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ESTIMATION OF CALCIUM HYDROXIDE IN OPC, OPC/PFA AND OPC/PFA/POLYMER MODIFIED SYSTEMS

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ABSTRACT

Formation of calcium hydroxide in a hydrating ordinary Portland cement (OPC) not only determines the process of cement hydration but also influences the ultimate mechanical properties. Calcium hydroxide is a well crystallized material and possesses a typical morphology which can change upon the incorporation of any additives and admixtures capable of altering the hydration mechanisms in a given cement paste, thus resulting into varying degrees of calcium hydroxide formations. The additives used in the present work are the pulverized fuel ash (PFA) and a Versicol W13 polymer.

Thermogravimetric (TG) and differential thermal analysis (DTA) techniques have been used to estimate the quantity of calcium hydroxide present in the hydrating OPC, OPC/PFA and OPC/PFA polymer systems. The results have shown that by incorporating PFA and W13 polymer into OPC the quantity of calcium hydroxide formed is reduced apparently due to a secondary reaction taking place between calcium hydroxide and silica present in PFA.

INTRODUCTION

Calcium hydroxide is one of the major phases in set Portland cements. It results from the hydration of two major compounds, i.e. tricalcium silicate (C_3S) and dicalcium silicate (C_2S) in cement. The reactions take place as follows:

$$2(3CaSiO_2) + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 \quad (1)$$

$$2(2CaSiO_2) + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \quad (2)$$

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In contrast to the phase $3CaO \cdot 2SiO_2 \cdot 3H_2O$, also known as the C–S–H gel, calcium hydroxide has a well defined crystallinity with a definite stoichiometry [1].

Calcium hydroxide occupies approximately 20–25%, by volume, of the mature paste [1,2]. During the hydration of silicates, particularly tricalcium silicate (C_3S), the calcium hydroxide largely nucleates and grows within free capillary pore spaces. Calcium hydroxide morphology may vary from system to system, being largely affected by the presence of additives and admixtures causing an alteration in the hydration pattern. Calcium hydroxide growing in situ can therefore have a significant effect on the engineering properties of the paste containing additives, particularly in the present case where the pastes are being incorporated with the PFA and a Versicol W13 polymer, respectively. Several methods have been used to estimate the amount of calcium hydroxide in cementitious materials including chemical, optical and X-ray diffraction, methods [3–5].

Various authors have suggested the thermogravimetric technique (TG) for estimating free calcium hydroxide [6–11]. Recent papers by Midgley, Ramachandran and Bhatty et al. have shown thermal analysis techniques to be very reliable for estimating calcium hydroxide in set Portland cement [12–15]. In the present investigation, both the TG and DTA techniques have been used to estimate the calcium hydroxide in OPC, OPC/PFA and OPC/PFA/polymer pastes.

MATERIALS

Calcium hydroxide

Calcium hydroxide used for calibration purposes was obtained by calcining calcium carbonate (Analar) to 1000°C for 3 h and hydrating the resulting calcium oxide in distilled water. The precipitated calcium hydroxide was filtered at the pump and dried in an oven at 105 ± 1.0°C for 3 h.

Cement

Ordinary Portland cement, ASTM Type I, was used. Its specifications are given in Table 1.

Polymer

A non-ionic polymer, Versicol W13 (pH = 8.9 at 20% concentration), was used.

TABLE 1

Chemical and physical properties of the cement and PFA

Description		Cement	PFA
Chemical analysis (wt.%)			
SiO_2		20.37	49.2
Al_2O_3		5.78	28.8
Fe_2O_3		2.52	10.7
CaO		63.10	3.1
MgO		2.37	1.7
SO_3		2.75	0.95
Na_2O			2.0
K_2O			3.8
TiO_2			1.0
Insoluble residue		0.63	
Loss on ignition		1.02	
Others		1.20	
Physical properties			
Time of set (Vicat Needle)	Initial	2 h 30 min	
	Final	3 h 31 min	
Surface area, Blaine		300 $m^2 kg^{-1}$	

Pulverized fuel ash (PFA)

The PFA was obtained from a Fiddlers Ferry power station. The chemical analysis of PFA is also given in Table 1.

