Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 85–90

THERMAL STUDIES ON THE HARDENING BEHAVIOUR OF CEMENTS GROUND WITH ADDITIVES

I. Teoreanu[1]*, G. Guslicov*[2] *and A. Volceanov*[1]

[1]University 'Politehnica' Bucharest, Catedra SIMO, P.O. Box 12-134, Bucharest, Romania
[2]National Institute for Cement, Bulevarddul Preciziei 6, 77562 Bucharest, Romania

(Received January 15, 2000; in revised form June 30, 2000)

Abstract

A study was carried out on the effects on the hardening of Portland cements of the surfactants (dihydroxy alcohols and ethers and aminoalcohols) used as grinding additives. The effects were found to depend on the molecular mass of the surfactants and to correlate with the surface forces in the given reactant systems.

Keywords: aminoalcohols, dihydroxy compounds (alcohols and ethers), grinding additives, hardening of cements, surfactants

Introduction

The surfactant additives used to intensify cement grinding bring consequences as concerns the behaviour of the cement behaviour during handling and utilization, and particularly during hardening. These effects must not lead to a decreased performance of the cements during operation.

In previous papers [1, 2], we reported results of chemical and structural-mechanical studies concerning the hardening behaviour of Portland cements ground with surface-active additives belonging to different functional classes [1, 2], discussed factors that influence this behaviour. Complementary studies involving thermal and spectroscopic analysis, X-ray diffraction (XRD), microscopy and many other techniques can furnish additional information of interest (e.g. [3–5]).

The present paper reports results of investigations in which methods of thermal analysis (DTA and TG) were applied.

Experimental conditions and procedures

Cements obtained from ordinary Portland clinker were examined (Table 1). The clinkers were ground with additives in a proportion of 0.05%, considered to have the optimum effect on the grinding process intensity.

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Table 1 Mineral characteristics of the used clinker

Clinker type	Bogue potential mineral composition/%			
	$3CaO \cdot SiO_2$	$2CaO \cdot SiO_2$	$3CaO \cdot Al_2O_3$	$4CaO \cdot Al_2O_3.Fe_2O_3$
D	52.86	19.52	13.20	9.76

The additives used were from different classes:

(i) the dialcohols ethylene glycol (EG) and propylene glycol (PG); (ii) the ether (polyglycol) polypropylene glycol (PPG) and (iii) the aminoalcohols monoethanolamine (MEA) and triethanolamine (TEA).

The pastes were prepared for a water/cement ratio, *W/C*=0.5, hardened for different curing periods and then subjected to thermal analysis. In certain cases, information obtained from XRD analysis and IR spectroscopy was used to confirm some of the results.

Results and discussions

The results of thermal studies are presented for illustration in Figs 1, 2 and Table 2.

The results of the thermal analysis for the hydrated cements hardened for 28 or 360 days (Table 2) show three groups of mass loss and thermal effects: (i) in the temperature range 20–485°C, the loss of hygroscopic water, capillary water (particularly from the gel) and chemically bound water from alumina and aluminosulphate-based compounds; (ii) in the temperature range 420–665°C, effects that essentially corre-

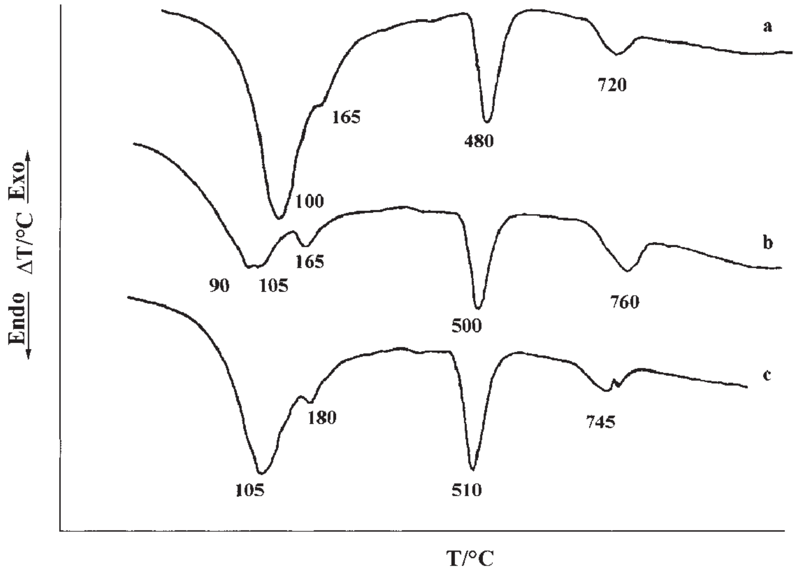

Fig. 1 DTA patterns of cement pastes – reference and with glycols as grinding additives, hardened after 28 days: a – sample E; b – sample EG; c – sample PG (symbols are according to Table 2)

