

## Effect of heat treatment on properties of steam cured fly ash–lime compacts

S MAITRA\*, S DAS, A K DAS<sup>†</sup> and A BASUMAJUMDAR<sup>†</sup>

Government College of Engineering and Ceramic Technology, WB University of Technology, Kolkata 700 010, India

<sup>†</sup>Department of Chemical Technology, University of Calcutta, Kolkata 700 009, India

MS received 4 June 2005

**Abstract.** Four different varieties of class F fly ashes, collected from different sources from the state of West Bengal (India) were mixed with lime in 9 : 1 wt ratio, followed by compaction of the mixes. The compacts were subjected to steam curing to develop an optimum strength by the reaction between fly ash and lime. The steam cured compacts were heated at different elevated temperatures and free lime content, compressive strength, bulk density and water absorption tendency of these compacts were measured and FTIR spectral changes were studied as a function of the heating temperatures. Kinetics of thermal dehydration of the compacts was also studied from thermogravimetric measurements under non-isothermal condition to ascertain the order of dehydration process and the associated activation energy.

**Keywords.** Fly ash–lime; compacts; curing; heat treatment.

### 1. Introduction

Fly ash has a tendency to react with lime to form different lime bearing silicates/aluminates hydrates due to its pozzolanic properties. These hydrates possess cementitious properties and are responsible for the development of strength in fly ash–lime compacts, which are used as structural products, like bricks and blocks suitable for use in masonry works just like common burnt clay bricks.

Different researchers worked on the fly ash based structural products. Song *et al* (1996) studied the manufacture and properties of coal fly ash–clay bodies. They suggested that bulk substitution of coal fly ash for clay in building bricks and tiles was possible because the chemical composition of fly ash was mostly  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  and its properties were very similar to those of clays. Kumar (2002) made a perspective study on fly ash–lime–gypsum bricks and hollow blocks for low cost housing development. It was observed that these bricks and hollow blocks had sufficient strength for their use in low cost housing development. It was also observed that the hot water curing leads to a greater degree of hardening and higher strength, earlier compared to ordinary water curing. Zhu (1994) analysed effects of solidifiers (such as lime, cement, cement–lime and lime–gypsum), process parameters (including raw materials and compacting pressure) and production processes on properties of fly ash silicate products. Muntcan *et al* (1987) reported that the physico-mechanical properties of autoclaved siliceous limestone

with 10–30% fly ash was superior compared to the product obtained from lime and sand only under similar condition. Barbier (1986) studied on the possible uses of coal fly ash in brick industry with respect to the availability and characteristics of fly ash. Tsunematsu *et al* (1987) observed that in hydrothermal reaction of fly ash with lime and gypsum at 180°C a good correlation existed between  $\text{Al}/(\text{Si} + \text{Al})$  and ratio of glass phase and the yield of hydrogarnet. Ma and Brown (1997) observed that the variation in reactivity of fly ash with  $\text{Ca}(\text{OH})_2$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in hydrothermal reaction depends on the presence of  $\text{Ca}(\text{OH})_2$  or  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Wang *et al* (1996) studied on the reaction mechanism of fly ash–lime–water system and proposed a model of the reaction. Ma and Zhao (1993) developed a method for the manufacture of fired hollow blocks of fly ash with adequate mechanical strength. Liu *et al* (1994) worked on press forming of sintered hollow brick with high fly ash content and related the rate of temperature rise and highest sintering temperature to the fly ash content of the bricks. Basumajumdar *et al* (2005) developed correlation between free lime remaining in steam cured and water cured fly ash–lime compacts under equilibrium conditions with the chemical composition of fly ash.

Though, a lot of work has been done in different laboratories on the fly ash–lime compact systems, but a scanty attention has so far been paid on the thermal stability of these compacts. In the present investigation, therefore, steam cured fly ash–lime compacts were subjected to heat treatment to ascertain the thermal stability and related changes by measuring free CaO content, compressive strength, studying the FT–IR spectroscopy and

\*Author for correspondence (maitra\_s@vsnl.net)

determining the kinetic parameters under non-isothermal conditions from the DTGA studies.