TEST PROCEDURES

The water/(OPC + PFA) ratio was kept at 0.40. The cement was replaced by 30% of PFA. The cement and PFA were blended together before mixing with water. The addition of Versicol W13 was added in the pastes at 0.25, 0.50 and 0.75% by weight.

The experimental procedures for the preparation of OPC, OPC/PFA and OPC/PFA/polymer pastes have been described previously [16]. In this study samples crushed from the strength tests were first dried in an oven at $105 \pm 1.0°C$ for a period of 24 h to remove the evaporable water (free water). After cooling the sample in a desiccator both TG and DTA were carried out.

Calibration

For TG and DTA calibration synthetic mixtures of calcium hydroxide and dead burnt alumina were prepared at 1, 2.5, 5.0, 7.5, 10.0, 15.0 and 20.0% by weight of calcium hydroxide.

Experimental

A Stanton-Redcroft thermobalance TG750 and DTA 673.4 were used for TG and DTA experiments. The sample holders for the TG and DTA were made of Pt/Rh. For the TG experiments, the mass of the sample taken was 7–10 mg. The mass of sample for DTA experiments was 10 mg and alumina was used as reference. The heating rate in each case was 10°C min^{-1} and dry nitrogen was used as flowing gas at 100 ml min^{-1}. The sample was equilibrated for 30 min before being subjected to heat treatment.

RESULTS AND DISCUSSION

Figure 1 shows typical calcium hydroxide endotherms obtained for the various systems in the region 400–600°C. These results show that as the hydration process continues, the calcium hydroxide peak increases. The peak temperature of calcium hydroxide is also shifted.

The peak area of the decomposition of calcium hydroxide was determined in the temperature range 410–560°C. Figure 2 shows the calibration curve of the endothermal peak areas due to decomposition of calcium hydroxide in $Ca(OH)_2$–Al_2O_3 mixtures containing different amounts of calcium hydroxide. A good linear relationship for samples containing up to 20% calcium hydroxide attests the applicability of the DTA. Ramachandran showed a linear relationship up to 33% [13].

Figure 3 shows plots of calcium hydroxide formed vs. time for OPC from the TG and DTA results. The results are also given in Table 2. It is apparent

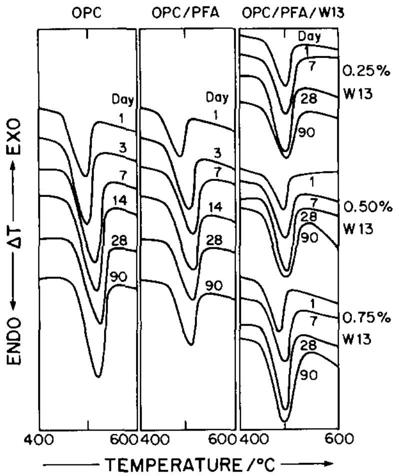

Fig. 1. Typical DTA plots for OPC, OPC/PFA and OPC/PFA/W13 at varying W13 concentrations.

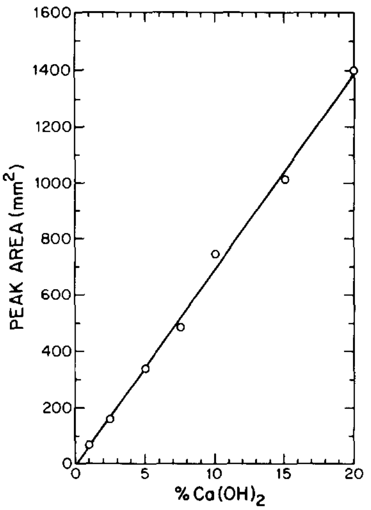

Fig. 2. Calibration curve between endothermal peak areas and the estimated amounts of decomposed calcium hydroxide.

from these data that both TG and DTA show close agreement between the two methods. A plot of calcium hydroxide estimated by TG and by DTA for OPC at various times shows good linear relationship (Fig. 4). Means of both TG and DTA results have therefore been quoted for all the other results.