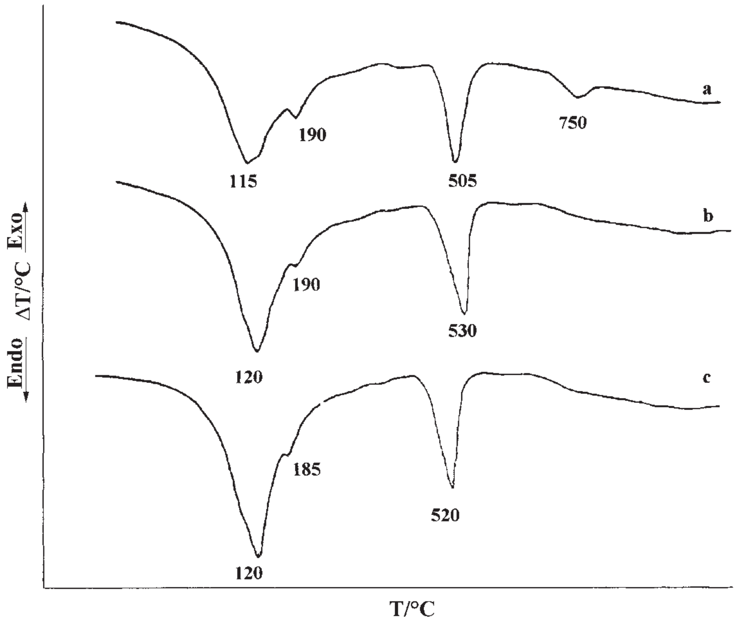

Fig. 2 DTA patterns of cement pastes – grinding additives from ethers or aminoalcohols class, hardened after 28 days: a – sample PPG; b – sample MEA; c – sample TEA

spond to dehydration of calcium hydroxide, formed as a consequence of the hydrolysis of Portland clinkers minerals, and especially of tricalcium silicate; (iii) in the temperature range 550–965°C, effects corresponding to the complete dehydroxylation of calcium hydrosilicates, simultaneously with the formation of related anhydrous phases, and to the decomposition of $CaCO_3$ (generated by carbonation of calcium hydroxide) or of other carbonate phases. Figures 1 and 2 present a selection of DTA patterns that support the above observations.

The quantitative and qualitative data on the effects of the grinding additives and the hardening duration on the processes of interaction with water, the mechanisms of these processes and the development of the hardening structure relating to the resulting hydrated phases (Table 2 and Fig. 3, showing histograms for the calcium hydroxide formed) permit some conclusions.

In the case of cements obtained by grinding with surfactants during long hardening periods (28 and 360 days) an obviously higher amount of calcium hydroxide results from cement hydrolysis. This is a consequence of increasing of the transformation degree α, of the anhydrous cement, due to its interaction with water, and of the intensification of the hydrolysis reactions themselves (even if α=constant).

The increase in α leads to an increased amount of water chemically bound as hydroxide ('hydroxyl water') when the hydrolysis reaction itself is not intensified (the intensity of this process being determined by the amount of released $Ca(OH)_2$ relative to the unit mass of anhydrous binder hydrolyzed). If the hydrolysis reaction is intensified, the basicity of the formed hydrosilicates decreases, and, as a consequence, their characteristic ratio H_2O/SiO_2 will also decrease. The proportion of 'hydroxyl water' therefore decreases, indicated by the mass loss Δm in the DTA patterns which accompanies the high-temperature thermal effects (ranging between 550 and 965°C). Δm for cements with grinding additives is significantly lower values than that for the reference cement, especially when aminoalcohols and EG are used as grinding additives. For the given hardening time, this suggests a lower basicity of the formed hydrosilicates as a consequence of hydrolysis intensification without any change in typology, i.e. the hydrosilicate class they belong in remains the same. Both XRD analysis and IR spectroscopy support this conclusion.

Table 2 Mass loss of samples hardened for 28 or 360 days

Sample	T_{range}/°C	Mass loss/%	T_{range}/°C	Mass loss/%
	Hardening time 28 days		Hardening time 28 days	
E (reference cement)	20–420	25.8	20–450	16.0
	420–550	2.8	450–610	3.3
	550–800	3.0	610–965	4.5
	20–800	31.6	20–965	23.8
EG (cement with 0.05% ethylene glycol)	20–420	21.8	20–450	16.0
	420–570	3.0	450–640	3.5
	570–900	1.3	640–965	4.0
	20–900	26.1	20–965	23.5
PG (cement with 0.05% propylene glycol)	20–440	24.0	20–450	17.0
	440–590	3.5	450–650	4.0
	590–850	2.5	650–940	3.3
	20–850	30.0	20–940	24.3
PPG (cement with 0.05% polypropylene glycol)	20–430	22.6	20–450	18.5
	430–550	3.0	450–650	4.0
	550–880	2.8	650–920	2.8
	20–880	28.4	20–920	25.3
MEA (cement with 0.05% monoethanolamine)	20–450	23.3	20–450	15.0
	450–610	4.0	450–620	4.3
	610–800	1.3	620–960	3.5
	20–800	28.6	20–960	2.8
TEA (cement with 0.05% triethanolamine)	20–450	27.1	20–485	17.3
	450–590	3.8	485–665	4.0
	590–820	1.5	665–920	3.5
	20–820	32.4	20–920	24.8

The mass loss accompanying the process in the low-temperature range (20–485°C) is also affected by the presence of grinding additives, for a given hardening time; however, the corresponding effects are not highly significant for a hardening time of 360 days, but more obvious for a hardening time of 28 days.

