

# ADDITION OF LIMESTONE IN THE LOW HEAT PORTLAND CEMENT Part 1.

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Submitted March 11, 1999; accepted November 13, 1999.

*The substitution of about 50 wt.% of gypsum by limestone in Portland cement affects the particle size distribution, decreases the total porosity and accelerates the rate of hydration of cement paste. The effect of partially up to fully substitution of gypsum in the laboratory prepared low heat Portland cement on the characteristics of the hardened cement pastes up to 90 days of hydration was studied. The results show that the substitution of 60 wt.% of gypsum by fine limestone improves the rate of hydration at early ages up to 28 days. In addition, the elevated amount of limestone increases the heat of hydration and enhances the compressive strength at early ages.*

## INTRODUCTION

To discuss the effect of limestone on the physico-mechanical properties of low heat Portland cement, the attention must be paid to whether it is a substitution of the gypsum or an addition to the clinker. Not all clinkers accept the same percentage of limestone; it depends considerably on the fineness and the composition of the cement, i.e. the reactivity of the clinker [1].

The effect of fillers on cement properties has been subject of many experimental studies. The change in strength occurs due to several mechanisms: filler action leading to change the particle size distribution filling the space by substituting fine particles of cement [2-5], acceleration of the hydration process, formation of calcium monocarboaluminate hydrate, modification of the thermodynamic assemblage and the morphology of the hydration reactions.

According to Regourd [6], limestone fillers improve the compactness of composite cements. The consumption of calcite, the formation of carboaluminate, the acceleration effect on the hydration of  $C_3A$  and  $C_3S$ , the changes in the C-S-H as well as the depth of the "transition area" between the filler and the cement paste are different factors specific to the reactivity of limestone filler.

The addition of calcium and magnesium carbonate increases the rate of hydration and compressive strength [7, 8]. The higher strength was attributed to the formation of a dense structure and crystallization of a highly polymerized calcium silicate hydrate.

Negro [9] concluded that replacement of gypsum by limestone up to 50 wt.% was possible without adverse effects on the set, shrinkage and compressive properties of Portland cement. At low-

-level limestone also acts as an active component in the hydration reaction. Puchyr and Toborsky [10] found that cement ground with 2-5 wt.% limestone had no decrease in the physical properties but improved binding properties.

The characterization of high – strength concrete using low heat Portland cement was studied [11]. The workability of high strength concrete is inferior to that of concrete with ordinary Portland cement due to low water cement ratio, moreover, thermal cracking occurs because high strength concrete contains a great amount of cement. To solve this problem, the application of low heat Portland cement and limestone powder as high strength concrete was examined. The slump of high strength as well as long term compressive strength of low heat Portland cement concrete is higher than that of ordinary Portland cement concrete.

The aim of the present work is to study the characteristics of laboratory prepared low heat Portland cement containing fine limestone as setting retarder instead of gypsum. The gypsum content (5 wt.%) was gradually substituted by the limestone. The physico-mechanical properties of the cement pastes such as the water of consistency, setting time, total porosity, bulk density and compressive strength were determined. In addition, the kinetics of hydration such as the heat of hydration, free lime and combined water contents were estimated up to 90 days.

## EXPERIMENTAL PROCEDURE

The materials 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.

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	43.02
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	0.92	5.20

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	36.0	39.52	1.74	17.81

Table 3. Water of consistency and setting time of the cement pastes.

physical properties	mix no.					
	M <sub>0</sub>	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>	M <sub>4</sub>	M <sub>5</sub>
water of consistency (wt.%)	28.5	28.5	28.0	28.0	27.5	27.0
initial setting time (min)	135	125	120	110	105	100
final setting time (min)	245	230	215	210	205	195

The materials were ground in a laboratory steel ball mill to pass through sieve No. 200, B.S. To prepare the low heat Portland cement (ASTM specification C150 – 68 and BS: 1370 : 1991), the ingredients of the mix were thoroughly homogenized, mixed with water, molded into a compact mass and heated at 1200 °C for two hours, then ground (200 mesh), remolded with CCl<sub>4</sub> and fired at 1450 °C for two hours. The complete reaction was tested by determining free lime content and insoluble residue. The clinker was ground with 5 wt.% gypsum, which was gradually substituted by limestone in the ratios 1, 2, 3, 4 and 5 wt.%. The mixes were denoted as M<sub>0</sub>, M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub>, M<sub>4</sub> and M<sub>5</sub> respectively. The chemical and mineralogical composition of the prepared low heat Portland cement (ASTM specification (C150 – 68) are given in table 2.

