

Hydration Characteristics of Limestone Filled Cement Pastes

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Abstract. The physico-mechanical properties of hardened limestone-filled cement pastes were studied. Five filled-cements were prepared from 0, 5, 10, 15 and 20 wt. % of limestone and OPC. The water of consistency of filled-cement pastes was 0.275, 0.275, 0.275, 0.272, and 0.270, respectively. The pastes are moulded into one inch cubic moulds and left within the moulds at 100% relative humidity for 24 h, then demoulded and cured under tap water for 3, 7, 28, and 90 days. At each hydration time, the combined water, bulk density, total porosity and compressive strength of the hardened filled-cement pastes were determined. Some selected filled-cement pastes were investigated using differential thermal analysis (DTA) and scanning electron microscope (SEM) Techniques. Addition of limestone to Portland cement causes an increase of hydration at early ages inducing a high early strength, but it can reduce the later strength due to the dilution effect. The results indicate that the addition of limestone up to 5 wt. % improves the physico-mechanical properties of ordinary Portland cement which acts as a nucleating agent and accelerates the hydration of filled cement pastes. The addition of 5 wt. % limestone can be used in the production of portland cement according to the international specifications. On the other side, the addition of 10-20 wt. % limestone can be used in the production of blended or mixed cements.

1 Introduction

The objective of the present work is to prepare the kind of new coating which prevents iron rust; this rust causes corrosion of bodies fabricated of iron like reinforced steel in buildings construction, cars, ships and others. Which is a natural material prepared chemically of kaolin and ceramic waste but after many studies have proven the coating role as corrosion inhibitor, which is no longer, confined to add color, but many researchs [1] discovered important functions such as protecting metals from corrosion when used in the concrete industry. Limestone is an important material for cement manufacture.

The addition of limestone to ordinary Portland cement may significantly improve several cement properties such as compressive strength, water demand, workability, durability [1-5], and can also decrease the production costs. The effect of small limestone additions on both compressive strength and heat of hydration is relatively well known, but less is known about the dependence of this effect on the clinker properties (for example C_3S content), fineness of cement and other factors. The influence of limestone depends on C_3A content of clinker because $CaCO_3$ produces calcium carboaluminate hydrate during the reaction with C_3A [1, 6]. There is also some evidence that finely ground limestone influences C_3S hydration [7-10]. Limestone filler addition to Portland cement produces several effects on the kinetics of cement hydration. Limestone filler causes a hydration acceleration of Portland clinker grains

(especially the C_3S [11]) at early ages. It improves also the particle packing of the cementitious systems [12], provides new nucleation sites for calcium hydroxide [13], and forms calcium carboaluminate hydrate as results of the reaction between $CaCO_3$ from and C_3A from Portland clinker [14].

Researchers [15], revealed that the reaction between C_3A and $CaCO_3$ takes place by a solid state mechanism and the addition of $CaCO_3$ modifies the initial reaction of C_3A with water, due to the rapid formation of hydrated calcium carboaluminate ($C_3A.CaCO_3 \times H_2O$) developed on the surface of C_3A grains. Accordingly [16], hydrated calcium carboaluminate can be formed from the hexagonal (C_4AH_{13}) and cubic (C_3AH_6). Hydration reactions of C_3A in the presence of gypsum have been discussed [17]. Initially ettringite crystallizes and then if the sulfate is consumed before C_3A consumption, the ettringite conversion to monosulfoaluminate occurs. The limestone addition modifies these reactions. First, the ettringite formation is accelerated by the presence of $CaCO_3$ [14].

Secondly, the ettringite conversion to monosulfoaluminate hydrate will be delayed or stopped when a large amount of carbonate is present in the paste. This phenomenon occurs because some sulfate ions can be interchanged by carbonate ions during C_3A hydration [18]. Carbonate additions also influence the C_3S hydration [7], which accelerated when the amount and fineness of $CaCO_3$ increase.

It was found that C-S-H incorporates a significant amount of $CaCO_3$ into its structure. Additionally, [19],

calcium silicocarbonate hydrates during the hydration of C3S in the presence of large quantities of carbonate were formed. It was also found that limestone filler increases the hydration rate from 1 to 90 days [20]. The present work aims to study the physico-mechanical properties of the Portland limestone cements.

