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Thermochimica Acta 247 (1994) 381–388

thermochimica
acta

Effect of temperature on the hydration of ordinary Portland cement in the presence of a superplasticizer

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Received 8 October 1993; accepted 24 April 1994

Abstract

The hydration of ordinary Portland cement in the presence of 2% licosuperplast superplasticizer was studied at 25, 50 and 75°C by determining the setting time, and the free lime and non-evaporable water contents. X-ray diffraction and DTG studies of the hydrated samples were also made. Results indicated that setting times are decreased with temperature. In addition, it was observed that up to three days, the extent of hydration increased with temperature, whereas after this time the values were lowest at 75°C and highest at 50°C. The mechanism of hydration is discussed.

Keywords: Cement; DTG; Hydration; Plasticizer; Superplasticizer; XRD

Cement nomenclature

OPC	ordinary Portland cement
w/s	water/solid
C	CaO
S	SiO_2
A	Al_2O_3
F	Fe_2O_3
H	H_2O
C_3S	tricalcium silicate
C_2S	dicalcium silicate

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SSDI 0040-6031(94)01867-G

C_3A	tricalcium aluminate
C_4AF	tetracalcium aluminoferrite
$C\bar{S}H_2$	gypsum
$C\bar{C}$	$CaCO_3$
E	$C_3A \cdot 3CaSO_4 \cdot 32H_2O$ (ettringite)
M	$C_3A \cdot CaSO_4 \cdot 12H_2O$ (monosulphate)
LOI	loss on ignition

1. Introduction

The hydration of Portland cement and its constituents is affected significantly by changing temperature. When certain additives are present in the hydrating cement at different temperatures, the process becomes much more complicated. Very few data are available for the hydration of ordinary Portland cement under these conditions [1–4]. This paper describes the study of the hydration of ordinary Portland cement in the presence of 2% licosuperplast superplasticizer at 25, 50 and 75°C.

2. Experimental

2.1. Materials

Ordinary Portland cement was used for the hydration studies. The oxide and mineralogical compositions are given in Table 1.

The Blain surface area was 2815 $cm^2\ g^{-1}$. Licosuperplast was used as a superplasticizer. The basic component of the superplasticizer is naphthalene formaldehyde condensate.

2.2. Methods

Preparation of hydrated samples

OPC (10 g) was weighed in different polythene bags and mixed with superplasticizer solution in water in such a way that the concentration of the superplasticizer

Table 1
Oxide composition of ordinary Portland cement

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	LOI [a]
Composition in %	62.2	22.2	6.3	2.8	2.4	1.4	2.7

Mineralogical composition of ordinary Portland cement

	C_3S	C_2S	C_3A	C_4AF
Composition in %	47.7	25.2	12.0	8.5

[a] Loss on ignition.

with reference to OPC was 2% and w/s was 0.5. The air in the bags was removed in order to avoid carbonation, and the bags sealed and kept at 25, 50 and 75°C in an incubator. The hydration was stopped at different time intervals by washing with isopropyl alcohol and ether several times. The samples were dried at 105°C in an electric oven for 1 h. The hydrated samples were then sealed in polythene bags and stored in a desiccator.

Determination of setting time

The setting time of OPC in the presence of 2% superplasticizer was determined using a Vical apparatus at 25, 50 and 75°C in the normal way [5]. The water/solid ratio varied at different temperatures, as given in Table 2.

Determination of free lime

The percentage of free lime in the hydrated samples (w/s = 0.5) was determined by the Franke extraction method [6]. Approximately 1 g of the sample was placed in a round-bottomed flask, and 40 ml of an isopropyl alcohol and acetoacetic ester mixture (in the ratio of 20:3) was added to it. The mixture was refluxed on a sand bath for approximately 1 h and then allowed to cool for about half an hour. The solution was filtered quickly through a G4 sintered glass crucible and washed with isopropyl alcohol. The filtrate was titrated with 0.1 N HCl using bromophenol blue as an indicator. At the end point, the colour of the solution changed from blue to yellow. The percent free lime was calculated using the equation: % free lime = $0.2804(V/W)$ where V is the volume of 0.1 N HCl and W the weight of the sample. The results are given in Table 3.

Non-evaporable water content W_n

Approximately 1 g of the hydrated sample (w/s = 0.5) was heated in a platinum crucible at 105°C for 1 h, cooled and weighed, and then heated at 1000°C for another hour, cooled and weighed. From the loss in weight, the non-evaporable water content was calculated. The results are given in Table 3.

Table 2
Setting time

Temperature in °C	w/s	Concentration of superplasticizer in %	Initial setting time in min	Final setting time in min
25	0.25	0	155	205
		2	153	308
50	0.30	0	40	140
		2	120	240
75	0.312	0	25	85
		2	75	130

Table 3
Free lime and non-evaporable water content, w/s = 0.5

Sample	Hydration time in days	25°C		50°C		75°C	
		f_{CaO} in %	W_n in %	f_{CaO} in %	W_n in %	f_{CaO} in %	W_n in %
1	1	1.26	4.6	2.64	13.9	2.72	15.8
2	3	2.16	12.2	2.80	16.5	3.29	17.2
3	7	3.22	17.3	3.45	18.0	1.96	16.0
4	15	3.51	17.4	3.95	19.8	1.93	16.6
5	28	4.35	17.7	5.36	21.7	1.85	16.8

DTG studies

DTG studies of hydrated samples (w/s = 0.5) were made using a PL 1000 thermogravimetric analyser from ambient temperature to 990°C. The heating rate was 10°C min^{-1}.

