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Kinetics of hydration of $2CaO{\cdot}SiO_2$–xMn_2O_3 system

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Abstract

Samples of dicalcium silicate using xMn_2O_3 ($x = 0.5$–5.0% by mass of C_2S) were prepared and hydrated with a view to studying the effect of concentration of Mn_2O_3 on the kinetics of hydration of pure and Mn_2O_3 doped phase. Hydrated samples of different age intervals from 3–180 days were investigated by DTA/DTG and X-ray diffraction techniques. Hydration of Mn_2O_3 doped dicalcium silicate phase indicates that the hydration increases with increase in Mn_2O_3 from 0.5 to 0.7% and then declines to become minimal at 5.0% Mn_2O_3 concentration. The degree of hydration and extent of hydration uniformly increase at all concentrations, reaching a value of 69% at 90 days age for pure C_2S and 99% at 90 days age for 0.7% Mn_2O_3 dopant. However, only 86% of hydration is observed for 0.5% Mn_2O_3 dopant at the above age.

Keywords: Thermogravimetric analysis; Dicalcium silicate; Hydration; X-ray diffraction

1. Introduction

Manganese is generally a minor constituent in cement raw materials and is mainly derived from limestone or slag [1]. Dicalcium silicate [2] exists in various polymorphic forms but the most predominant in ordinary Portland cement is β-C_2S. Dicalcium silicate phase of Portland cement is often referred as belite [3]. The stabilization of polymorphs of C_2S depends upon the type and concentration of the stabilizer [4,5]. The addition of $BaO + Mn_2O_3$ to the raw mix, has a mineralizing effect on clinker formation, and cements, thus produced show higher hydration [6,7] rates and strength development than ordinary Portland cement [8]. Savelev et al. [9] have studied the hydration activity of calcium orthosilicate and cements made from it and concluded that the fixation of C_2S in α-form by the addition of MgO and MnO_2 in clinker increases the hydration reactivity of high C_2S cements.

It has been reported from the study of the kinetics of hydration of doped C_2S that the stabilizers enhance the rate of hydration of C_2S phase if present in suitable range of doped amounts [10–14]. The present paper incorporates the systematic study of the kinetics of hydration of C_2S in the presence of 0.5–5.0% Mn_2O_3 using thermal and X-ray diffraction techniques.

2. Experimental

Calcium carbonate and quartz (>99.0% pure) in the mole ratio of $2CaO{:}SiO_2$ were mixed, ground wet with AR grade dry acetone and dried to pass 45 μ sieve. The dry mass was pelletized at a pressure of 500 kg/cm^2 for 2 min and the resulting pellets were repeatedly fired at 1450 °C till virtually no free lime (CaO_f) was left. The absence of CaO and quartz were confirmed from XRD patterns. The time and temperature of firing were fixed to simulate the burning conditions in the cement rotary kiln. Formation of dicalcium silicate, was determined by XRD. In the same way, dicalcium silicate was ground to pass 90 μ and doped with 0.5, 0.7, 1.0 and 5.0% Mn_2O_3 by weight, homogenized, and fired at 1400 °C with a retention time of 30 min and air cooled to ambient temperature. The pellets were grounded to pass 45 μ.

Pure dicalcium silicate and Mn_2O_3 doped dicalcium silicate phase were mixed with distilled water (w/s=2), sealed and kept in an incubator at 40 °C for different ages. The hydration of the paste was arrested by treating with anhydrous

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acetone and dried under vacuum for 2 h. The dried samples were grounded to pass through 90 μ sieve and stored in sealed vials. X-ray diffraction study was undertaken with Rigaku Rad Max system with wide angle goniometer having Cu Kα target, Ni filter, and graphite monochromator for establishing the mineral composition. Thermal study was performed by Netz thermal analyzer up to 1050 °C, using α-Al_2O_3 (already heated to 1500 °C) as a standard and keeping heating rate at 10 °C/min.

