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THERMAL MONITORING OF FLASH SETTING IN PORTLAND CEMENT CLINKERS

JAVED I. BHATTY

Mineral Resources Research Center, 56 East River Road, University of Minnesota, Minneapolis, MN 55455 (U.S.A.)

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ABSTRACT

Flash setting behavior of a Type I Portland cement clinker with and without the presence of gypsum (calcium sulphate dihydrate) used as a set regulator has been studied by using thermogravimetry and differential thermal analyzing techniques. The effect of sulphate addition in controlling the flash set is monitored over the critical initial period of hydration and its consequences on the ultimate setting properties of clinker are discussed. A correlation between degree of hydration and flash setting, caused mainly by a rapid reaction between water and the phase tricalcium aluminate present in the clinker, is also established by estimating the amount of chemically bound water and free calcium hydroxide incorporated in the hydration products formed from clinker–water and clinker–calcium sulphate–water systems. It is shown that the addition of sulphate ions effectively controls the early clinker hydration possibly by reacting with tricalcium aluminate to form ettringite that shields it from further rapid hydration.

INTRODUCTION

The phenomenon of set regulation in a hydrating cement paste containing gypsum is well known. Gypsum is ground with clinker to avoid flash setting during water–cement mixing. When ground cement clinker is mixed alone with water the phase tricalcium aluminate (C_3A) * in the clinker undergoes a rapid hydration reaction to form calcium aluminate hydrate (C_4AH_{13}) which results in a marked increase in irreversible stiffening generally referred to as flash setting [1]. The reaction takes place in the presence of calcium hydroxide, also formed during hydration, according to the following equation.

$$C_3A + 12H + CH \rightarrow C_4AH_{13} \qquad (1)$$

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* In cement chemistry notation: $C = CaO$; $A = Al_2O_3$; $H = H_2O$; $S = SiO_2$; $F = Fe_2O_3$; $\bar{S} = SO_3$.

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With the presence of gypsum in the solution, however, an immediate reaction with C_4AH_{13} takes place to form ettringite which deposits on the surface of C_3A and inhibits further flash setting. The reaction occurs as follows:

$$C_4AH_{13} + 3C\bar{S}H_2 + 14H \rightarrow \underset{\text{(ettringite)}}{C_6A\bar{S}_3H_{32}} + CH \qquad (2)$$

The underlying process of clinker hydration in presence of gypsum is of vital technical importance because of its influence on the initial rheological and subsequent setting behavior of cement pastes. Present investigations have therefore been aimed to elucidate further the effects of gypsum in controlling clinker hydration. Both DTA and TGA techniques, because of their ability to easily detect chemical changes, have been used to monitor the hydration process [2–11]. The systems under investigation are clinker–water and clinker–gypsum–water, which are hydrated under identical conditions for up to 24 h and their degrees of hydration are estimated in terms of free calcium hydroxide and bound water formed in the hydration products. Particular attention is given to the initial part of hydration (up to 1 h or so) when the process of rapid C_3A hydration and the counter set regulation by sulphate ions are effective.

MATERIALS AND METHODS

Ordinary Portland cement (type I) clinker was provided by the Northwestern States Portland Cement Company, Mason City, Iowa. The clinker was kept in air-tight containers to avoid any surface conversions suspected of atmospheric carbonation. Approximate composition limits [12] of the clinkers are given in Table 1. The clinker was divided into two identical portions. One portion was ground as received in a rod mill to a Blaine fineness of 3500, whereas the other portion was mixed with 4% gypsum and also ground to 3500 Blaine fineness. Representative samples from each portion were then individually mixed with deionized water (50 wt.%) and allowed to hydrate for durations of 30 min, 1 h, 3 h, 5 h and 24 h. After each

TABLE 1

Approximate composition limits of the cement clinker [6]

Compound composition	Weight (%)
C_3S	41–60
C_2S	20–41
C_3A	2–10
C_4AF	8–13

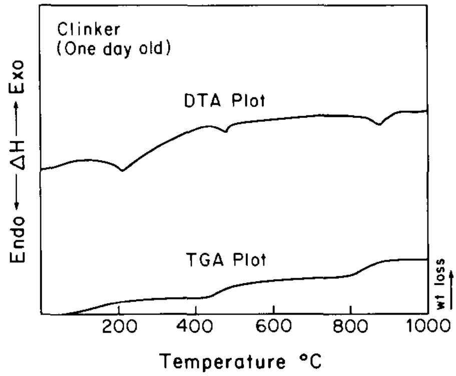

Fig. 1. Typical DTA and TGA plots for the Portland cement clinker hydrated for one day without the presence of gypsum (w/s ratio = 0.5).

duration the samples were washed with methanol to wash out loose moisture and then air dried. The samples were then subjected to oven drying at 105 ± 2 °C followed by simultaneous DTA and TGA testing conducted in a Stanton Redcroft thermobalance equipped with temperature, heat and weight recordings. The experiments were run from ambient to 1000 °C in a nitrogen atmosphere. The sample heating rate was kept at 20 °C min^{-1}.