X-ray diffraction studies

The X-ray diffraction patterns of the hydrated samples (w/s = 0.5) were recorded at IIT Kanpur using Cu $K\alpha$ radiation.

3. Results and discussion

Table 2 shows that both the initial and final setting times increase in the presence of 2% superplasticizer, and that the values decrease with increasing temperature. It has already been reported that setting time decreases with rising temperature up to 30°C, but beyond this there is no effect [5]. However, the present results show that setting times decrease even up to 75°C (the temperature of the experiment) although the decrease is not linear with temperature. Furthermore, as the temperature is increased, the water/solid ratio for making a normal paste increases. It appears that as the temperature increases, the amount of hydration products responsible for the setting process also increases. The increase in hydration may require more water and the presence of more hydration products may decrease setting times. As a result, the setting times are decreased with the rise in temperature (25–75°C).

The free lime content in the hydrated samples in the presence of superplasticizer increased with time at 25 and 50°C and the values are higher at 50°C. This simply shows that the extent of hydration is higher at higher temperatures (50°C). Also, the values are higher after 1 and 3 days of hydration at 75°C than those for the same times at 25 and 50°C, and in the latter stages of hydration, i.e. 7, 15, and 28 days, the values decrease, becoming much lower than the corresponding values at lower temperature (25 and 50°C). It is found that at 75°C up to 3 days of hydration, the amount of calcium hydroxide formed is significantly higher as a result of increased hydration. The larger amounts of hydration products formed

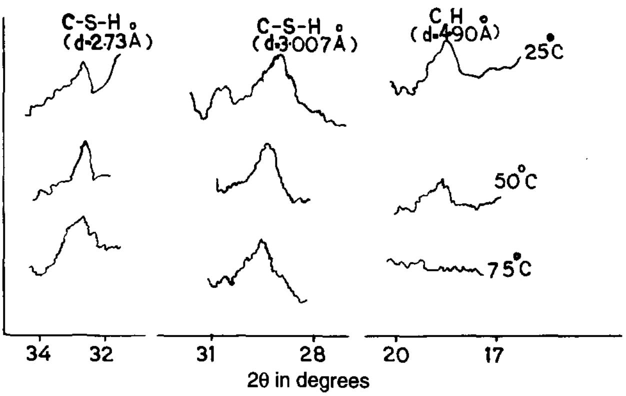

Fig. 1. X-ray diffraction patterns of samples hydrated for 90 days in the presence of 2% superplasticizer.

may cover the unhydrated grains and further hydration may decrease. As the amount of hydration products increases, the $Ca(OH)_2$ diffuses into the interlayer spacing and intersperses with the C–S–H. This process may depend on the temperature of hydration, the amount of hydration products and the time of hydration. Singh et al. [7] have found that licosuperplast solution dissolves $Ca(OH)_2$ with a colour change. Spectroscopic studies have shown that there is some sort of chemical interaction between $Ca(OH)_2$ and licosuperplast which may increase with temperature and, as a result, there may be very little free $Ca(OH)_2$ at 75°C.

X-ray diffraction patterns of samples hydrated for 90 days ($w/s = 0.5$) in the presence of 2% superplasticizer are shown in Fig. 1. The amount of $Ca(OH)_2$ formed at 75°C ($d = 4.90$ Å) is almost negligible, whereas at 25 and 50°C the quantity is appreciable but not substantial. It appears that when larger amounts of $Ca(OH)_2$ are formed, it may be mostly in the amorphous state which cannot be detected by XRD [8]. However, the extraction method also indicates that less $Ca(OH)_2$ is formed at 75°C. More C_3S is hydrated ($d = 2.73$ Å) at 50°C than at 25 and 75°C, and the extent of hydration is lowest at 75°C. At 90 days of hydration, crystalline C–S–H ($d = 3.007$ Å) is also formed and the amount is lowest at 75°C. It appears that the formation of C–S–H is also affected by the presence of superplasticizer at 75°C.

