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A STUDY ON THE HYDRATION OF PORTLAND LIMESTONE CEMENT BY MEANS OF TG

S. Tsivilis[1], *G. Kakali*[1], *E. Chaniotakis*[2] *and A. Souvaridou*[1]

[1]National Technical University of Athens, Chemical Engineering Department, Labs of Inorganic and Analytical Chemistry, 9 Heroon Polytechniou St., 15773 Athens, Greece
[2]TITAN Cement Company S.A., Department of Research & Development, Kamari Plant Viotias, P.O. Box 18, 19200 Elefsis, Greece

Abstract

Subject of this paper is to investigate the hydration process of Portland limestone cement containing 10–35% limestone. Cements, produced by co-grinding of clinker, limestone and gypsum, were hydrated for periods 6 h to 28 d and were studied by means of TG and XRD. The $Ca(OH)_2$ content of the cements containing limestone is higher than in pure cements, specifically for 10% limestone content and ages more than 1 day. These results are in accordance with the strength development of the studied cements. In earlier ages the $Ca(OH)_2$ content is slightly lower in the limestone cements and independent of the limestone content. After 1 day curing, the increase of limestone addition causes a relative increase of the non evaporable water. The XRD patterns indicated the presence of carboaluminates in the hydrated limestone cements.

Keywords: calcium hydroxide, hydration, limestone cement, non evaporable water, TG

Introduction

There are important reasons, both technical and economical, for producing Portland cement containing limestone, co-ground or mixed with clinker, as main constituent. The technical reasons are the satisfactory mechanical properties of the Portland limestone cement as well as the reduction of the water demand of the cement and improvements of its workability [1–5]. Furthermore the above cement type leads to energy saving, because of the reduction of the clinker proportion in cement as well as to environmental impact reducing [6, 7].

The new European Standard EN 197-1 (1996) identifies 2 types of Portland limestone cement containing 6–20% limestone (type II/A-L) and 21–35% limestone (type II/B-L). The limestone must meet three requirements: a) $CaCO_3$ content greater than 75%, b) clay content, determined with methylene blue test (MBA), less than 1.20 g/100 g, c) total organic carbon (TOC) less than 0.5% [8].

Cement is a system composed of numerous minerals which react with water at different rates, give hydration products of different composition and crystal-

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linity, and influence the engineering properties of the final product – concrete – in different ways. The two most important clinker components primarily responsible for the cement setting and strength development respectively, are tricalcium aluminate (C_3A)* and tricalcium silicate (C_3S). C_3S and C_3A react with water, in the presence of gypsum, according to the following Eqs (1)–(3). It must be noticed that the reactions are much more complex than shown below [9].

$$C_3S \xrightarrow{H_2O} C\text{–}S\text{–}H + nCH \text{ (calcium hydroxide)} \tag{1}$$

$$C_3A + 3C\underline{S}H_2 + 26H \rightarrow C_3A\cdot 3C\underline{S}H_{32} \text{ (ettringite)} \tag{2}$$

$$C_3A\cdot 3C\underline{S}H_{32} + 2C_3A + 4H \rightarrow 3C_3A\cdot C\underline{S}H_{12} \text{ (monosulphate)} \tag{3}$$

The hydration rate of cement can be evaluated by measuring the mass loss of hydrated samples up to 800°C. Hydrated ordinary Portland cement is a complex mineral comprised mainly of calcium silicate hydrates (C–S–H). C–S–H is nearly an amorphous material, containing water of various energy level. Six DTG peaks have been reported when hydrated cement is heated in thermobalance [10]:

1.	~100°C:	dehydration of pore water
2.3.4.	100–300°C:	different stages of C–S–H dehydration
5.	~500°C:	dehydroxylation of $Ca(OH)_2$
6.	~700°C:	decarbonation of $CaCO_3$

The effect of limestone on the cement hydration has been mostly studied in pure clinker phases and $CaCO_3$ and in cements produced by blending OPC with ground limestone (non co-ground). The data found in the literature do not seem to be in total agreement, particularly concerning the determination of limestone percentage incorporating in the hydration products. But they generally agree that limestone participate in the hydration reactions rather than be an inert filler [11–17].

Despite growing use of limestone as a cement constituent, little attention has been paid on the study of the limestone behavior when it is co-ground with clinker and gypsum to produce Portland limestone cement. The co-grinding is expected to affect the hydration process due to the modifications of particle size distributions and the mechanical activation of components' grains [18–20]. In the present paper TG is used in order to study the cement hydration, while XRD is used for the identification of the hydrated products in limestone cement produced by co-grinding of components. This work is a part of a project, developed in our laboratories, concerning the properties of limestone cement and concrete.