## 2. Experimental

In the present investigation, four different varieties of class F fly ash samples from different power plants of West Bengal (India) were collected following IS:1528–1974, Part-VII specification. Chemical analyses of the ash samples were carried out following sodium carbonate fusion process. 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 specification IS: 1528–1974, Part-IX. All the physicochemical properties of the ash samples are given in table 1. Pulverized lime with high percentage of CaO (> 80 wt%) and considerable surface area (10,800 cm<sup>2</sup>/g) was used in the present investigation. The test compacts were prepared by mixing fly ash and lime in the weight ratios of 9 : 1 in a laboratory mixer with sufficient mixing time (6 h) to ensure thorough mixing. The mix thus obtained was compacted with 5% moisture with a hydraulic press at a pressure of 250 kg/cm<sup>2</sup> (Basumajumdar et al 2005). The test compacts were steam cured in an autoclave at an average steam pressure and temperature of 2.5 kg/cm<sup>2</sup> and 120°C for a period of 10 h, respectively (Basumajumdar et al 2005). The free lime content in the test specimens was measured chemically using the procedure described by Hanna et al (1938, 1939).

## 3. Results and discussion

Fly ash: lime in the ratio of 9 : 1 was used in the present investigation to study the possibility of the maximum utilization of fly ash. Various types of calcium silicate and calcium alumino-silicate hydrates are formed by the reaction between fly ash and lime (Watt and Thorne 1996). When the fly ash-lime compacts were subjected to elevated temperatures, water molecules associated with the structures were progressively lost depending on the binding energy of the system. This loss of water affected the physico-mechanical properties of fly ash-lime compacts. To study this effect the free lime content and compressive strength of the fly ash-lime compacts were measured as a function of heating temperature.

### 3.1 Effect of heating on free lime content

The free lime content of the fly ash-lime compacts did not change significantly up to a heating temperature of 300°C and after that it suddenly increased as evident

from figures 1 and 2. It suggested that water molecules were mostly lost up to a period of 300°C, and the calcium silicate/aluminosilicate bonds mostly remained unaffected within this temperature range. A rapid increase in the free lime concentration indicated the dissociation of calcium silicate/aluminate bonds, which probably started after a temperature of 300°C. The free lime generation in the heated masses increased from 300–450°C and after that it started to increase from a heating temperature of 500°C. Therefore, the calcium silicate hydrate of two different ranges of stability was formed in the cured fly ash-lime compacts.

### 3.2 Effect of heating on compressive strength

With heating the compressive strength increased up to a period of 250°C and after approximately 350°C, the com-

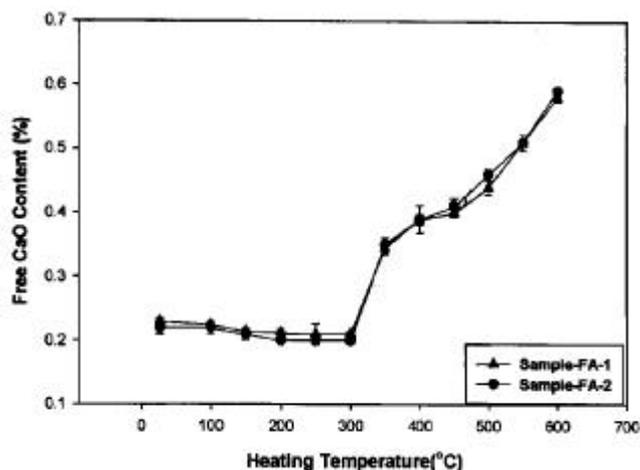


Figure 1. Effect of heating on the free CaO content of steam cured fly ash-lime compacts.

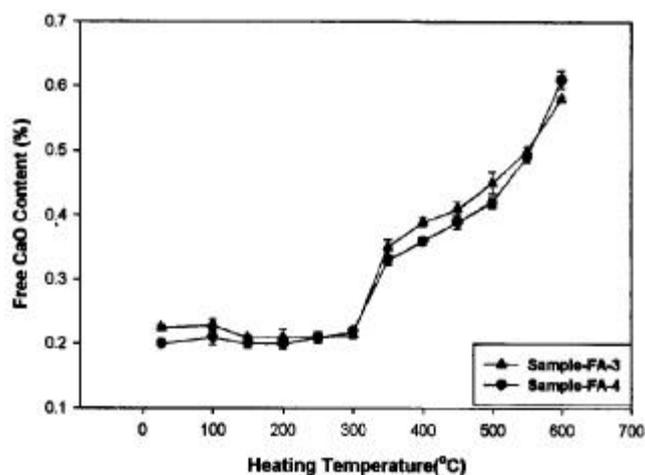


Figure 2. Effect of heating on the free CaO content of steam cured fly ash-lime compacts.

pressive strength decreased with the increase in heating temperature as evident from figures 3 and 4. Within this heating temperature, concentration of free lime generated from the lime–fly ash compacts did not change significantly, but water molecules got removed from the hydrates within this temperature range. Loss of these water molecules did not change the compressive strength of the compacts significantly. Beyond 350°C, the compressive strength decreased due to the breakage of calcium silicate/calcium aluminate hydrates.