2 Experimental Programs

2.1 Material and composition of mixture.

The starting materials used in this work were OPC and limestone provided from Suez Cement., Co. and Helwan area, Cairo respectively. The limestone sample was ground to pass 90 μ m sieve. The chemical composition of these materials is shown in Table (1). The mix composition of the different cement blends is given in Table (2). Each dry mix was first blended in a porcelain ball mill using three balls for one hour in order to attain a complete homogeneity, then kept in an airtight container. The water of consistency, initial and final setting times of each cement were determined according to ASTM designations [21]. The dry mix was mixed using the corresponding water of consistency to study the hydration characteristics of cement pastes. The cement pastes were demoulded after 24 hrs of casting and cured under tap water up to 90 days. The bulk density was determined from the weight both in air and suspended in water using Archimedes principle [22].

Table 1. Chemical compositions of starting materials, wt %

Composition (% of mass)	O.P.C.	Limestone
CaO	64.12	54.58
SiO ₂	21.51	1.07
Al ₂ O ₃	4.34	0.18
Fe ₂ O ₃	3.62	0.09
MgO	1.67	0.37
SO ₃	1.09	0.10
Na ₂ O	0.51	0.01
K ₂ O	0.12	0.09
L. O.I	2.95	43.17

Figure (1) illustrates the XRD pattern of the limestone sample collected from Helwan area. It shows only the presence of calcite (cc). The determination of compressive strength of hardened cement pastes was carried out using ELE Auto-Test 2000, (England) testing machine with pace rate of 2.40 KN/sec. After the compressive strength determination, the broken pieces were used for stopping the hydration using methanol/acetone mixture (1:1 v/v). The total water of the saturated paste as well as the dried paste at 105 °C for 24 hr was determined after firing at 1000 oC for 1 hr. These two values were corrected by subtracting the anhydrous ignition loss of the dry blend.

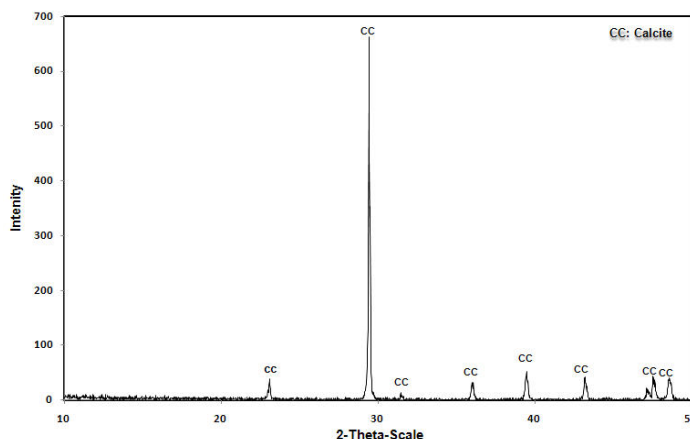


Fig. 1. XRD patterns of limestone sample.

Table 2. Mix composition of filled cements, wt %

Mix No.	OPC	Limestone
M0	100	-
MLH1	95	5
MLH2	90	10
MLH3	85	15
MLH4	80	20

The free water was calculated from the total water and combined water as follows:

$$\text{Free water} = \text{total water} - \text{combined water}$$

The total porosity was also calculated from the equation [23].

$$\varepsilon = \frac{0.99W_e X B.D X 100}{1 + W_t}$$

W_e: free water, W_t: total water, B.D: bulk density and ε : total porosity. The thermal analysis of cement paste was identified using (DT- Thermal Analyzer (Shimadzu Co, Japan. A sample of 50 mg (-45 μ m) was used. The heating rate was adjusted at 20 °C/ min. in nitrogen atmosphere.

3 RESULTS AND DISCUSSION

3.1. Water of Consistency and Setting Time.

Figure (2) shows the water of consistency as well as initial and final setting times of filled cement pastes. The water of consistency slightly decreases with limestone content in cement blend; this is related to the different particle size distribution of the samples. Limestone

cements despite their higher fineness have wider particle size distributions compared with Portland cements [24]. Addition of 5-10 wt. % limestone is associated with a notable decrease in the setting times (initial and final), due to the nucleating effect which accelerates the rate of hydration. The addition of 20 wt. % limestone has no effect on the initial setting time but slightly elongates the final setting. The elongation of final setting time may be due to the decrease of cement which has hydration properties in comparison with the limestone.

