

# ADDITION OF LIMESTONE IN THE LOW HEAT PORTLAND CEMENT

## Part 2.

HAMDY EL-DIDAMONY, EL-SAYED EL-ALFI\*

*Faculty of Science, Zagazig University,  
Zagazig, Egypt*

*\*National Research Centre,  
Dokki, Cairo, Egypt*

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The influence of substitution of clinker by fine limestone on the properties of the low heat Portland cement pastes up to 90 days was studied. The results show that the substitution of 4-6 wt.% of clinker by fine limestone (76  $\mu\text{m}$ ) improves the rate of hydration up to 90 days. In addition, as the amount of limestone increases the heat of hydration and the free lime content slightly enhance, while the total porosity decreases and the compressive strength enhances at early ages.

### INTRODUCTION

The rise in temperature in the interior of a large concrete bodies due to the heat developed by the hydration of cement can lead to serious cracking. For this reason, it is necessary to limit the rate of heat evolution of the cement paste by using the low heat Portland cement (Type IV). In some application, a very low early strength of this cement may be a disadvantage. Therefore, the substitution of clinker by fine limestone in the low heat Portland cement with the aim *to improve* its physico-mechanical properties was studied.

Many authors have been tried to explain the influence of finely ground limestone on the physico-mechanical properties of filled cement [1 - 3]. Most common *hypotheses* are the filler effect of fine particles, the increase of rate of hydration of the clinker, the formation of monocarboaluminate and the modification of microstructure of hardened cement paste.

The addition amount of filler to Portland cement reduces the rate and total heat released as well as the heat evolution time [4]. Increasing filler content therefore reduces the temperature rise in the concrete body. The acceleration of hydration due to the action of calcite on the aluminates and  $\text{C}_3\text{S}$  becomes evident from the microcalorimetry. Barker and Mattheus [4] found that the increase amount of limestone filler in Portland cements progressively decreases the rate of heat evolved during the first 72 hours.

The effect of calcium and magnesium carbonate addition on the hydration of Portland cement is reported to the rate of hydration and compressive strength [5, 6]. The higher strength was attributed to the formation of a dense structure and to the crystallization of a highly polymerized calcium silicate hydrate.

The addition of limestone to cement paste affects the activation of hydration and crystallization of CSH, which ultimately affects the physico-mechanical properties of the cement [7]. The effect of  $\beta\text{-C}_2\text{S}$  and  $\text{C}_3\text{S}$  contents on compressive strength,  $\text{Ca}(\text{OH})_2$  and water contents are described.

The characterization of high-strength concrete using low heat Portland cement was studied [8]. The workability of the concrete is inferior to that of concrete with ordinary Portland cement due to low water to cement ratio. Moreover, there are concerns about thermal cracking as the high strength concrete contains a great amount of cement. To solve this problem, the application of low heat Portland cement with the addition of limestone to high strength concrete was examined. The slump and long-term compressive strength of low heat Portland cement concrete was higher than that of ordinary Portland cement concrete.

The aim of the present work is to study the influence of substitution of cement clinker by limestone up to 10 wt.% on the physico-mechanical properties and the kinetics of hydration of laboratory prepared low heat Portland cement pastes.

### EXPERIMENTAL PART

The material used in this study, namely limestone, clay, pyrite ash and gypsum were provided by Suez Portland Cement Company, Egypt. Table 1 shows the chemical analysis of these materials. The materials were ground in laboratory steel ball mill to pass through a 200-mesh sieve. To prepare the low heat Portland cement [9], the ingredient were homogenized, mixed with water, moulded into a compact mass and fired at 1200 °C for two hours, then ground, remoulded with  $\text{CCl}_4$  and refired at 1450 °C for two hours. The clinker

Table 1. Chemical composition of starting materials (wt.%).

