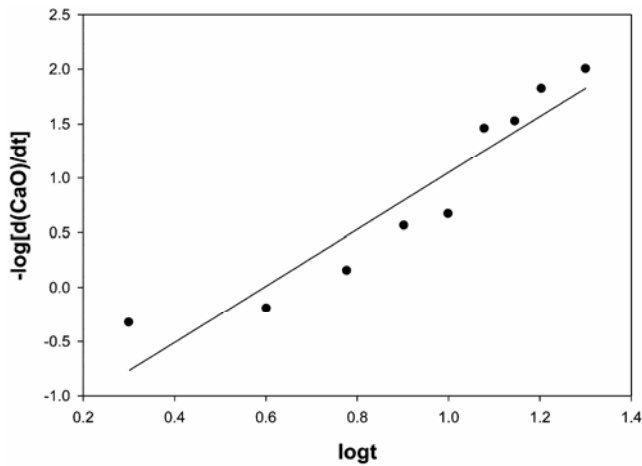
For water curing of the fly ash–lime compacts it was observed that the order of the reactions was  $<1$  and with



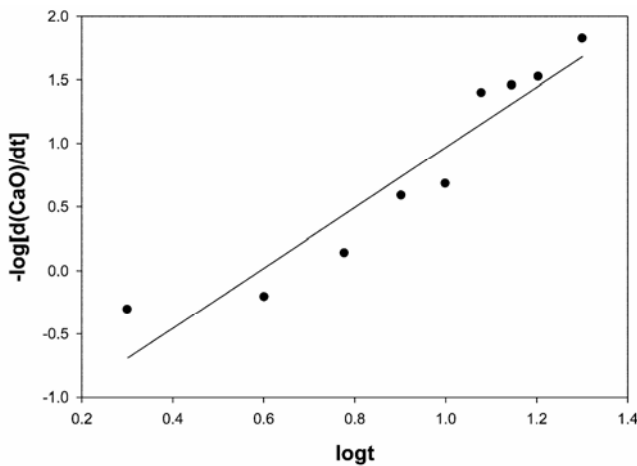
**Figure 7.** Linear plot of  $-\log[d(CaO)/dt]$  vs  $\log t$  for water curing of 4 : 1 FA–lime compacts (SE = 0.1828; C.C = 0.9515).



**Figure 8.** Linear plot of  $-\log[(dCaO)/dt]$  against  $\log(t)$  for steam curing of 4:1 FA–lime compacts (SE 0.4013; C.C 0.9218).



**Figure 9.** Linear plot of  $-\log[d(\text{CaO})/dt]$  vs  $\log t$  for steam curing of 9:1 FA-lime compacts with 0.5%  $\text{MgCl}_2$  (SE 0.3313; C.C 0.9434).



**Figure 10.** Linear plot of  $-\log[(d(\text{CaO})/dt)]$  vs  $\log t$  for steam curing of 9:1 FA-lime compacts with 0.5%  $\text{FeCl}_3$  (SE 2684; CC 0.9492).

the increase in the lime content both the order of the reactions and also the reaction rate constants increased. For steam curing the order of the reactions in all the compositions were more than 1.5. The influence of the additives on the kinetics of the reactions was apparent from the higher value of the order and the reaction rate constants. The order of the reactions almost reached 2 in presence of the additives.  $\text{MgCl}_2$  imparted slightly higher reaction rate compared to  $\text{FeCl}_3$ .

#### 4. Summary and conclusions

Fly ash and lime compacts were cured under water and hydrothermal conditions separately. The rate of decrease in free lime content in water cured compacts was maximum up to 50–55 days of curing, whereas in the case of steam curing the rate of decrease was maximum up to a curing period of 10 h.  $\text{MgCl}_2$  and  $\text{FeCl}_3$  were used as additives for the compacts made by hydrothermal curing. Up to a period of 4 h the additives exhibited no significant effect on the reaction. But afterwards the additives improved the rate of reaction between fly ash and lime, which was evident from a higher drop in free CaO content in the compacts with the additives.  $\text{MgCl}_2$  exhibited better effect in improving the rate of reaction between fly ash and lime. The order of the reaction and reaction rate constant values were more for steam cured samples compared to the water cured samples.

#### References

- Barbier U 1986 *Ind. Ital. Laterizi* **40** 53
- Basumajumdar A, Das A K, Bandyopadhyay N and Maitra S 2005 *Bull. Mater. Sci.* **28** 131
- Brown P M 1986 *J. Am. Ceram. Soc.* **73** 345
- Farry A L A, Bijen J M and de Haan Y M 1989 *Cem. Concr. Res.* **19** 235
- Jiang W and Roy D M 1992 *Am. Ceram. Soc. Bull.* **71** 642
- Kumar S 2002 *Constr. Build. Mater.* **16** 525
- Lokken R O, Shade J W and Martin P F C 1990 *Mater. Res. Soc. Symp. Proc.* **176** 23
- Ma W and Brown P W 1997 *Cem. Concr. Res.* **27** 1237
- Maitra S, Das S, Das A K and Basumajumdar A 2005 *Bull. Mater. Sci.* **28** 697
- Maitra S, Das A K and Basumajumdar A 2005 *InterCeram* **54** 4749
- Maitra S, Bandyopadhyay N and Das A 2007 *J. Am. Ceram. Soc.* **903** 712
- Muntcan M, Paul F and Haret B 1987 *Mater. Constr.* **17** 226
- Pietersen H S, Farry A L A and Bijen J M 1990 *Mater. Res. Soc. Symp. Proc.* **176** 139
- Roy D M and Silsbee M R 1992 *Mater. Res. Soc. Symp. Proc.* **245** 153
- Song J T, Yun S D, Ryan D W and Han K S 1996 *J. Korean Ceram. Soc.* **33** 262
- Swenson E G and Thorvaldson T 1951 *Can. J. Chem.* **29** 140
- Tsunematsu S, Inow N and Hara N 1987 *Gypsum and Lime* **211** 362