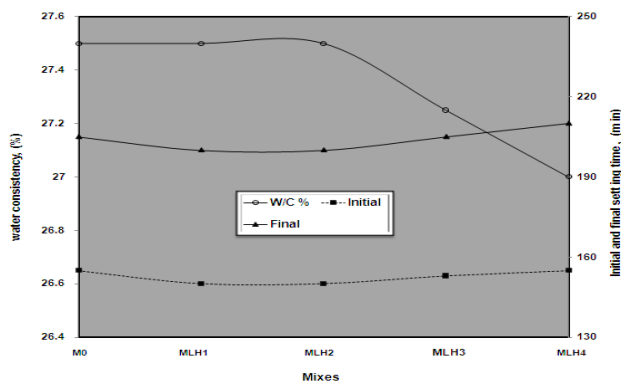


Fig. 2: Water of consistency and setting time of limestone-filled cement pastes

3.2 Thermal Analysis.

Figure (3) illustrates DTA thermograms of filled-cement pastes with 5 wt. % limestone cured in tap water for 3, 7, 28 and 90 days. The endothermic peaks located at (57.16 oC, 72.47 °C, 78.60 oC and 76.79 °C), are due to the loss of free water and CSH. The endothermic peaks at temperatures (154.47 °C, 155.55 °C, 153.43 °C and 159.21 °C), are characteristic to the dehydration of ettringite as well as carboaluminate hydrate. The intensity of peaks increases with curing time up to 90 days, due to the continuous hydration. Also, the endotherms at (481.19 °C, 480.05 oC, 476.71 °C and 478.89 °C) related to the dissociation of $\text{Ca}(\text{OH})_2$, and increase with curing time up to 90 days, due to the continuous hydration of C_2S and C_3S liberating $\text{Ca}(\text{OH})_2$.

On the other side, the endotherms located at (741.23 °C, 738.33 oC, 731.32 °C and 729.95 °C), are related to the calcination of CaCO_3 and the intensity of peaks increases up to 90 days, due to the effect of carbonation of some of portlandite $\text{Ca}(\text{OH})_2$.

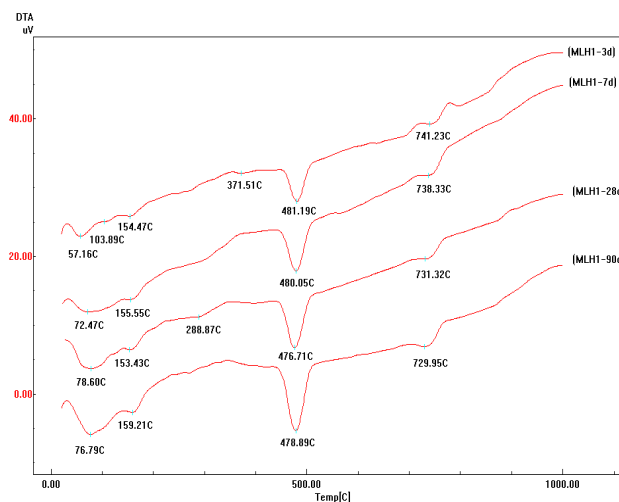


Fig. 3: DTA thermo grams of filled-cement pastes with 5 wt. % limestone immersed in tap water up to 90 days

Figure (4) shows DTA thermograms of filled-cement pastes containing 0, 5, 10, 15 and 20 wt. % limestone cured in tap water for 90 days. The endotherms at temperatures (75.24 °C, 77.31 °C, 76.79 °C, 79.96 °C and 75.19 °C), are also due to the loss of free water and CSH, while these located at (160.20 °C, 158.46 °C, 159.21 °C, 160.48 °C and 160.76), are related to the dehydration of sulphoaluminate (ettringite) as well as carboaluminate hydrates. Also, the endothermic peaks at temperatures (482.48 °C, 480.24 °C, 478.89 °C, 482.99 °C as well as 477.55 °C), are characteristic to the dehydroxylation of $\text{Ca}(\text{OH})_2$ and the intensity of peaks decreases at 20 wt. % limestone. This is also due to the dilution of portland cement. The endothermic peaks at (879.73 oC, 750.02 °C, 729.95 °C, 767.97 °C and 772.74 °C), are due to the calcination of CaCO_3 and increases with limestone content. The endotherms at ≈ 880 °C is due to the carbonation of some $\text{Ca}(\text{OH})_2$ liberated from the hydration of OPC (M0).

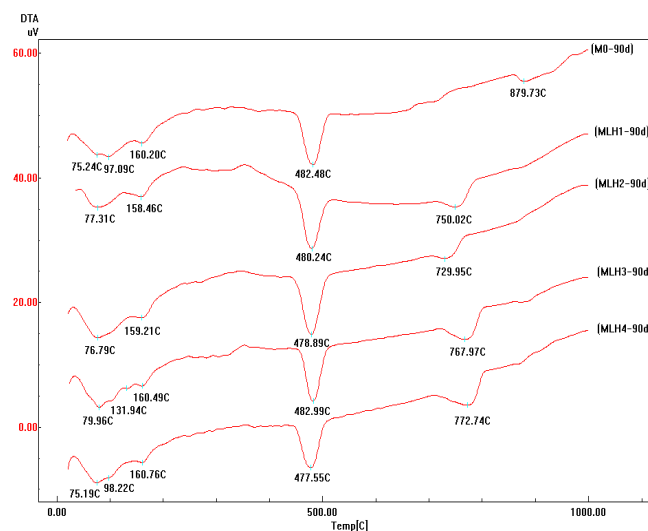


Fig. 4: DTA thermograms of filled-cement pastes with 0, 5, 10, 15 and 20 wt. % limestone at 90 days