It is apparent from Fig. 3 that as the OPC is aged, the concentration of calcium hydroxide increases. The explanation for this is that upon OPC hydration, increasing amounts of calcium hydroxide are formed by the reaction of unhydrated tricalcium silicate and dicalcium silicate with water. Initially, the rate of formation of calcium hydroxide is rapid (1–3 days) then

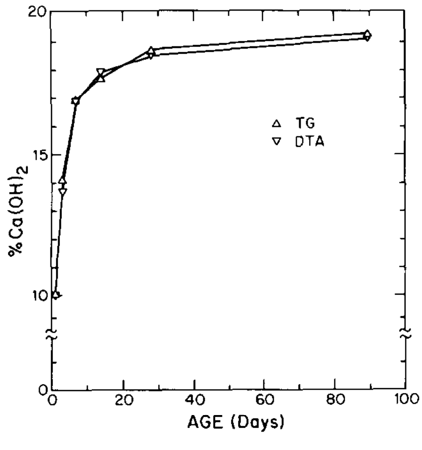

Fig. 3. Comparison of TG and DTA plots on calcium hydroxide formation in hydrating OPC.

TABLE 2

Estimation of calcium hydroxide (wt.%) during hydration of OPC at different curing times using both TG and DTA data

Curing time (days)	Thermal technique used	
	TG	DTA
1	10.10	10.00
3	14.30	13.65
7	16.95	16.85
14	17.60	17.80
28	18.65	18.55
90	19.20	19.00

the rate decreases as is shown in Fig. 3. Hydration of tricalcium silicate is more vigorous than the dicalcium silicate in the early part of hydration [1].

The overall effect of introducing PFA in cement pastes reduces the concentration of calcium hydroxide. Due to their fine particle size and generally noncrystalline character, the fly ashes usually show adequate pozzolanic behavior [17]. In accordance to the ASTM C 595 specification [18] a pozzolan is defined as "a siliceous or a siliceous and aluminous material which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties". In the Portland cement/fly ash system the compounds tricalcium silicate and dicalcium silicate, upon their hydration,

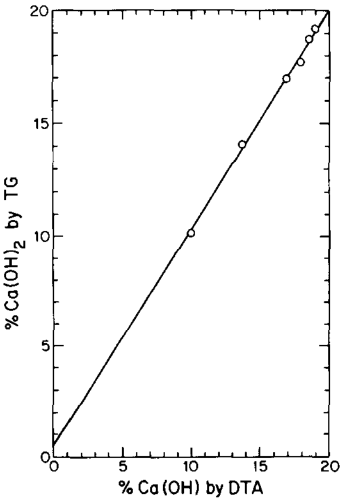

Fig. 4. Relationship between the TG and DTA plots on the estimation of calcium hydroxide in hydrating OPC.

release substantial amounts of lime to initiate pozzolanic reaction with the fly ashes. There are three generally accepted modes of action known as physical, chemical and pozzolanic reactions in which PFA interacts with the constituents in a concrete mix [19]. These are summarized as follows:

(i) A physical effect of noticeable workability in the concrete mix occurs mainly due to balling effect of the spherical PFA particles causing lubrication without further water demand. Conventionally, PFA for replacing part of cement in concrete mixes is used to influence its rheological behavior, thus enhancing the workability of mixes and giving the benefit of reducing the water content without affecting the engineering properties of concrete.

(ii) A chemical reaction takes place when soluble ions from PFA react with the calcium aluminates in the cement and retard their hydration.

(iii) A pozzolanic reaction occurs when silica (and alumina) from the PFA react with calcium hydroxide produced from the hydration reactions of the compounds tricalcium silicate (C_3S) and dicalcium silicate (C_2S) present in cement, as is already explained in eqns. (1) and (2).