The variation of non-evaporable water contents in the presence of superplasticizer increases with time at 25 and 50°C and the values are higher at 50°C. This is simply a result of the higher degree of hydration. However, the values at 75°C are higher up to 3 days of hydration, and after that the values are lower as compared to the corresponding times at 25 and 50°C. Verbeck and Helmuth [9] suggested that rapid hydration leads to encapsulation of the cement grains by product layers of low porosity. It appears that at 75°C, because of encapsulation of cement grains by the hydration products up to 3 days, the hydration may become slow. It is also possible that the nature of the hydration products may change and some of the products may enter into the interlayer spacing of the other products

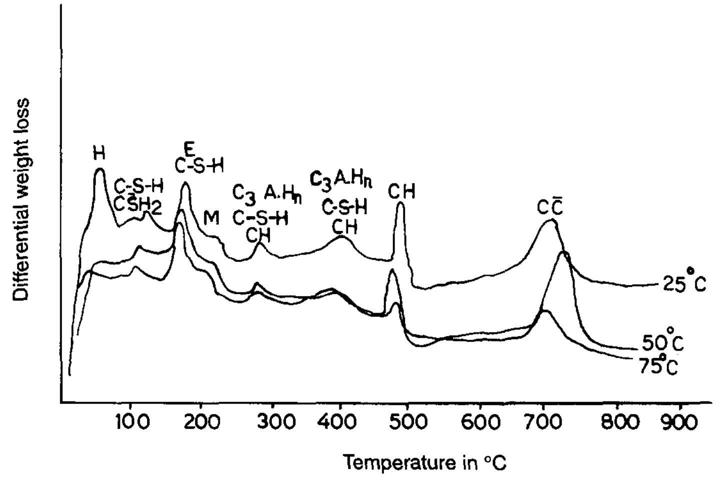

Fig. 2. DTG curves of OPC hydrated in the presence of 2% superplasticizer for 28 days at 25, 50 and 75°C.

and the dehydration process may be very slow. Furthermore, because of increased chemical interaction between superplasticizer and $Ca(OH)_2$ at 75°C, there is very little free calcium hydroxide and as a result the values of W_n are lower. It is also reported [1] that as the temperature is increased, the main peak of the heat evolution curves is shifted to shorter reaction times. The pattern of peaks also changes implying that the reactions of the different phases are affected in different ways. Ghorab et al. [10] also found that strength formation is significantly reduced at 70°C and above, and that even at 60°C ettringite tends to be replaced by monosulphate. These changes may affect the values of non-evaporable water contents at higher temperatures.

DTG curves of OPC hydrated in the presence of 2% superplasticizer for 28 days at 25, 50, and 75°C are given in Fig. 2. The curves for all three samples are similar, indicating that the hydration products are almost identical. The only difference is in the peak areas at different temperatures. The peaks between 44 and 66°C are due to removal of adsorbed water which is much higher for the paste hydrated at 25°C and much lower for the paste hydrated at 50 and 75°C. The peaks between 101 and 120°C are due to decomposition of $C\bar{S}H_2$ and C–S–H. The peaks between 166 and 172°C are due to decomposition of C–S–H and ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$). The peaks between 204 and 223°C are due to decomposition of monosulphate ($C_3A \cdot CaSO_4 \cdot 12H_2O$). The peaks between 269 and 277°C and between 238 and 396°C may be due to the decomposition of C–S–H and the hydrated aluminate phases as well as due to amorphous C–H. The peaks between 475 and 496°C are primarily due to decomposition of CH^-. However, there are two sources of error in the estimation of CH^- in this temperature range. The decomposition of AF_m may also occur in this temperature range and the decomposition of CH^- may not be complete. The peaks for the decomposition of CH^- decreased with temperature and are minimum for the paste hydrated at 75°C. This sugegsts that a smaller amount of CH^- is decomposed at 75°C. This may be due to the following reasons:

(1) Less CH^- is formed, as discussed above.

(2) More CH^- may have migrated deep into the C–S–H lattice. It has been reported that this process is facilitated in the presence of admixtures [11].

(3) A larger amount of $Ca(OH)_2$ reacts with superplasticizer and free calcium hydroxide is diminished.

The peaks between 699 and 713°C are due to (i) decomposition of $CaCO_3$ formed during hydration as a result of carbonation of $Ca(OH)_2$ and C–S–H; and (ii) the final stages of the dehydration of C–S–H and aluminate phases. The peak areas for the paste hydrated at 75°C are much lower. This may be due to the fact that a lower amount of CH^- is present at this temperature and as a result the amount of $CaCO_3$ formed is smaller.

4. Conclusions

From the results it may be concluded that

(1) In the presence of superplasticizer, the setting times decrease from 25 to 75°C and the w/s ratio is increased.

(2) Free lime and non-evaporable water contents are increased from 25 to 50°C at all hydration times (up to 90 days). At 75°C, the values are higher up to 3 days but after this the values are much lower.

(3) X-ray diffraction and DTG studies indicate that at 75°C and 90 days, the amount of calcium hydroxide is negligible.

(4) Calcium hydroxide interacts chemically with the superplasticizer and the interaction is increased with temperature. As a result the amount of free $Ca(OH)_2$ in the hydrated sample (90 days) at 75°C is negligible. This might also be due to diffusion of $Ca(OH)_2$ into the interlayer spacings of the other hydration products.

Acknowledgements

The authors thank Professor S. Giri, Head, Chemistry Department, Gorakhpur University, Gorakhpur for providing laboratory facilities. Financial support from CSIR, New Delhi is gratefully acknowledged.

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