The brief explanations and considerations presented above concerning the information provided by thermal analysis, point out that the processes that take place during hardening and the nature of the resulting phases are not basically modified in the presence of grinding additives; their ratios and their kinetics are affected, however.

The effects of the grinding additives on the processes controlling the hardening of Portland cements displays a certain regularity, correlated with their functional class and the length of the hydrocarbon radical.

For a given hydrocarbon radical, the aminoalcohol surfactants exert more significant effects than those of glycol type do; the information in Table 2 can be compared with respect to the behaviour of cements ground with the same amount of EG or MEA. A parallelism was established between the effects revealed during hardening and those resulting from the grinding operation [1, 2, 6], both being a consequence of the modifications induced by additive adsorption in the surface features of the admixed cements and related surface phenomena [1, 2, 6].

The same features can be used to explain the differences that occur in the behaviour of cements ground with PG (a dihydroxy alcohol) and PPG (dihydroxy ether). In this case, the differences are less significant. Thus, the intensification of the hydrolysis process, for the given hardening periods exhibits less evident differences, and as a rule is less significant for PPG. This is certainly due to the longer hydrocarbon chain; the higher polarity of the functional groups would have justified the opposite behaviour.

With the same functional groups of the surfactant, the increase of hydrocarbon chain beyond a certain length could modify the direction of a process, e.g. the direction of hydrolysis intensification with calcium hydroxide release; in this way, it might be explained (Fig. 3) why the hydrolysis process is intensified when PPG is used as

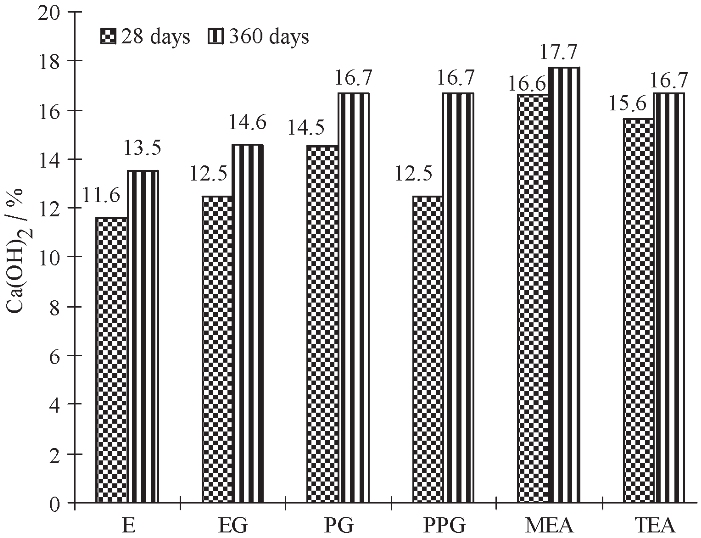

Fig. 3 Histograms regarding the amount of calcium hydroxide formed by cements hydrolysis – reference and with additives after a hardening time of 28 and 360 days, respectively

grinding additive instead of EG and, in contrast, why the same process is attenuated when TEA is used as grinding surfactant instead of MEA.

Conclusions

The thermal analysis methods used to investigate the hardening behaviour of cements containing grinding additives have shown that the processes that take place during hardening, and the nature of the resulting phases are not modified; only their ratio and their kinetics are affected. Especially the intensification of the hydrolysis reactions is emphasized followed by an alteration in the basicity of the formed hydrosilicates, without change in their typological nature.

The mechanism of action of grinding surfactants in the hardening process, and the correlations between the induced effects and the nature of the additives (considered in terms of their functional groups and hydrocarbon radicals) can be understood via the physics and chemistry of the surface. In this context, a parallelism was found between the effects of the grinding additives and the behaviour of the admixed cements during the hardening process, thereby providing additional supports for the interpretations developed previously [1, 2, 6], as regards the physical chemistry of the surfaces in consequence of the action of the grinding surfactant additives.

References

1 I. Teoreanu and G. Guslicov, Materiale de Constructii, 25 (1995) 215 (in Romanian).
2 I. Teoreanu and G. Guslicov, Proc. Fifth NCB Internat. Seminar, New Delhi (India), Vol. II, National Council for Cement and Building Materials-NBC Publishers, 1996, p. 41–50.
3 S.Tsivilis, G. Kakali, E. Chaniotakis and A. Souvaridou, J. Therm. Anal. Cal., 52 (1998) 863.
4 K. Kovler, Cem. Concr. Res., 28 (1998) 523.
5 K. Kovler and A. Bentur, Proc. of Israeli–Hungarian Biannual Conf. on Thermal Analysis and Calorimetry of Materials, Ein Bokek, Israel 1996, p. 15.
6 I. Teoreanu and G. Guslicov, Proc. of the VII Conf. of Materials Science and Engineering, CONSILOX, Vol. I, 1996, UPB Publishing House, Constanța, Romania, p. 33–45.