The amount of β-C_2S present in dicalcium silicate phase in unhydrated and hydrated system could be established by XRD and gives the degree of hydration of β-C_2S at different ages. Degree of hydration is the ratio of hydrated β-C_2S at specified age to unhydrated β-C_2S at 0 day. The formula used for degree of hydration is as follows:

$$\text{Degree of hydration} = \frac{100(\text{unhydrated } \beta\text{-C}_2\text{S at 0 day} - \beta\text{-C}_2\text{S at specified age})}{\text{unhydrated } \beta\text{-C}_2\text{S at 0 day}}$$

It can be illustrated taking 90 days of hydration of pure C_2S (Table 4)

Unhydrated β-C_2S at 90 days = 30.8%

Unhydrated β-C_2S at 0 day = 100%

$$\text{Degree of hydration} = \frac{100(100 - 30.8)}{100} = 69.2$$

Extent of hydration is the ratio of hydrated β-C_2S to unhydrated β-C_2S, taking into account of fixed water calculated from thermogravimetry. The formula used for extent of hydration is as follows:

$$\text{Extent of hydration} = \frac{100 - (\text{fixed water (\%)} + \text{unhydrated } \beta\text{-C}_2\text{S (\%) at specified age})}{100 - \text{fixed water (\%)}} \times 100$$

It can also be illustrated taking 90 days of hydration of pure C_2S (Table 4)

Fixed water = 16.1%,

unhydrated β-C_2S at 90 days = 30.8%

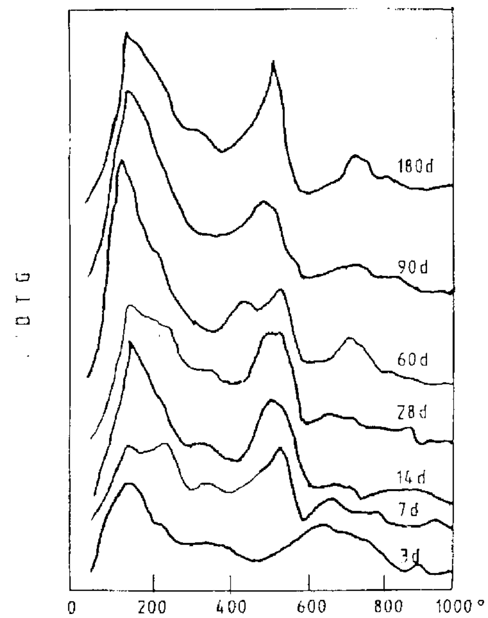

Fig. 1. DTG curves of pure hydrated C_2S at different ages.

$$\text{Extent of hydration} = \frac{100 - (16.1 + 30.8)}{100 - 16.1} = 63.29$$

Calcium silicate hydrate gel and $Ca(OH)_2$ represent fixed water and is determined by thermal gravimetric technique. Fixed water is the total water at 1000 °C minus superficial water. The amount of CSH gel formed and its composition can be calculated using fixed water and calcium hydroxide determined thermogravimetry and per cent unhydrated β-C_2S left at a given age by XRD, using 10% silicon as an internal standard. CSH gel composition is obtained by calculating the unhydrated β-C_2S in per cent by subtracting the unhydrated β-C_2S and fixed water from 100 at that particular age. The amount of CaO and H_2O present is calculated in $Ca(OH)_2$ which is obtained from the weight loss between 400–550 °C from TG curves. The amount of SiO_2 and CaO present in the hydrated C_2S is calculated. Subtracting the amount of CaO from total CaO obtained from the hydrated β-C_2S, gives the amount of CaO present in CSH. Also, subtracting water present in $Ca(OH)_2$ from fixed water to obtain the amount of H_2O present in CSH. Then dividing percentage of SiO_2, CaO and H_2O by their respective molecular weights. The ratio of CaO and H_2O with respect to SiO_2 is calculated. This gives the composition of calcium silicate

Table 1
Weight loss (%) at 1000 °C for undoped and Mn_2O_3 doped hydrated C_2S at different ages