RESULTS AND DISCUSSION

Typical DTA and TGA plots of clinker–water and clinker–gypsum–water systems show three main regions of decomposition, i.e. dehydration region between 105 and 440 °C, dehydroxylation region between 440 and 580 °C and decarbonation region between 580 and 1000 °C. Their corresponding endothermic peaks and associated weight losses as recorded in the thermal plots are shown in Figs. 1 and 2. Estimations of weight losses due to free and chemically bound water, and free calcium hydroxide incorporated in the hydration products along with respective degrees of hydration for each system are given in Tables 2 and 3.

The higher values of bound water in the clinker–water system, as compared to those of the clinker–gypsum–water system hydrating under identical conditions, reveal that the clinker hydrates faster thus giving higher and increasing degrees of hydration. It may be postulated that the faster hydrating rates of the clinker–water systems correspond to their flash setting behavior, whereas the slower hydration rates of clinker–gypsum–water systems is the result of controlled setting caused by gypsum addition.

In flash setting the irreversible stiffening [1] in the cement paste takes place earlier on in the hydration process and is primarily due to the rapid reaction between C_3A and water in the presence of calcium hydroxide to

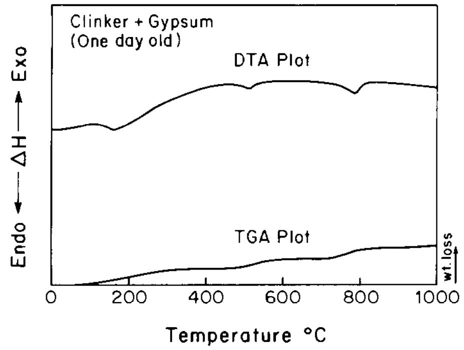

Fig. 2. Typical DTA and TGA plots for the clinker hydrated for one day in the presence of gypsum (w/s ratio = 0.5).

form C_4AH_{13} according to eqn. (1). In the presence of gypsum a reaction between calcium sulphate and the calcium aluminate hydrate (C_4AH_{13}) immediately follows to form ettringite according to eqn. (2). Ettringite is insoluble in alkaline calcium sulphate solution and is deposited on the hydrating C_3A providing a protective layer against further flash setting.

In the present investigation of the clinker–gypsum–water system the virtually stable hydration of up to 1 h or so is due to set regulation caused

TABLE 2

Weight losses during various decomposition regions in the clinker–water and clinker–gypsum–water systems

Curing time	Weight losses (%) during			Actual water loss (Ldh + Ldx)	Ignition loss (Ldh + Ldx + Ldc)
	Dehydration 105–440 °C (Ldh)	Dehydroxylation 440–580 °C (Ldx)	Decarbonation 580–1000 °C (Ldc)		
Clinker – water					
5 min	0.9	0.2	0.6	1.1	1.7
30 min	1.3	0.3	0.6	1.6	2.2
1 h	1.3	0.4	0.6	1.7	2.3
2 h	1.6	0.6	0.8	2.2	3.0
5 h	1.9	0.4	1.2	2.3	3.5
24 h	2.5	0.8	2.3	3.3	5.6
Clinker – gypsum – water					
5 min	0.9	0.4	0.3	1.3	1.6
30 min	0.8	0.5	0.3	1.3	1.6
1 h	0.8	0.5	0.3	1.3	1.6
2 h	1.1	0.3	0.5	1.4	1.9
5 h	1.3	0.3	0.7	1.6	2.3
24 h	1.8	0.5	1.5	2.3	3.8

TABLE 3

Values of free and chemically bound water, free calcium hydroxide and degree of hydration for clinker–water and clinker–gypsum–water systems