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	ignition loss
limestone	2.61	0.93	0.38	52.58	0.05	0.12	43.03
clay	69.96	9.17	3.91	4.50	1.09	1.61	4.55
pyrite ash	7.92	11.45	66.15	3.92	2.05	0.95	5.17

Table 2. Chemical and phase composition of the prepared low heat Portland cement.

chemical composition (wt.%)						mineralogical composition (wt.%)			
SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	alite	belite	aluminate	ferrite
23.20	4.39	5.86	61.39	1.15	1.68	35.80	39.62	1.78	17.81

was tested by determining the insoluble residue and free lime contents.

The chemical and mineralogical composition (using Bogue equation) of the prepared low heat Portland cement [ASTM C150-92] Type IV are given in table 2.

The prepared clinker (specific surface area 3150 g cm<sup>-2</sup>) was substituted with 0, 2, 4, 8 and 10 wt.% of fine limestone (76µm) with constant amount of gypsum (5 wt.%). The water of consistency [10] and the setting time [11] were determined. The pastes were mixed with the water of consistency, moulded in 0.5-inch cubic moulds for 24 hours, demoulded then immersed in tap-water up to 90 days. The kinetic of hydration were followed by the determination of heat of hydration [12], free lime [13] and combined water contents after firing at 1000 °C for 30 minutes minus the weight of water in Ca(OH)<sub>2</sub>.

The total porosity, bulk density and compressive strength were also measured up to 90 days. The mixing, moulding, curing and stopping of hydration were described elsewhere [14].

## RESULTS AND DISCUSSION

The water of consistency as well as initial and final setting time of the cement pastes are presented in figure 1. The results show that the water of consistency as well as setting time of all cement pastes slightly decrease with limestone content. This is because the limestone increases the number of precipitation sites for deposition of C-S-H gel and calcium hydroxide from solution. In addition, the limestone forms monocarbo-aluminate hydrate, which needs less water amount than that of ettringite.

The heat of hydration of cement pastes cured up to 90-days is presented in figure 2. The heat of hydration increases with curing time for all hardened cement pastes due to the continuous hydration of the cement paste accompanied by the heat liberation. In addition, it can be seen that the heat of hydration enhances at early ages up to 90 days when the amount of the limestone

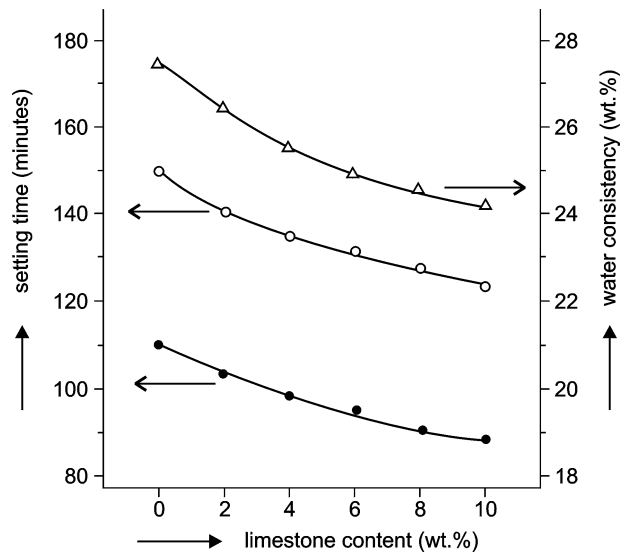


Figure 1. Water of consistency, initial and final setting times of low heat Portland cement pastes with different amounts of limestone.

△ - water of consistency, ● - initial setting time, ○ - final setting time

content increases. The addition of limestone accelerates the hydration of C<sub>3</sub>S especially at the early ages. This accelerating effect may be related to a modification of the hydrating C<sub>3</sub>S surface and its nucleating effect [1 - 3]. The low heat Portland cement without limestone shows sharp increase of heat up to 7 days, slight increase from 7 - 28 day and then sharp increase up to 90 days. The first sharp increase is mainly due to the hydration of alite in the early ages. The slow and then rapid increase within 7-90 day is mainly attributed to the hydration of belite.