Mn_2O_3 (%)	Weight loss (%) by mass after age of hydration (days)						
	3	7	14	28	60	90	180
0.0	6.10	9.00	11.77	12.59	13.58	16.55	12.30
0.5	4.59	7.80	11.08	11.64	13.05	16.38	15.15
0.7	7.08	11.41	14.86	16.11	15.58	16.38	17.20
1.0	7.98	8.26	12.03	13.26	15.27	14.79	15.57
5.0	–	–	–	–	–	0.55	–

hydrates. It can be illustrated taking 90 days of hydration of pure C_2S. Fixed water = 16.01, unhydrated β-C_2S = 30.8, hydrated β-C_2S = 100−(30.8 +16.01) = 53.19, $Ca(OH)_2$ = 12.55, CaO in $Ca(OH)_2$ = 9.5, H_2O in $Ca(OH)_2$ = 3.05, H_2O in CSH = 16.01−3.05 = 12.96 (Table 4).

$$\%SiO_2 \text{ in hydrated } \beta\text{-}C_2S = \frac{53.19 \times 60.09}{172.25} = 18.56\%$$

$$\%CaO \text{ in hydrated } \beta\text{-}C_2S = \frac{53.19 \times 56.08 \times 2}{172.25} = 34.63\%$$

$$CaO \text{ in CSH} = 34.63 - 9.50 = 25.13$$

SiO_2 (S)	CaO (C)	H_2O (H)
$\frac{18.56}{60.09} = 0.309$	$\frac{25.13}{56.08} = 0.448$	$\frac{12.96}{18} = 0.72$
$\frac{0.309}{0.309} = 1$	$\frac{0.448}{0.309} = 1.45$	$\frac{0.72}{0.309} = 2.33$

$C_{1.45}SH_{2.33}$.

3. Results and discussion

3.1. Thermogravimetric study

Total weight loss obtained from TG curves at 1000 °C at different concentrations for a given age and for the same concentration at different ages is given in Table 1.

The data indicate that the loss in weight in pure C_2S and 0.5% Mn_2O_3 doped hydrated C_2S increases continuously from 3 to 90 days and then declines. In case of 0.7% Mn_2O_3 doped hydrated C_2S, loss in weight increases continuously up to 28 days and then slightly decline at 60 days and again increases up to 180 days. In case of 1.0% Mn_2O_3 doped hydrated C_2S, the loss in weight increases up to 60 days and then remains almost the same up to 180 days. In case of 5.0% Mn_2O_3 doped hydrated C_2S, the loss in weight is only 0.55% at 90 days indicating poor hydration even at later ages. The loss in weight indicates per cent of combined water corresponding to the extent of hydration at various ages. It is evident that the weight loss in general increases