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* Cement chemistry notation: $C=CaO$, $A=Al_2O_3$, $S=SiO_2$, $F=Fe_2O_3$, $\underline{S}=SO_3$, $H=H_2O$, $\underline{C}=CO_2$

Experimental

The co-grinding of clinker, limestone and gypsum, was carried out in a pro-pilot plant ball mill. Four cements containing 0% , 10%, 20% and 35% limestone correspondingly were produced and referred as C1, C1L1-10, C1L1-20 and C1 L1-35 respectively. The gypsum content was 5% of the clinker mass. The chemical and mineralogical composition (Bogue) of the used clinker is shown in Table 1. The chemical analysis of the limestone is given in Table 2. The main constituent of the limestone is calcite containing also dolomite and quartz as minor constituents. The specific surface, according to Blaine apparatus, the compressive strength after 1 , 2, 7 and 28 days, the standard consistency and the setting time of the produced cements are given in Table 3.

Pastes were prepared with water to solid ratio of 0.3 using carbon dioxide-free distilled water. After a period of 6 h the cement cores were extracted and wet-cured at 20°C in sealed polythene containers. This procedure has been se-

Table 1 Chemical and mineralogical composition of the clinker

Chemical composition/%							
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3
21.79	5.13	3.59	66.42	1.71	0.55	0.09	0.52

Mineralogical composition/%			
C_3S	C_2S	C_3A	C_4AF
65.15	13.32	7.54	10.92

Table 2 Chemical composition of the limestone

Chemical composition/%							
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	LOI
0.61	0.15	0.17	53.36	1.47	0.02	0.00	43.54

Table 3 Properties of the cements

Code	Specific surface/ $cm^2\ g^{-1}$	Compressive strength/ $N\ mm^{-2}$				Standard consistency/ %	Setting time/ min	
		1	2	7	28		initial	final
C1	3110	14.5	24.7	40.3	53.8	25.8	145	200
C1L1-10	3830	15.0	25.9	44.0	53.3	25.0	145	195
C1L1-20	4330	11.0	21.4	37.6	45.9	23.2	110	180
C1L1-35	5150	7.5	15.9	27.2	33.5	22.8	100	165

lected in order to avoid the conduct of samples with air and prevent the transformation of $Ca(OH)_2$ to $CaCO_3$. Samples hydrated for periods 6 h, 1, 7 and 28 days were subjected to acetone and isopropyl ether treatment and then dried for 24 h in vacuum.

TG was used for the determination of non evaporable water, calcium hydroxide and calcium carbonate in unhydrated and dried cement paste samples using a TA Instruments Thermal Analyst 3000. The samples (~50 mg) were heated over the range 20 to 900°C at a constant rate of 15°C min^{-1} in an atmosphere of carbon dioxide free nitrogen, flowing in 90 cm^3 min^{-1}.

Powdered samples, with particle size less than 54 micron, were measured on a Siemens D5000 diffractometer and the data were evaluated using Siemens "Diffrac Eva" software in order to identify the hydrated products.

Results and discussion

Figure 1 presents, indicatively, the TG and DTG curves of sample C1L1-20, 6 h. As it is shown the curves can be divided into three major parts, representing three different kinds of reactions:

– up to 300°C: removal of water from hydrated products which are likely to include, among others, most of the C–S–H. Several minor steps are likely to take place in this area, attributed to capillary pore water, interlayer water and ad-

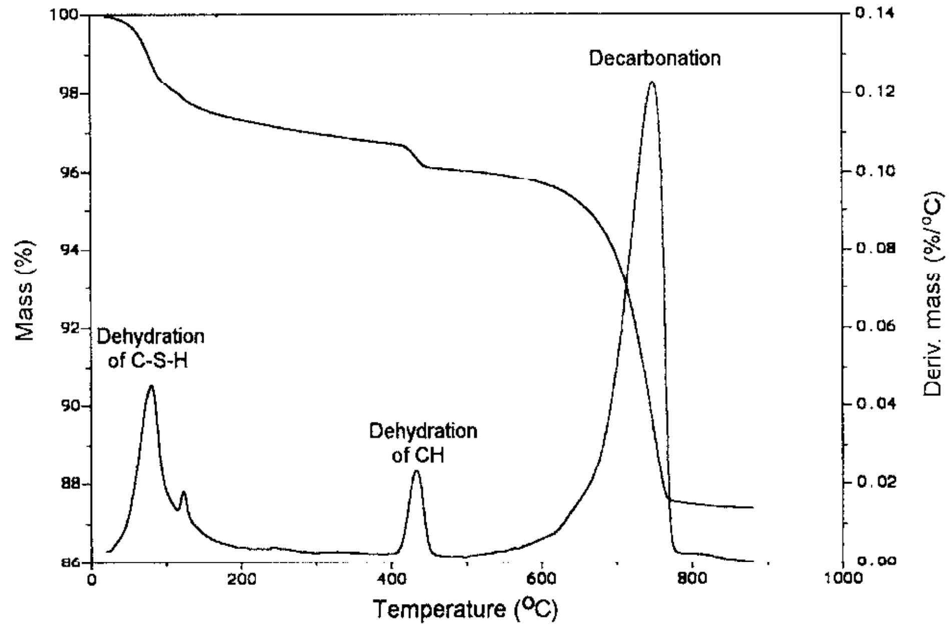

Fig. 1 TG and DTG curves of sample C1L1-20 (6 h)

sorbed water respectively. The corresponding peaks overlap each other because of the dynamic heating process,