3.3 Bulk Density.

The bulk density of limestone-filled cement pastes cured up to 90 days is graphically plotted as a function of curing time in Fig. (5). It is found that the bulk density of all cement pastes increases with curing time, due to the formation of more hydration products which are deposited in some open pores then increase the bulk density. The bulk density decreases with limestone content. This is attributed to the decrease of the amount of calcium silicate hydrate which has higher bulk density in comparison with hydrated calcium carboaluminate as well as the decrease of specific gravity of limestone in comparison with Portland cement. The decrease of tobermorite (CSH) in filled cement is due to the dilution of OPC on the expense of limestone content. Also, the mix 5 wt. % limestone has higher bulk density than the other limestone-filled cement pastes which acts as a nucleating agent that accelerates the rate of hydration forming more hydration products and therefore the bulk density increases [21].

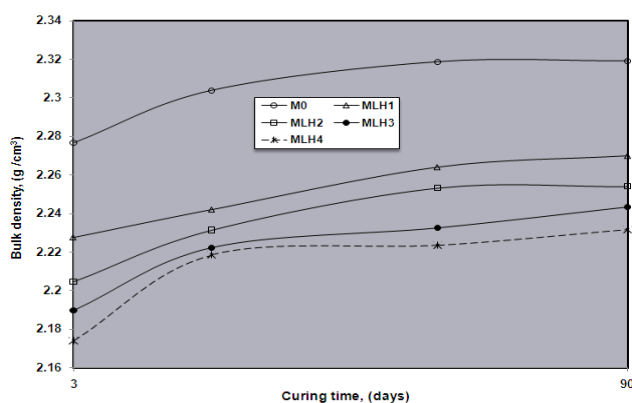


Fig. 5: Bulk density of limestone-filled cement pastes up to 90 days

3.4 Compressive Strength.

The values of compressive strength of limestone-filled cement pastes cured up to 90 days is graphically plotted as a function of curing time in Fig. (6). It is clear that the compressive strength increases with curing time due to the formation of more hydration products deposited in the open pores. Therefore, the total porosity decreases and then the bulk density as well as the compressive strength increase. The strength development depends primarily on the formation of hydrated calcium silicate as the main hydration product, which is precipitated into the water filled spaces to form a more compact body with high strength. This is mainly attributed to the crystallization of initially formed hydrates, having strong binding forces and/or their transformation into other hydration products having weaker binding forces [25, 26]. It is clear that the hardened filled cement paste with 5 wt. % limestone shows higher compressive strength up to 7 days than that of the other cement pastes. This is due to the formation of dense structure and crystallization of highly polymerized calcium silicate hydrate, as well as the nucleating agent which accelerates the rate of hydration at early ages.

The hydration products especially CSH are proportional to the compressive strength. There is a small difference in the compressive strength of filled cement pastes containing 10-20

wt. % limestone. It can be said that 5 wt. % acts as a nucleating agent for portland cement and can be used in portland cement production. On the other side, the addition of 10-20 wt. % limestone produces blended or mixed cement with low strength.