In the OPC/PFA system the calcium hydroxide concentration is increased up to 14 days and then decreases (28–90 days). This can be explained in terms of the reaction of calcium hydroxide with silica present in PFA to form calcium silicate hydrate [1,6]. The PFA used in the present investigation is a low-calcium fly ash (< 5% CaO). The presence of nonreactive crystalline alumino-silicates such as mullite and sillimanite at the cost of non-crystalline compounds reduces the reactivity of the ash [20], at least in the initial stages of hydration (up to 14 days), during which the concentra-

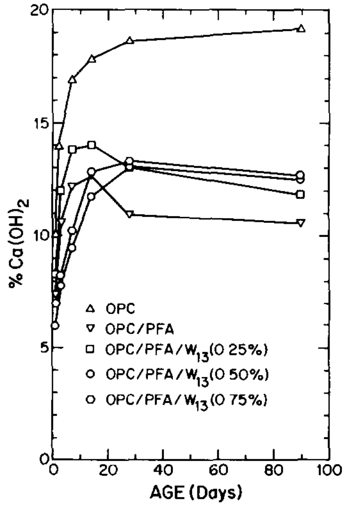

Fig. 5. Effect of PFA and W13 additions on calcium hydroxide formation in given systems.

TABLE 3

Estimation of calcium hydroxide (wt.%) during hydration of OPC/PFA/W13 pastes at different curing times and varying W13 concentration

Curing time (days)	OPC	OPC/PFA	OPC/PFA/W13 at W13 (wt.%)		
			0.25	0.50	0.75
1	10.05	7.35	8.32	6.05	7.05
3	13.98	10.65	12.00	7.85	8.10
7	16.88	12.20	13.85	9.45	10.25
14	17.70	12.75	14.05	11.78	12.85
28	18.60	11.95	13.10	13.15	13.25
90	19.10	10.38	11.55	12.65	12.85

tion of calcium hydroxide in the system continues to increase (see Fig. 5). The pozzolanic reactivity beyond this point, however, clearly increases, resulting in a lower calcium hydroxide concentration as shown in Fig. 5.

Similar observations on gradual decrease in lime concentration beyond 28 days in fly ash-containing cement mixes have also been reported by other workers [21]. They have directly related the progressive decrease in lime released in the mix to the increased pozzolanic activity of fly ash incorporation. The rate of formation of calcium hydroxide by incorporating PFA in the system is also reduced.

The effect of adding Versicol W13 on OPC/PFA pastes is shown in Fig. 5. It is apparent that calcium hydroxide content is reduced by W13 compared to neat OPC paste whilst it is either increased or decreased, depending on the concentration of W13, compared to the OPC/PFA. Data on the estimation of calcium hydroxide for these systems is presented in Table 3. The rate of formation of calcium hydroxide is also dependent on the concentration of W13. It increases with time for W13 at all concentrations except at 90 days at 0.25% concentration when it is lowered.

It may be that the polymer W13 effectively competes for the silica (and alumina) in the PFA thus leaving the growth of calcium hydroxide in the system unhindered. At higher W13 concentration, i.e. at 0.50% and 0.75%, this effect is more obvious. At 0.25% concentration, however, the amount of W13 is perhaps too low to check the reaction between silica and calcium hydroxide; therefore at the recorded values of calcium hydroxide at 28 and 90 days, curing of the OPC/PFA/W13 systems is much less than those for W13 = 0.50% and 0.75%.

CONCLUSIONS

The presence of PFA slows down the hydration rate in a cement paste thus lowering the amount of calcium hydroxide in the products, apparently due to a secondary reaction taking place between the calcium hydroxide formed originally in the paste and the silica (and alumina) present in the PFA.

The retarding effect of PFA is perhaps countered by the presence of W13 polymer, which most probably attaches to silica and inhibits its potential reaction with the calcium hydroxide being formed in the OPC pastes.

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