The addition of limestone increases the rate of hydration and then the amount of heat liberated at early ages up to 28-days. This is because the limestone activates the hydration reaction of the alite and maybe the belite. The cement with 6 wt.% limestone gives the

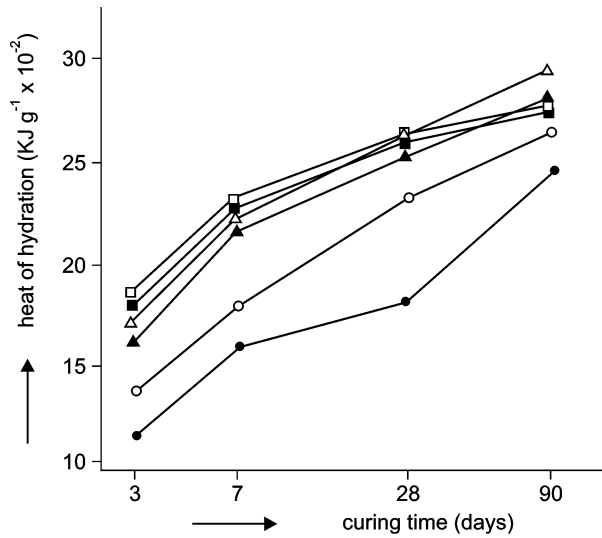


Figure 2. Heat of hydration of low heat Portland cement pastes with different ratios of limestone.  
 ● - 0 wt.%, ○ - 2 wt.%, ▲ - 4 wt.%, △ - 6wt.%, ■ - 8 wt.%, □ - 10 wt.% limestone

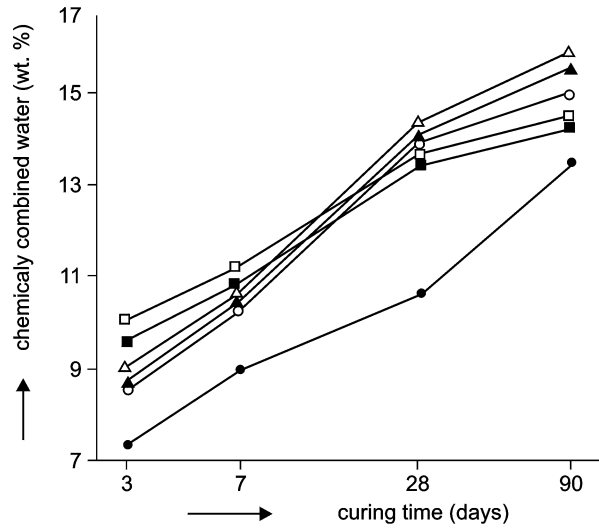


Figure 3. Combined water content of low heat Portland cement pastes with limestone in relation to curing time.  
 ● - 0 wt.%, ○ - 2 wt.%, ▲ - 4 wt.%, △ - 6wt.%, ■ - 8 wt.%, □ - 10 wt.% limestone

highest rate of hydration as well as the amount of heat liberated than the others at later ages (90 day). The addition of limestone also increases the rate of hydration and the amount of liberated heat at later ages 7 - 90 day. The increased of limestone content is accompanied by a decrease in the clinker content of the cement and, therefore, the rate of hydration is slightly increases.

The combined water content of cement pastes is plotted as a function of curing time in figure 3. The combined water content increases with curing time for all hardened cement pastes. As the amount of limestone increases the combined water content enhances at early ages. On the other side, the low heat cement without limestone gives a lower amount of combined water up to 28-days than those containing limestone. This indicates that the limestone plays an important role in the hydration of low heat Portland cement. In addition, cements with 4 and 6 wt.% limestone give a higher amounts of combined water at 28-90 days than the other cement pastes. The increase of limestone is accompanied by a decrease in the clinker content. Therefore, the cements with 8 and 10 wt.% limestone give a higher amount of combined water at 3-days and a lower amount at 90 days. This shows the role of limestone in activation of  $C_3S$  and maybe  $\beta-C_2S$  at early ages of hydration. The addition of a small amount of limestone (4 - 6 wt.%) also increases the combined water content with curing time up to 90 days.