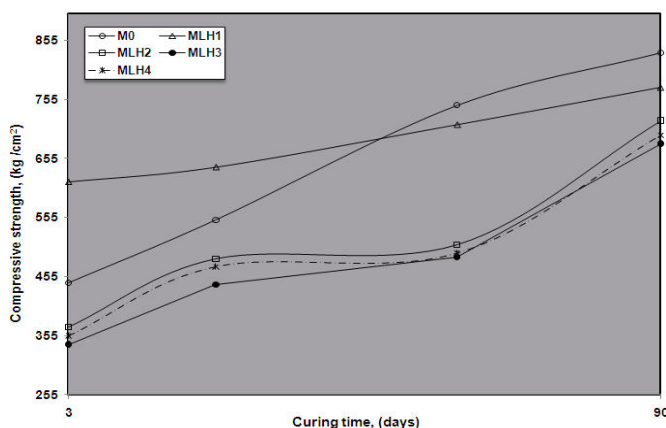


Fig. 6: Compressive strength of limestone-filled cement pastes up to 90 days

3.5 Scanning Electronic Microscope Observation.

Figure (7) clarifies SEM photomicrographs of OPC and limestone filled –cement pastes with 5 and 20 wt. %. Plate (a) represents OPC paste at 3 days of hydration and contains small amount of fibrous tobermorite (CSH) and small portlandite (CH). On the other side, (b) shows filled-cement paste with 5 wt. % limestone at 3 days where CSH filling the pores of sample and this evidence shows that the addition of 5 wt. % limestone increases the compressive strength at early ages of hydration. Fig. 7 (c) clarifies OPC paste at 28 days, it is seen that the amount of fibrous tobermorite increases with hydration filling the pores present in the sample with some cubic portlandite. Fig. 7 (d) represents the filled-cement paste with 5 wt. % limestone at 28 days, which shows crystalline gehlenite hydrate (C_2ASH_8) formed at later ages of hydration leading to the decrease of the compressive strength in comparison with OPC at 28 days. Also, Fig. 7 (e) illustrates filled- cement paste with 5 wt. % limestone at 90 days where the surface coated with gel CSH. The presence of calcium carboaluminate hydrates accelerates the rate of hydration while the compressive strength decreases if compared with OPC paste at 90 days. Fig. 7 (f) shows the hydration of filled-cement paste with 20 wt. % limestone at 90 days. It is noted that the amount of calcium carboaluminate hydrate increases with limestone content up to 28 days. The increase of carbonate ions in the cement paste produced in the transformation of monosulfaluminate to monocarboaluminate which accelerates the rate of hydration while the compressive strength decreases with the limestone content.

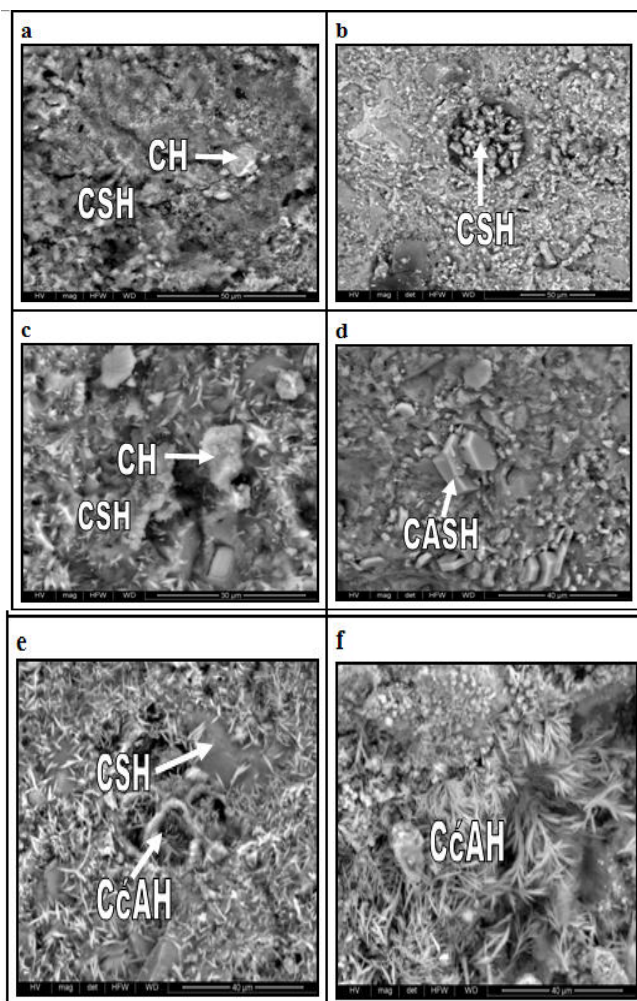


Fig.7: SEM photomicrographs. (a): OPC paste at 3 days, (b): 5 wt. % limestone at 3 days, (c): OPC paste at 28 days, (d): 5 wt. % limestone at 28 days, (e): 5 wt. % limestone at 90 days and (f): 20 wt. % limestone at 90 days.

4 Conclusions

From the above results, it can be concluded that:

1. Addition of 5-10 wt. % limestone is associated with a notable decrease in the setting times (initial and final), due to the nucleating effect which accelerates the rate of hydration. While the addition of 20 wt % limestone elongates the final setting time due to the decrease of cement which delays the hydration properties.
2. Limestone fills the pores between the cement particles due to the formation of carboaluminate phases.
3. The replacement of OPC by 5 wt. % of limestone increases the compressive strength at early ages, due to the nucleating effect and can be used in portland cement production. The addition of 10-20 wt. % limestone can be used in the production of blended cement.

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