- 400°C–500°C: dehydroxylation of calcium hydroxide,
- 600°C–800°C: decarbonation of calcium carbonate.

The CH and non evaporable water determined by TG are shown in Table 4. Both CH and non evaporable water are expressed as a percentage of mass of clinker+gypsum rather than clinker+gypsum+limestone (cement) since this enables the effect of limestone addition on hydration to be illustrated more clearly. Figures 2 and 3 present the non evaporable water and CH *vs.* hydration time and limestone content correspondingly.

Table 4 Non evaporable water and $Ca(OH)_2$ content of the hydrated cements

Code	Non evaporable water/%				$Ca(OH)_2$/%			
	6 h	1 day	7 days	28 days	6 h	1 day	7 days	28 days
CI	7.05	12.02	17.38	16.37	5.39	9.43	14.55	16.05
CIL1-10	4.57	9.98	17.90	18.15	3.63	9.10	20.59	19.80
CIL1-20	4.81	10.45	17.17	19.02	3.64	8.95	18.52	18.35
CIL1-35	4.94	11.75	21.38	21.16	3.58	9.98	16.03	16.13

As illustrated in Fig. 2 the limestone seems to have a positive role in the cement hydration, specifically for ages more than one day. For ages up to one day the non evaporable water is slightly lower in Portland limestone cements.

As shown in Fig. 3, up to one day, there is a slightly decrease of CH in limestone cement samples, which is independent from the limestone content. After 7 days samples containing 10% limestone exhibit higher rates of hydration.