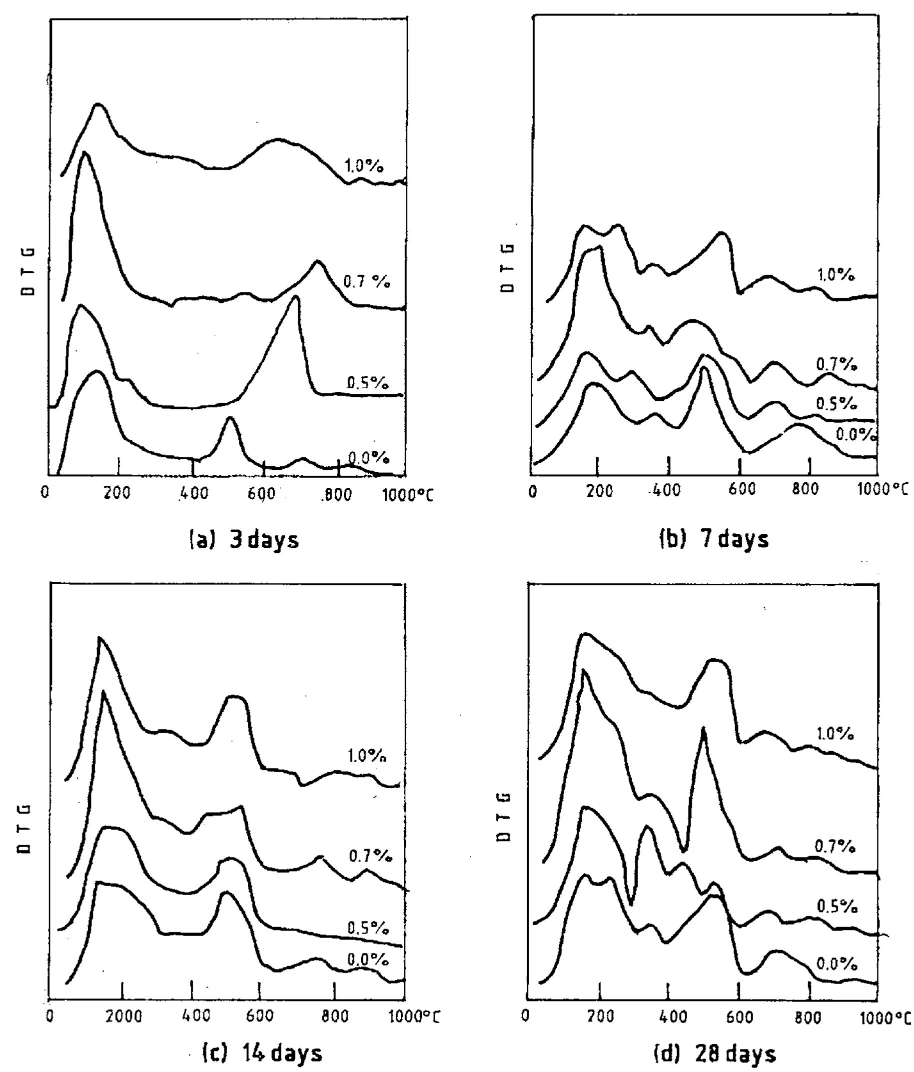

Fig. 2. DTG curves (a–g) of hydrated C_2S doped with Mn_2O_3.