The pastes were molded in 0.5 inch cubic moulds, cured in humidity chamber at 23 ± 1 °C for 24 hours, then immersed in fresh water for the time of testing. The mixing of the paste was carried out with the water of consistency [12] and the setting time was determined [13]. The kinetics of hydration was followed by the determination of the heat of hydration [14], free lime [15] and combined water contents. The total porosity, bulk density and compressive strength were also measured. The combined water content was estimated on the basis of ignition loss of dried sample heated at 1000 °C for 30 minutes minus the weight of water in

Ca(OH)<sub>2</sub>. The stopping of hydration of cement pastes was described elsewhere [16]

## RESULTS AND DISCUSSION

The water of consistency as well as initial and final setting times of cement pastes is shown in table 3. The results show that the water of consistency as well as the initial and final setting times of all cement pastes slightly decrease with limestone content. This is because the addition of limestone increases the plasticity of cement paste. This may be attributed to the effect of limestone as an active component in the hydration reaction of Portland cement, i.e. the rate of hydration increases and the amount of hydration products enhances. In addition, the limestone forms monocarboaluminate hydrate, which needs less water than that of ettringite.

The heat of hydration of cement pastes cured for 3, 7, 28 and 90 days are presented in figure 1. The heat of hydration increases with curing time for all hardened cement pastes. This is due to the increase in rate of hydration of cement paste, which is accompanied by the liberation of heat. In addition, as the amount of fine limestone increases, the heat of hydration liberated enhances at early ages (3 and 7 days). This is because the fine limestone activates the hydration reaction of C<sub>3</sub>S [6]. At later ages (28 and 90 days), when the amount of the limestone addition increases, the rate of

hydration reaction and the liberated heat increase due to the same effect of the fine limestone on the hydration of  $\beta$ -C<sub>2</sub>S. The results show that cements (M<sub>0</sub>) and (M<sub>1</sub>) have lower amount of heat of hydration at all ages of curing than the other cements. This indicates that limestone activates the hydration of alite and probably belite phases of the cement.

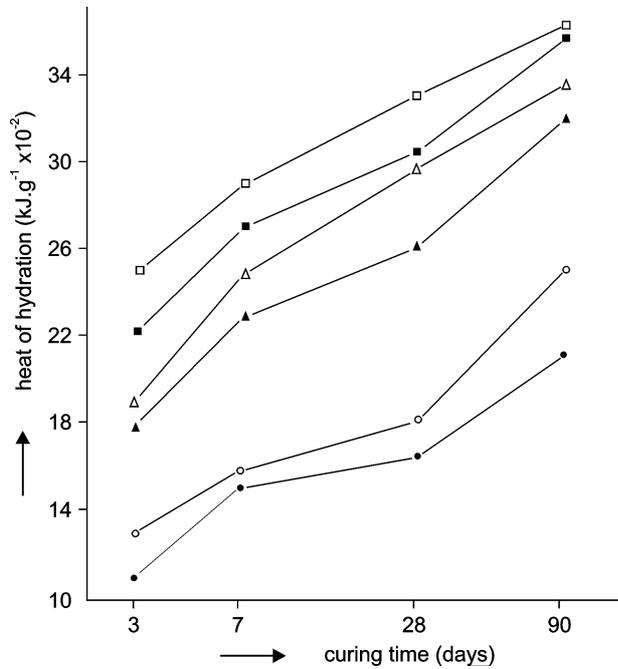


Figure 1. Heat of hydration of the low heat Portland cement pastes.

● - M<sub>0</sub>, ○ - M<sub>1</sub>, ▲ - M<sub>2</sub>, △ - M<sub>3</sub>, ■ - M<sub>4</sub>, □ - M<sub>5</sub>

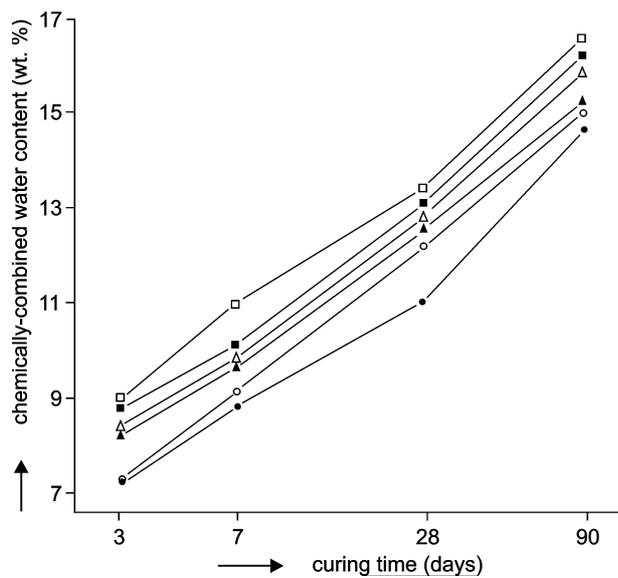


Figure 2. Combined water content of the low heat Portland cement pastes.