The free lime contents of hardened cement pastes are plotted as a function of curing time in figure 4. The free lime content increases with curing time for all cement pastes due to the continuous hydration of silicate phases that liberate free  $Ca(OH)_2$ . The most of free lime was liberated at early ages (3-days) while a

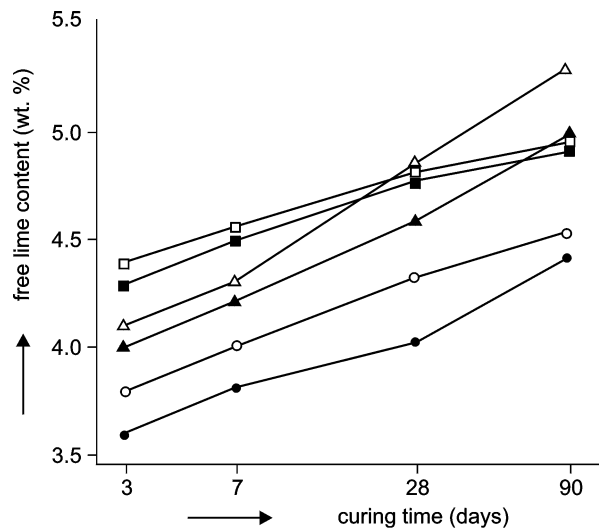


Figure 4. Free lime content of low heat Portland cement pastes as a function of curing time as well as limestone content.  
 ● - 0 wt.%, ○ - 2 wt.%, ▲ - 4 wt.%, △ - 6wt.%, ■ - 8 wt.%, □ - 10 wt.% limestone

slight increase was obtained at later ages up to 90-days for all cement pastes. This is mainly due to the fact that the low heat Portland cement contains lower amounts of alite liberating more  $Ca(OH)_2$  and having a higher rate of hydration at early ages than the belite, which amount is increasing at later ages. Also, as the amount of limestone increases the free lime content sharply enhances at early ages up to 3 days and then slightly up to 90 days. This is attributed to the activated alite that liberates more  $Ca(OH)_2$  than belite during the hydration

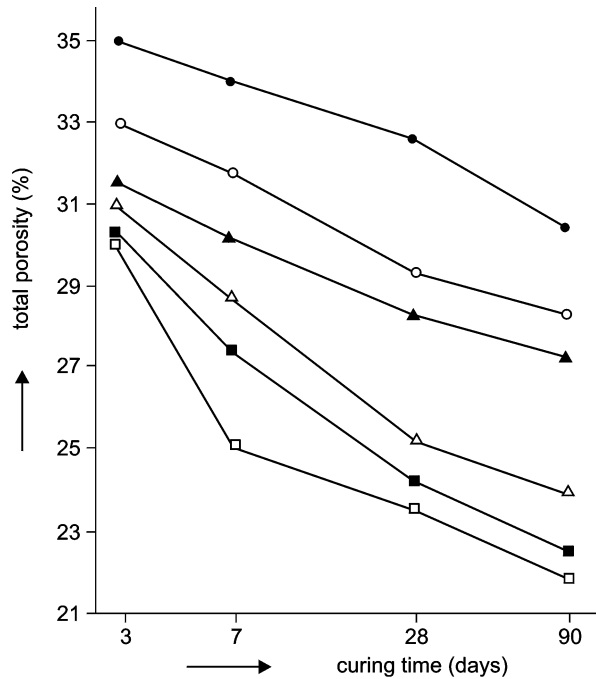


Figure 5. Total porosity of low heat Portland cement pastes with limestone additions.  
 ● - 0 wt.%, ○ - 2 wt.%, ▲ - 4 wt.%, △ - 6wt.%, ■ - 8 wt.%, □ -10 wt.% limestone