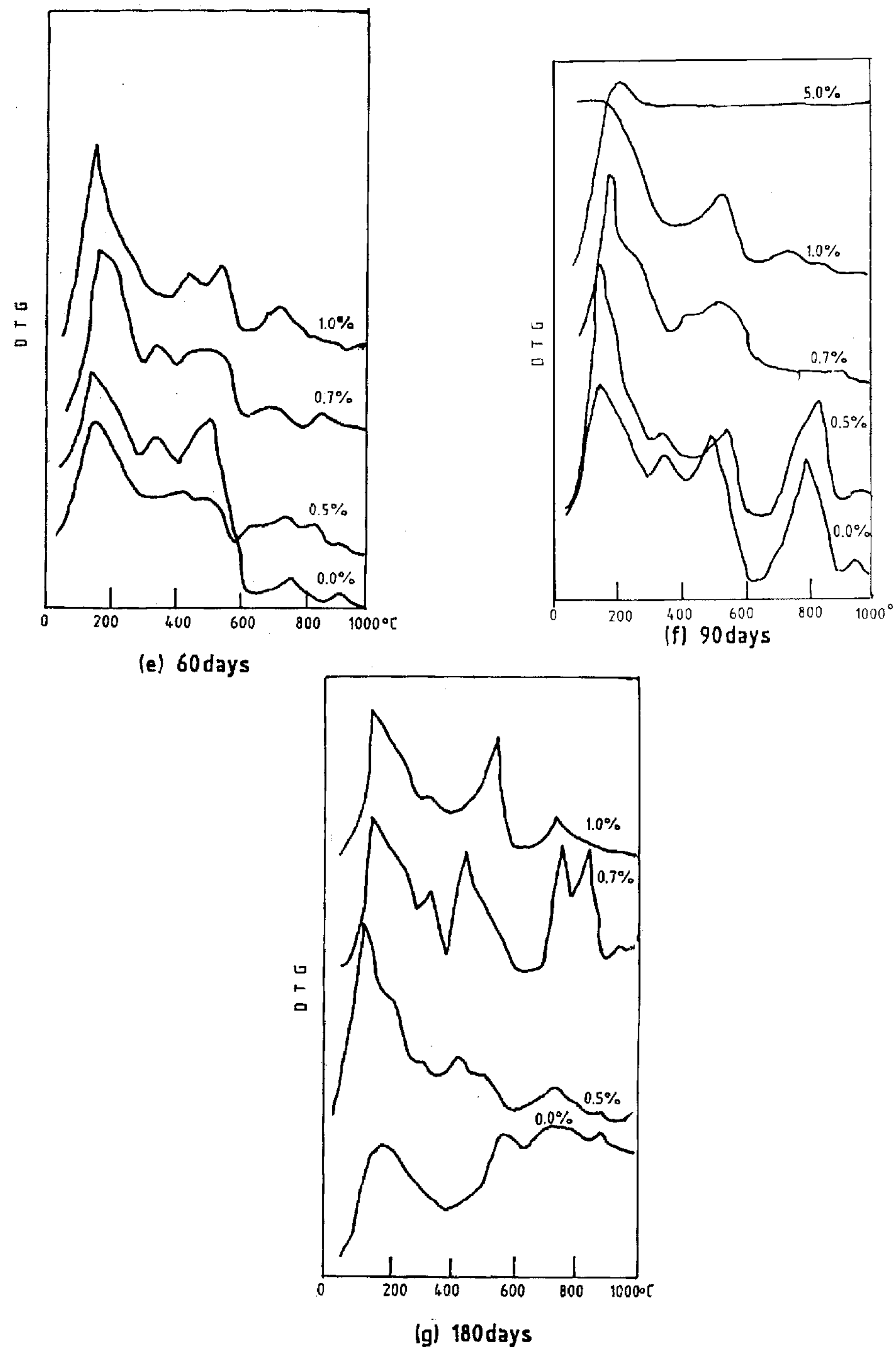

Fig. 2. (*Continued*).

with increase in age which is expected as the degree of hydration increases with age.

3.2. Differential thermogravimetric study of pure and Mn_2O_3 doped hydrated C_2S

Differential thermogravimetric study of pure and Mn_2O_3 doped hydrated C_2S were carried out for ages 3, 7, 14, 28, 60, 90, and 180 days. Differential weight loss was plotted against temperature for various ages (Fig. 1). In case of pure C_2S system, five peaks are identified with various products of hydration. Four of these peaks correspond to poorly crystallized hydrates of C_2S at temperature of 150, 350, 700–750 and 850–900 °C and fifth at around 500 °C corresponding to decomposition of calcium hydroxide. It is evident from the Fig. 1 that the peak at 850 °C is weak at 3, 7 and 14 days, becomes stronger at 28 and 60 days and disappears at 180 days. Such trends with variation here and there, are discernible for other peaks also. The shifting of peaks, appearing of new peaks and disappearance of some other peaks,

Table 2
Degree of hydration (%) in pure and Mn_2O_3 doped hydrated C_2S

Hydrated C_2S doped with Mn_2O_3 (%)	Age of hydration (days)					
	3	7	14	28	60	90
0.0	12	23	37	51	60	69
0.5	10	51	55	65	–	86
0.7	14	64	82	90	93	99

Table 3
Extent of hydration (%) in pure and Mn_2O_3 doped hydrated C_2S

Hydrated C_2S doped with Mn_2O_3 (%)	Age of hydration (days)					
	3	7	14	28	60	90
0.0	7	16	29	44	53	63
0.5	6	47	50	60	–	83
0.7	10	60	80	88	92	99

change in peak decomposition temperature, peak intensities, and the shape may be attributed to the dynamic nature of hydration. Similar trend is observed in Mn_2O_3 doped hydrated C_2S (Fig. 2). Generally, five peaks are observed corresponding to temperatures 150, 300, 550, 750, and 850 °C up to the dopant concentration of 1.0%. In case of 5.0% Mn_2O_3 doped hydrated C_2S for 90 days, only a single peak is observed.

3.3. Comparison of the hydration of pure and Mn_2O_3 doped C_2S

Comparison of the hydrated Mn_2O_3 doped C_2S with hydration rate of pure undoped C_2S indicate that the extent of hydration is higher with doped C_2S compared to undoped C_2S. Hydrated C_2S doped with Mn_2O_3 up to the dopant level of 1.0% indicates higher weight loss at the age of 180 days which at the level of 0.5% dopant, the weight loss is even higher at 90 days. The weight loss is observed to be higher from 7 to 60 days at the dopant level of 0.7% as compared to 0.5 and 1.0% dopant. At the level of 5.0% dopant, the weight loss is lower indicating poorer rate and extent of hydration. Manganese therefore, acts as retarder at 5.0% dopant concentration.