3.3 Change in FT–IR spectroscopy of compact during heating

With the increase in the heating temperature, % transmission of the IR radiation increased (figures 5a–d). In the

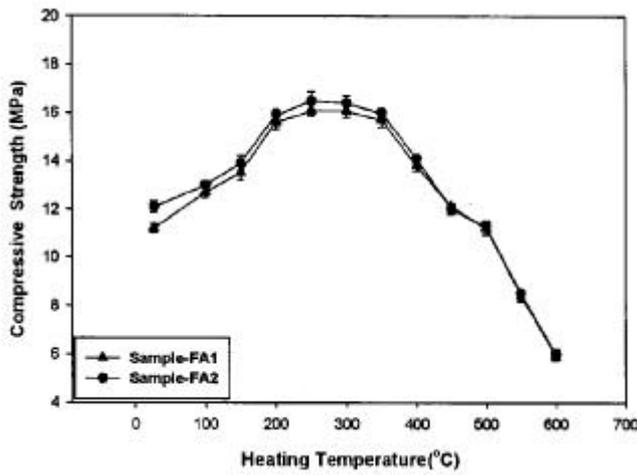


Figure 3. Effect of heating on the compressive strength of steam cured fly ash–lime compacts.

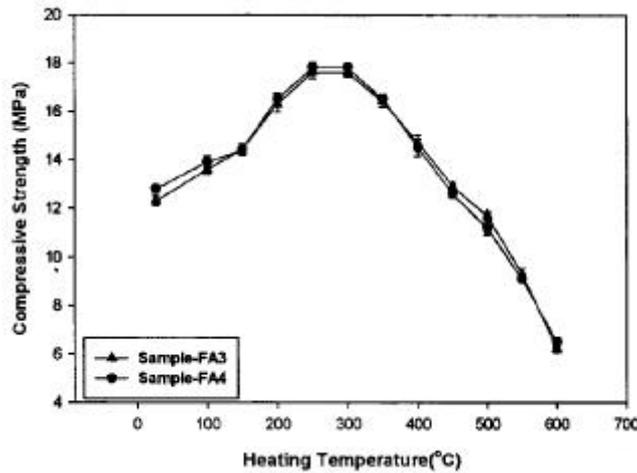


Figure 4. Effect of heating on the compressive strength of steam cured fly ash–lime compacts.