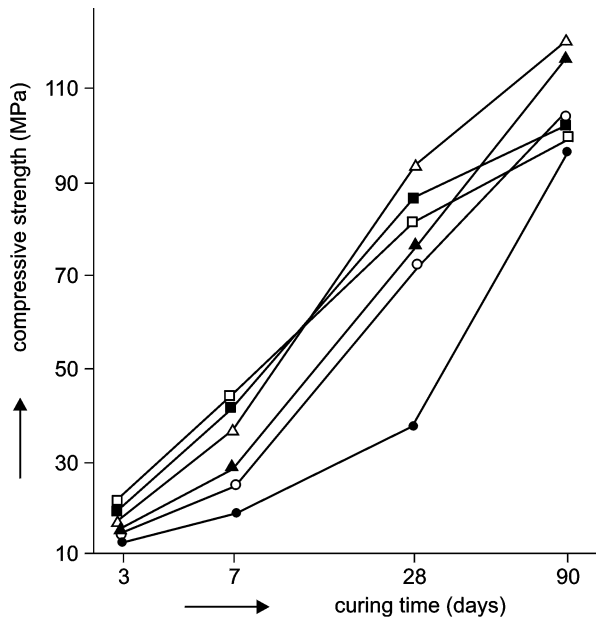


Figure 6. Compressive strength of low heat Portland cement pastes with different proportions of limestone.  
 ● - 0 wt.%, ○ - 2 wt.%, ▲ - 4 wt.%, △ - 6wt.%, ■ - 8 wt.%, □ -10 wt.% limestone

The total porosity of the hardened cement pastes cured up to 90 days is illustrated in figure 5. The total porosity of all hardened cement pastes decreases with curing time due to the filling up of a part of the available

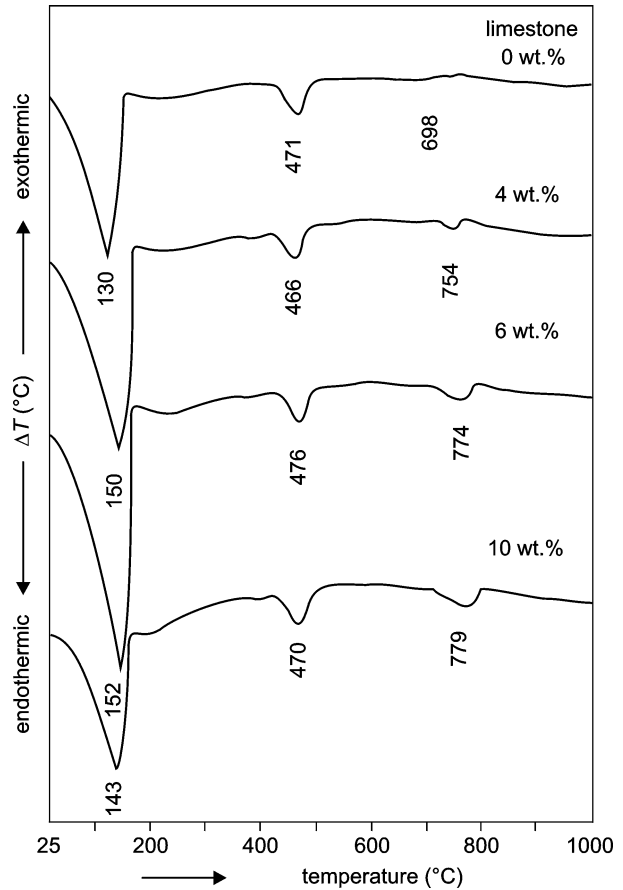


Figure 7. DTA thermograms of low heat Portland cement pastes with various proportions of limestone.  
 ● - 0 wt.%, ○ - 2 wt.%, ▲ - 4 wt.%, △ - 6wt.%, ■ - 8 wt.%, □ -10 wt.% limestone

pores with the hydration products. The low heat Portland cement pastes without limestone exhibit higher values of porosity than those with limestone up to 90 days. On the other hand, as the limestone content increases, the total porosity decreases, especially at early ages. Soroka [15-17] illustrated that the strength increase at a later age is similar for all fillers; while at early ages the effect of calcareous fillers is greater than the others. The author suggests that the limestone filler act as an accelerator and the filler effect is brought about by the increased rate of hydration associated with their incorporation in Portland cement mixes. The filler effect on strength is primarily an accelerating effect on the cement hydration with the filler serving as crystallization nuclei, and it increases with the fineness and content of the filler.