3.4. Degree of hydration

Degree of hydration (Table 2) shows a uniform increase with age for pure and 0.5 and 0.7% Mn_2O_3 doped hydrated C_2S, whereas only 69% of the pure C_2S phase is hydrated at 90 days. The degree of hydration is as high as 99% with 0.7% Mn_2O_3 doped hydrated C_2S at 90 days.

3.5. Extent of hydration

Extent of hydration uniformly increases with increase in age (Table 3). At early ages, the change is not appreciable but from 7 to 90 days, Mn_2O_3 doped hydrated C_2S has shown higher extent of hydration than the pure hydrated C_2S which means that Mn_2O_3 doped C_2S has higher extent and rate of hydration than pure C_2S. In case of pure C_2S, maximum change in extent of hydration is between 14 to 28 days while in Mn_2O_3 doped C_2S, it is from 3 to 7 days.

3.6. CSH gel compositions

In the case of undoped C_2S, the amount of CSH gel formed increases from 7.4 at 3 days to 56.6% at 90 days (Table 4). In the case of 0.5% Mn_2O_3 doped hydrated C_2S,

Table 4
Determination of CSH gel composition in pure and Mn_2O_3 doped hydrated C_2S

Mn_2O_3 doped C_2S (%)	Time (days)	Fixed water (%)	$Ca(OH)_2$ (%)	β-C_2S (%)	CSH Gel	
					Amount	Composition
0.0	3	4.81	4.53	88.1	7.4	$C_{0.51}SH_{5.02}$
	7	8.64	10.37	77.1	12.5	$C_{0.31}SH_{4.10}$
	14	11.23	12.68	63.3	24.0	$C_{0.84}SH_{3.06}$
	28	12.04	14.94	49.2	35.9	$C_{1.17}SH_{1.85}$
	60	13.02	16.63	40.5	42.9	$C_{1.17}SH_{1.85}$
	90	16.01	12.55	30.8	56.6	$C_{1.67}SH_{7.28}$
	180	10.83	9.84	21.0	69.2	$C_{1.66}SH_{2.33}$
0.5	3	4.42	0.93	90.0	9.1	$C_{1.67}SH_{1.19}$
	7	7.26	9.67	48.8	41.5	$C_{1.49}SH_{1.07}$
	14	10.54	12.72	45.0	42.3	$C_{1.34}SH_{1.60}$
	28	10.91	9.34	35.0	55.7	$C_{1.60}SH_{1.53}$
	90	19.64	13.46	13.8	72.7	$C_{1.53}SH_{2.35}$
0.7	3	4.72	1.52	85.7	12.8	$C_{1.63}SH_{4.32}$
	7	10.77	9.84	35.7	54.5	$C_{1.57}SH_{1.50}$
	14	13.77	13.42	17.6	69.0	$C_{1.57}SH_{1.47}$
	28	14.65	13.58	10.0	76.4	$C_{1.58}SH_{1.44}$
	60	14.85	14.32	6.6	79.1	$C_{1.58}SH_{1.39}$
	90	15.09	14.36	0.9	84.7	$C_{1.60}SH_{1.32}$

the amount of CSH gel formed increases form 9.1 at 3 days to 72.7 at 90 days, while in 0.7% Mn_2O_3 doped hydrated C_2S, the amount of CSH gel formed is even higher. The trend of CSH gel composition is different in pure C_2S and Mn_2O_3 doped C_2S which may be due dynamic nature of hydration process and does not achieve equilibrium at any fixed age or corresponds to any specific reaction.

4. Conclusions

Loss in weight continuously increases up to 90 days in pure C_2S and Mn_2O_3 doped hydrated C_2S indicating thereby continuous increase in hydration with age. The rate and extent of hydration is better in case of Mn_2O_3 doped hydrated C_2S than pure C_2S up to the concentration of 1.0% Mn_2O_3. 99% degree of hydration is observed in 0.7% Mn_2O_3 dopant at 90 days. At 5.0% dopant level, the situation is reversed. This shows that at higher doses, manganese acts as a retarder. Amount of calcium silicate hydrate gel increases with age in all the cases studied indicating continuous progress of hydration at all ages.

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