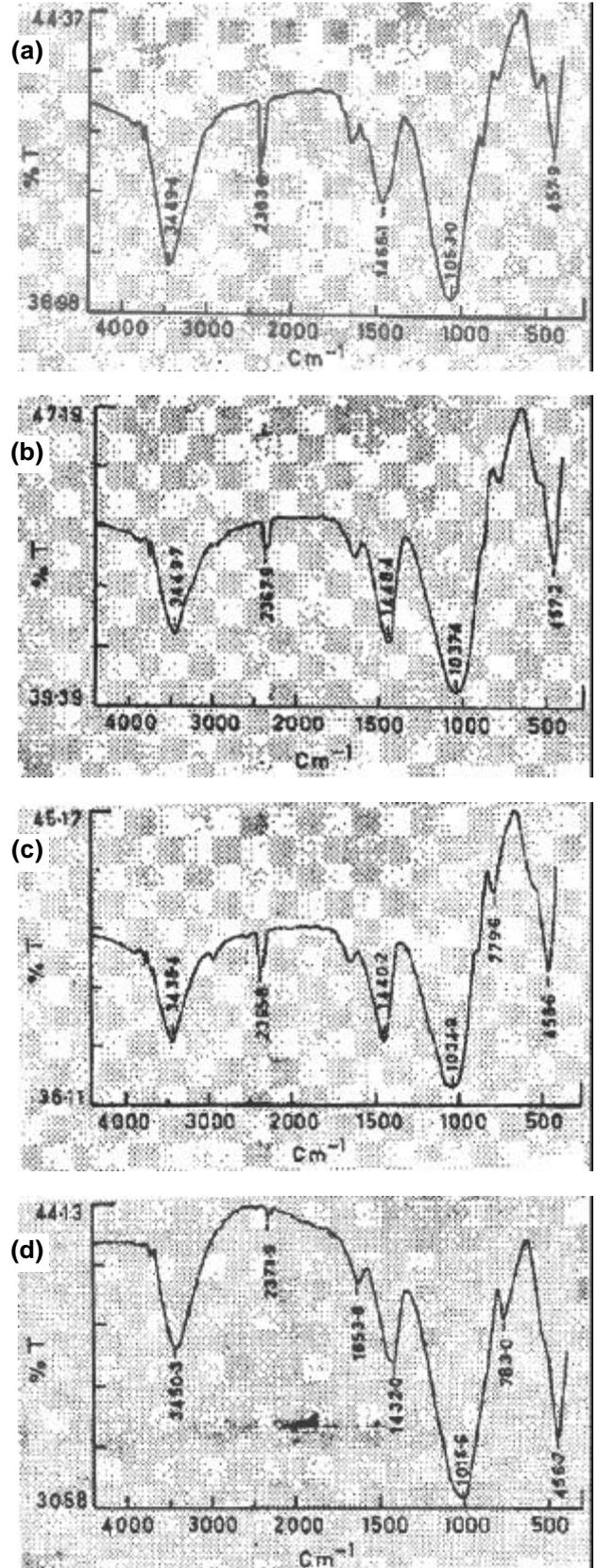


Figure 5. FTIR spectra of fly ash–lime (9 : 1) compacts after (a) steam curing, (b) after heating at 300°C, (c) after heating at 400°C and (d) after heating at 600°C.

FT-IR spectra of the samples vibration of Si-O stretching frequency decreased with the increase in heating temperature. For the sample without any heat treatment it occurred at  $1053\text{ cm}^{-1}$ , at  $1037.4\text{ cm}^{-1}$  after heating to  $300^\circ\text{C}$ , at  $1034.9\text{ cm}^{-1}$  after heating to  $400^\circ\text{C}$  and after heating to  $600^\circ\text{C}$  it was observed at  $1016.6\text{ cm}^{-1}$ . It could be due to reduced influence of water molecules (as the concentration was reduced) on the oxygen atom of Si-O bond as well as due to the increase in positive charge density as a result of the elimination of bonded water molecules. Similarly, vibration of Al-O stretching frequency more or less decreased with the increase in heating temperature. In the sample without heat treatment it was observed at  $457.9\text{ cm}^{-1}$ , at  $457.2\text{ cm}^{-1}$  after heating to  $300^\circ\text{C}$ , and at  $456.7\text{ cm}^{-1}$  after heating to  $600^\circ\text{C}$ . This also suggested the reduced pull on the Al-O bond by the water molecules with the increase in heating. O-H bending vibration was also observed to decrease with the increase

in heating temperature. In case of sample with no additive this vibration was observed at  $1466.1\text{ cm}^{-1}$ , at  $1448.4\text{ cm}^{-1}$  when heated to  $300^\circ\text{C}$ , at  $1440.2\text{ cm}^{-1}$  when heated to  $400^\circ\text{C}$  and at  $1423\text{ cm}^{-1}$  after heating to  $600^\circ\text{C}$ . Ca-O stretching vibration for free CaO was evident only after firing at  $400^\circ\text{C}$  at  $779.6\text{ cm}^{-1}$  and its frequency increased with the increase in firing temperature. -OH stretching vibration associated with Ca-O bond increased with the increase in heating temperature indicating a drop in the bonding strength of the -OH group in  $\text{Ca}(\text{OH})_2$ .

### 3.4 Kinetics of thermal dehydration of lime-fly ash hydrate compacts

At the later stage the kinetics of thermal dehydration of different lime-fly ash hydrates was studied under non-isothermal conditions. This study was expected to give an idea of the relative stability of the different hydrate phases and the nature of stability at different elevated temperatures. Non-isothermal differential thermogravimetric studies with 9 : 1 fly ash-lime compacts were carried out to determine the kinetic parameters. The dehydration was assumed to follow an arbitrary order 'n' and the kinetic parameters have been evaluated assuming various values of n. The rate equation of thermal dehydration of the hydrated phases is given by

Hydrated phases (s)  $\rightarrow$  dehydrated phases (s) + water vapour.