Curing time	Free water lost at 105 °C (wt.%)	Chemically bound water (wt.%)	Free calcium hydroxide (wt.%)	Degree of hydration (%)
Clinker – water				
5 min	0.36	1.35	1.83	5.63
30 min	0.40	1.85	2.24	7.71
1 h	0.68	1.95	2.65	8.25
2 h	0.84	2.53	3.81	10.54
5 h	0.69	2.79	3.66	11.63
24 h	4.37	4.21	7.15	17.54
Clinker – gypsum – water				
5 min	0.94	1.42	2.14	5.92
30 min	0.92	1.42	2.56	5.92
1 h	1.22	1.42	2.56	5.92
2 h	2.16	1.61	2.07	6.71
5 h	2.26	1.89	2.41	7.88
24 h	6.02	2.92	4.58	12.17

by sulphate–C_3A reaction in the presence of calcium hydroxide (CH) in the solution. The values of bound water and therefore of the degrees of hydration during that period of hydration are also constant at 1.42 and 5.92, respectively, identifying the existence of a controlled hydration process. Evidently the decisive factor in controlled hydration is the reactivity of C_3A in relation to the rate at which sulphate ions are freed from gypsum [12]. Degrees of hydration as a function of curing time during the earlier part of hydration for both the systems are shown in Fig. 3.

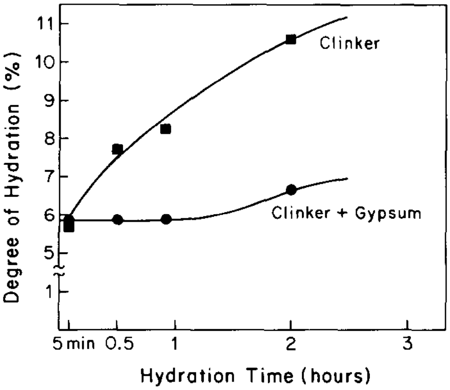

Fig. 3. Early hydration versus time profiles for hydrating clinker and clinker–gypsum systems.

Reaction (2) continues until all the sulphate ions are consumed [1,13]. When there are insufficient sulphate ions remaining in the solution to form ettringite (generally 8–16 h or so after the hydration has taken place [1]), C_3A starts reacting with the ettringite to form tetracalcium aluminate monosulphate ($C_4A\bar{S}H_{12}$), commonly known as monosulphoaluminate. The reaction takes place as follows:

$$\underset{\text{(ettringite)}}{C_6A\bar{S}_3H_{32}} + C_3A + 4H \rightarrow \underset{\text{(monosulphoaluminate)}}{3C_4A\bar{S}H_{12}} \tag{3}$$

Therefore the final product of the C_3A hydration in cement is a monosulphate–C_4AH_{13} solid solution.

In the meantime hydration gradually becomes active, especially in the clinker–gypsum–water system, thereby noticeably increasing the amounts of chemically bound water and free calcium hydroxide in the hydration products. Calculated amounts of individual products are given in Table 3. Plots of degrees of hydration versus curing time (up to 24 h) are given in Fig. 4 which clearly indicates much higher initial rates of hydration in clinker–water systems.

Only a certain concentration of sulphate ions, depending upon the amount of C_3A present in the cement, is required to form ettringite to maintain the process of set regulation for a given length of time. It may be emphasized that although the ettringite will stay stable longer with more gypsum in the system, this will cause C_3A to contribute little towards the early strength of the cement. On the other hand, as a result of a deficiency in sulphate ions in the system, conversion of ettringite to monosulphate and back to ettringite [13], when brought into contact with any fresh source of sulphate ions, can

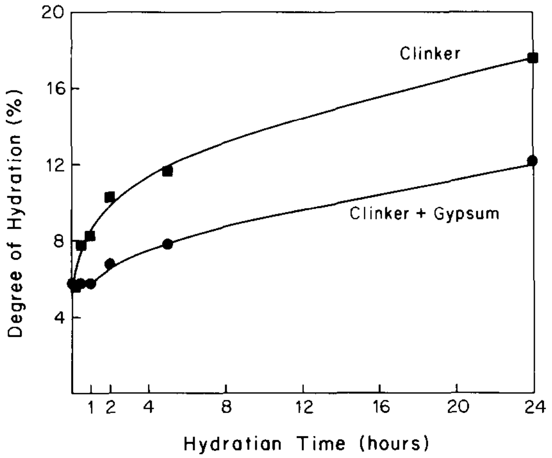

Fig. 4. Degree of hydration versus time plots for both the systems hydrated for longer periods.

make the cement prone to sulphate attack—a phenomenon that causes unsoundness in cement or concrete in the long run.

CONCLUSIONS

The phenomenon of flash setting of cement clinker and its control by gypsum addition is effectively demonstrated via thermal means. In the present investigation the effect of set controlling is monitored on a clinker–gypsum–water system over its early period of hydration, when the processes of flash setting and counter set retarding are in operation.

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