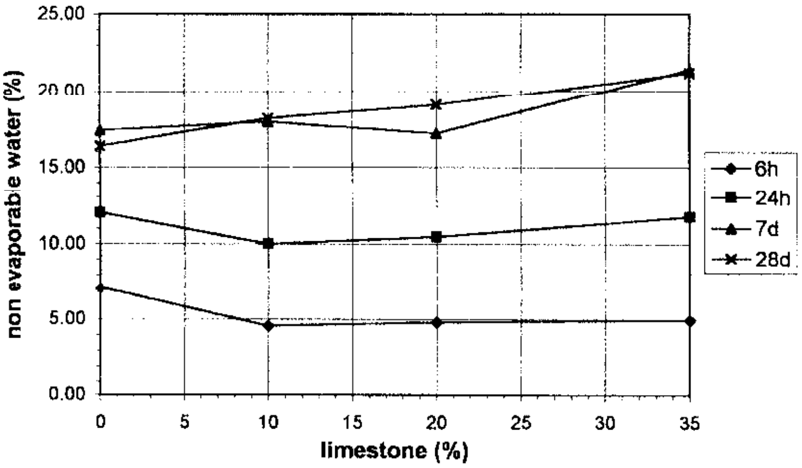

Fig. 2 Non evaporable water *vs.* hydration age and limestone content

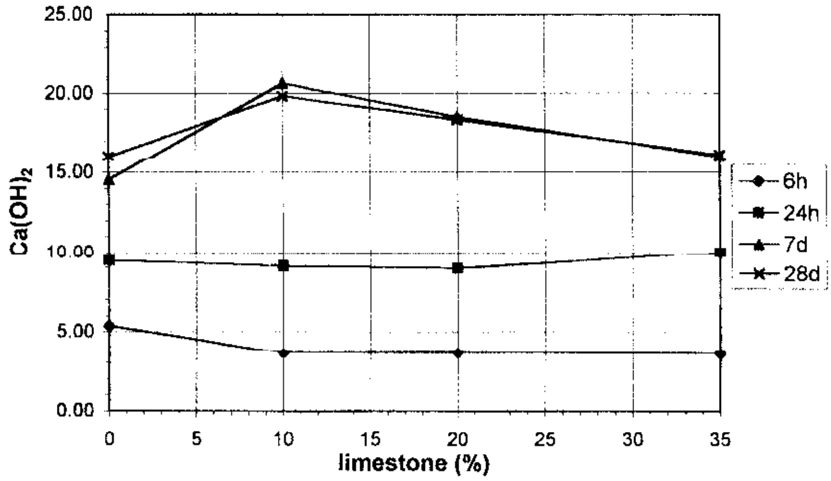

Fig. 3 $Ca(OH)_2$ *vs.* hydration age and limestone content

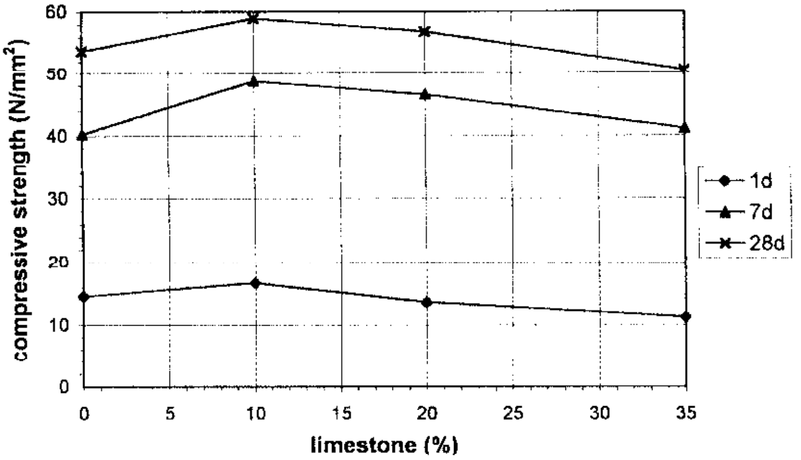

Fig. 4 Compressive strength *vs.* curing age and limestone content

In Fig. 4 the compressive strength of the cements, expressed per clinker+gypsum content, *vs.* the age and limestone content is presented. Comparing Figs 3 and 4 it is seen that the CH content at 7 and 28 days is strongly correlated with the corresponding compressive strength. Besides the non evaporable water seems to be independent of the relative compressive strength. The content of non evaporable water cannot be directly correlated with the CH% since a significant part of it is contributed to the capillary water and therefore is affected by the pore size distribution and the porosity of the paste.

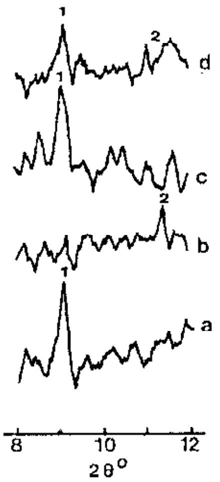

Fig. 5 XRD patterns of hydrated samples. a) C1 (1 day), b) C1L1-35 (1 day), c) C1 (7 days), d) C1L1-35 (7 days) 1. ettringite, 2. calcium carboaluminate hydrate

Figure 5 shows, indicatively, the XRD patterns of the samples a) C1 (1 day), b) C1L1-35 (1 day), c) C1 (7 days) and d) C1L1-35 (7 days). As it is observed limestone delays the formation of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 25H_2O$, *d*: 9.73, 5.61, 3.88 Å) and favors the formation of carboaluminates ($3CaOAl_2O_3CaCO_3\cdot 11H_2O$, *d*: 7.57, 3.85, 2.86 Å) during the first day of hydration. At later ages almost equal amounts of ettringite are found in both samples.

The delay of hydration in the first days can be associated with variations in both granulometry and hydration chemistry of the limestone cements. It may be attributed to the modified particle size distribution of limestone and clinker as limestone is ground in expense of clinker, due to its higher grindability. Besides, the limestone delays the formation of ettringite and favors the formation of carboaluminate during the first days of hydration. Furthermore the limestone presence alters the physical properties of paste (such as pore size distribution and porosity) affecting the formation and crystallization rate of the hydration.

The higher content of $Ca(OH)_2$, in the pastes made from limestone cements and for ages more than 1 day, indicates that limestone improves the clinker reactivity and the exploitation of its hydraulic potential. This effect may be related to the structure modification of the hydration products as well as to the nucleating action of the finely ground limestone.

Taking into consideration the results of the literature, mentioned in introduction, it is finally concluded that the co-grinding of Portland limestone cements leads to a different limestone behavior during hydration, specifically in early ages. The effect of limestone on the particle size distribution of clinker, the pore size distribution of paste and the hydration kinetics is the subject of a future paper.

Conclusions

The following conclusions can be drawn from the present study:

The $Ca(OH)_2$ content of the cements containing limestone is higher than in pure cements, specifically for 10% limestone content and ages more than 1 day. These results are in accordance with the strength development of the studied cements.

In earlier ages the $Ca(OH)_2$ content is slightly lower in the limestone cements and independent of the limestone content.

After 1 day curing, the increase of limestone addition causes a relative increase of the non evaporable water.

The presence of limestone inhibits the formation of ettringite and favors the formation of carboaluminates during the first days of hydration.

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