The rate of dehydration of the hydrated phase is given by

$$- dw/dt = kw.$$

Incorporating into this equation,  $k = A \exp(-E/RT)$  and heating rate,  $h = dT/dt$  and rearranging we get

$$[-(1/w) \cdot (dw/dt)] = A/h \cdot \exp(-E/RT).$$

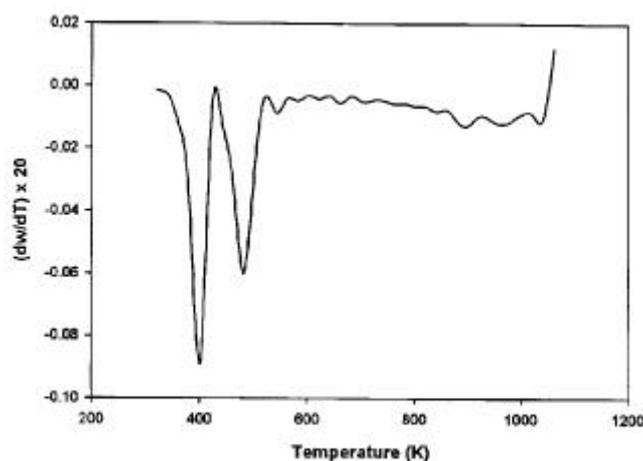


Figure 6. DTGA diagrams of fly ash-lime (9 : 1) compacts.

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

	1 Wt%	2 Wt%	3 Wt%	4 Wt%
A. Chemical compositions				
SiO <sub>2</sub>	54.30	60.20	62.72	52.00
Al <sub>2</sub> O <sub>3</sub>	23.30	23.90	29.93	23.00
Fe <sub>2</sub> O <sub>3</sub>	8.30	7.80	2.13	2.30
CaO	1.42	2.06	2.33	10.50
MgO	0.68	0.70	0.72	3.25
LOI	5.80	0.35	0.52	2.50
Na <sub>2</sub> O	1.43	0.51	0.19	1.33
K <sub>2</sub> O	1.38	0.73	0.25	1.88
SO <sub>3</sub>	0.23	1.97	0.19	0.63
TiO <sub>2</sub>	1.45	0.42	0.75	1.95
Cl	0.02	-	-	0.02
P <sub>2</sub> O <sub>5</sub>	-	-	-	-
B. Physical properties				
Bulk density (g/cm <sup>3</sup> )	0.91	0.82	0.77	0.84
Specific gravity	2.21	2.12	2.10	2.12
Surface area (Blain's, cm <sup>2</sup> /g)	3775	4120	4510	5172

The rate equation may also be expressed in terms of fractional conversion,  $X$  and reaction order,  $n$ , as follows,

$$[x = (w_o - w)/(w_o - w_a)] \\ - dx/dt = k(1-x)^n.$$

Incorporating expression of heating rate,  $h$  and rate constant,  $k$ , into the above equation, rearranging and integrating, the following equation is obtained

$$\int_0^x dx/(1-x)^n = A/h \int_0^T \exp(-E/RT)dT.$$

Among several approximate solutions the equation given by Coats and Redfern (1964) are the most commonly used and are as follows

$$\text{Ln}\{-\text{Ln}(1-x)/T^2\} = \\ \text{Ln}[AR/hE(1-2RT/E)] - E/RT \quad \text{for } n = 1.0,$$

and

$$\text{Ln}[-\text{Ln}\{1-(1-x)^{1-n}\}/(1-n)T^2] = \\ \text{Ln}[AR/hE(1-2RT/E)] - E/RT \quad \text{for } n \neq 1.0.$$

Therefore, a plot of  $\text{Ln}[-\text{Ln}(1-x)/T^2]$  vs  $1/T$  for  $n = 1.0$  and  $\text{Ln}[-\text{Ln}\{1-(1-x)^{1-n}\}/(1-n)T^2]$  vs  $1/T$  for  $n \neq 1.0$  gives us the value of  $E$  for both the methods.

The dehydration process takes place mainly at two different temperature ranges as two peaks were formed at 403 K and 533 K, respectively in the DTGA diagram (figure 6). This might be due to the difference in relative stability of the different hydrated phases formed by the interaction between lime and fly ash.

The order of the reactions and the activation energies in two different temperature ranges were calculated and the results are summarized in tables 2 and 3.

From the results it was evident that the dehydration at the first peak follows mostly 1st order reaction with an activation energy of 45.5692 kJ/mole which might be taken as the bond strength of the calcium silicate/aluminate hydrates formed in the cured fly ash–lime compacts within this temperature range. The dehydration at the second stage as indicated by the second peak followed mostly 2nd order reaction with an approximate activation energy of 57.765 kJ/mole. Therefore, dehydration at the two temperature zones takes place by different mecha-

nisms. The creation of voids and channels as a result of dehydration at the first stage accelerates the rate of dehydration at the second stage.