The compressive strength of the hardened cement pastes cured for 3, 7, 28 and 90 days is graphically plotted in figure 6. The compressive strength increases with curing time for all hardened cement pastes. This is attributed to the increasing amount of hydrated products (especially tobermorite gel) leading to an increase in the compressive strength of cement paste. The cement paste

without limestone has lower values of compressive strength at all ages than those containing limestone. In addition, as the limestone content increases, the hardening enhances especially at early ages up to 28-days. This is attributed to the higher degree of hydration of cement with limestone than those without limestone. In addition, when the limestone content increases, calcium hydroxide crystallizing in large crystals is concentrated in some areas to form bridge between the calcareous grains. The increased binding capacity of carboaluminate as compared to other  $C_3A$  hydrates is probably affected by its compact structure [18]. On the other side, the cements containing 4 and 6 wt.% limestone give the highest values of compressive strength at 90 days. This is because the small amount of limestone (< 5 wt.%) enhances the strength at early ages. This is attributed to the formation of a dense structure and crystallization of a highly polymerized calcium silicate hydrate [5, 6].

Figure 7 illustrates the DTA thermograms of the low heat Portland cement pastes containing 0, 4, 6 and 10 wt.% limestone hydrated up to 90 days. It is clear that the endothermic peak of the dissociation of  $Ca(OH)_2$  slightly increases with limestone content as revealed also from the results of the chemical analysis. In addition, as the amount of limestone increases up to 6 wt.% the dehydration of interlayer water of calcium silicate hydrate enhances. On the other side, the sample containing 10 wt.% limestone gives a lower amount of dehydration peak. An elevated content of limestone is accompanied by a decrease in the clinker content. Therefore, the cement containing 10 wt.% limestone gives a lower amount of interlayer water of hydrated products than the other cements at 90 days due to the decrease of the amount of clinker. These results are confirmed by the results of combined water content and the compressive strength, where as the limestone increases up to 6 wt.%, the low heat Portland cement is more activated and the amount of hydration product increases. The endothermic peak at 780 °C is mainly attributed to the decomposition of limestone. The intensity of the peak increases with the amount of  $CaCO_3$  added.

## CONCLUSION

The development of new process and better quality control will lead to a more active clinker, i.e. a clinker, which can be used in high performance concrete, but will need to be spread for the more common uses. The addition of filler is a possibility to achieve this in the most satisfactory way. The main results obtained from this investigation are summarized as follows:

The substitution of clinker by limestone slightly decreases the water of consistency as well as the setting time of cement paste.

The addition of 2-10 wt.% limestone to low heat Portland cements enhances the heat of hydration up to 90 days.

The combined water content increases with the limestone content at early ages and up to 6 wt.% at later ages.

The filled cement shows lower values of porosity and higher compressive strength than the pure low heat Portland cement especially at early ages. This suggests that the limestone acts as an accelerator and filler.

Till now there is no publication for the activation of belite by the addition of limestone. Therefore, the following studies will focus on the hydration characteristics of  $\beta$ - $C_2S$  by the addition of limestone.

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*Submitted in English by the authors.*

## PŘÍDAVEK VÁPENCE K PORTLANDSKÉMU CEMENTU S NÍZKÝM HYDRATAČNÍM TEPEM ČÁST 2

HAMDY EL-DIDAMONY, EL-SAYED EL-ALFI\*

*Faculty of science, Zagazig University, Zagazig, Egypt*

*\*National Research Centre, Dokki, Cairo, Egypt*

Byl studován vliv náhrady slínku vápencem na vlastnosti past portlandského cementu s nízkým hydratačním teplem během 90 dnů. Výsledky ukazují, že náhrada 4 - 6 hmotn.% slínku vápencem mletým vápencem (76  $\mu$ m) zvyšuje hydratační rychlost po dobu 90 dnů. Dále roste s obsahem vápence hydratační teplo a obsah volného vápna, zatímco celková porozita klesá a zvyšuje se pevnost v tlaku v počátečních stádiích tuhnutí.