#### 4. Conclusions

(I) When the fly ash–lime compacts were subjected to elevated temperature, both physically and chemically absorbed molecules remaining in the compacted mass was lost progressively. Above 300°C free lime content started to increase in two different stages. This suggested different temperature stability zone of calcium silicate hydrates. The compressive strength of the compacts increased up to a temperature of 250°C, which might be ascribed to the removal of loosely held mobile water from the structure. After this temperature compressive strength of the compacts decreased with the increase in temperature.

(II) From the FTIR spectra of the fly ash–lime sample during heating it was observed that the Si–O and Al–O stretching vibration frequency decreased with the increase in heating temperature, as a result of reduction in the water molecules from the silicate hydrate and aluminate hydrates which generally caused increase in the stretching vibration frequency on the Si–O and Al–O bonds. The bending vibration of bonded water molecules progressively decreased with the increase in heating temperature. The Ca–O stretching vibration frequency of free CaO was not observed till 300°C and after that it increased with the increase in heating temperature. The stretching vibration of –OH bond associated with Ca(OH)<sub>2</sub> increased with the increase in heating temperature due to reduction in concentration of water molecules.

(III) Kinetic study under non-isothermal conditions at two different temperature ranges, 403 and 533 K, respectively (from thermogravimetry) revealed that dehydration at the first peak follows mostly 1st order reaction with an activation energy of 46.5692 kJ/mole which might be taken as the bond strength of the calcium silicate/aluminate hydrates formed in the cured fly ash–lime compacts within this temperature range. The dehydration at the second stage as indicated by the second peak followed

**Table 2.** Order of the reaction and activation energy for the dehydration reaction.

$n$	$E$ (kJ/mole)	Standard error	Correlation coefficient
0.3	23.3474	1.7889	0.9453
0.5	31.8384	1.6724	0.9474
0.85	26.9656	1.4018	0.9484
0.95	22.6456	1.2224	0.9447
1.0	46.5692	0.5417	0.9972

Temperature range: 323–483 K.

**Table 3.** Order of the reaction and activation energy for the dehydration reaction.

$n$	$E$ (kJ/mole)	Standard error	Correlation coefficient
0.3	54.5830	0.6243	0.9952
0.5	51.4794	0.5602	0.9956
0.85	43.4838	0.5007	0.9951
0.95	36.8726	0.4330	0.9949
1.0	55.7636	0.5389	0.9965
1.5	65.4195	0.4559	0.9978
1.75	60.4502	0.3851	0.9984
2.0	57.7648	0.3473	0.9986

Temperature range: 483–583 K.

mostly 2nd order reaction with an approximate activation energy of 57.7648 kJ/mole.

### References

- Barbier U 1986 *Ind. Ital. Laterizi* **40** 53  
Basumajumdar A, Das A K, Bandyopadhyaya N and Maitra S 2005 *Bull. Mater. Sci.* **28** 131  
Coats A W and Redfern J P 1964 *Nature* **201** 68  
Hanna W C, Hicks T A and Saeger G A 1938 *Bull. Am. Ceram. Soc. Test. Mater.* **94** 47  
Hanna W C, Hicks T A and Saeger G A 1939 *Proc. Am. Soc. Test. Mater.* **39** 314  
Kumar S 2002 *Construction & Building Materials* **16** 519  
Liu Q G, Fu Y J and Xiao Q G 1994 *Guisuanyan Jianzhu Zhipin* **3** 27  
Ma J R and Zhao X J 1993 *Guisuanyan Jianzhu Zhipin* **4** 33  
Ma W and Brown P W 1997 *Cem. Concr. Res.* **27** 1237  
Muntcan M, Paul F and Haret B 1987 *Mater. Constr.* **17** 226  
Song J T, Yun S D, Ryan D W and Han K S 1996 *J. Korean Ceram. Soc.* **33** 154  
Tsunematsu S, Inow N and Hara N 1987 *Gypsum and Lime* **211** 362  
Wang X, Yang N and Zhang B 1996 *J. Chinese Ceram. Soc.* **24** 137  
Watt J D and Thorne D J 1996 *J. Appl. Chem.* **15** 585  
Zhu B X 1994 *Guisuanyan Jianzhu Zhipin* **1** 12