● - M<sub>0</sub>, ○ - M<sub>1</sub>, ▲ - M<sub>2</sub>, △ - M<sub>3</sub>, ■ - M<sub>4</sub>, □ - M<sub>5</sub>

The combined water content of cement pastes cured for 3, 7, 28 and 90 days are plotted in figure 2. It can be seen that the combined water content increases with curing time for all hardened cement pastes, due to the progress of hydration and to increasing the amounts of hydration products. In addition, as the amount of limestone increases, the combined water gradually enhances for all cement pastes with curing time. This indicates that the limestone plays an important role in the hydration of low heat Portland cement. On the other hand, M<sub>0</sub> has lower values of combined water than the other cement pastes at all ages of hydration and the amount of combined water content increases with the substituted limestone. Also, the results show that when about 50 wt.% of gypsum is substituted by a limestone the combined water increases linearly up to 90-days. This indicates that the substitution of 50 wt.% and more improves the hydraulic properties of the low heat Portland cement [9].

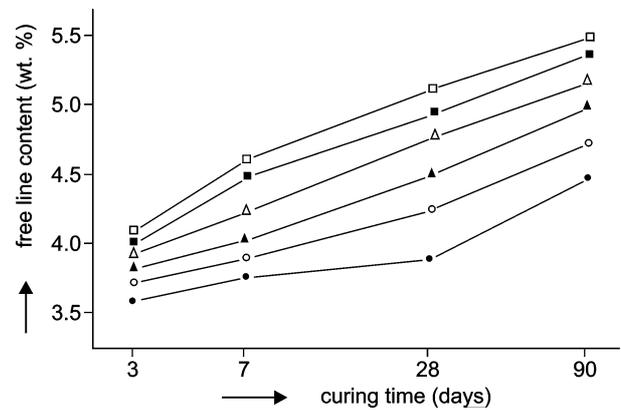


Figure 3. Free lime content of the low heat Portland cement pastes.

● - M<sub>0</sub>, ○ - M<sub>1</sub>, ▲ - M<sub>2</sub>, △ - M<sub>3</sub>, ■ - M<sub>4</sub>, □ - M<sub>5</sub>

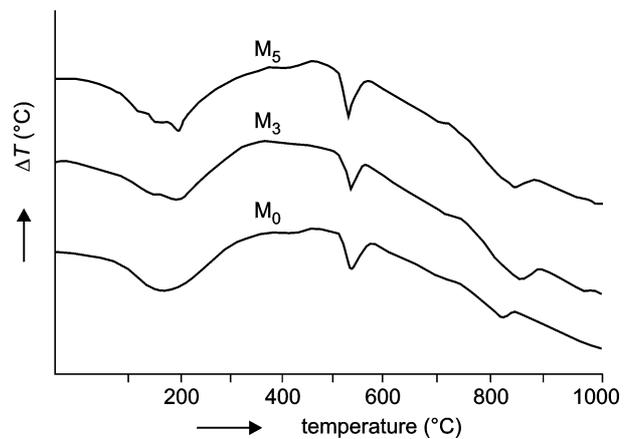


Figure 4. DTA thermograms of the cement pastes with 0, 3, 5 wt.% limestone.

The free lime contents of hardened cement pastes are plotted as a function of curing time in figure 3. The free lime content increases with curing time for all cement pastes due to the continuous hydration of silicate phases that liberate free  $\text{Ca(OH)}_2$ . It can be seen that most of the free lime content ( $\geq 3.5$  wt.%) was liberated at early ages (3 days) while a small increase was obtained at later ages up to 90 days ( $\geq 4.8$  wt.%) for all cement pastes. This is mainly due to the fact that the low heat Portland cement contains low amounts of alite phase that liberates more  $\text{Ca(OH)}_2$  and has a higher rate

of hydration at early ages comparing to belite, which amount is higher at later ages. The results show that as the limestone increases the free lime content slightly enhances. This can be seen also from the DTA thermograms of cement pastes containing 0, 3 and 5 wt.% limestone hydrated for 28 days figure 4. Sample with only 5 wt.% gypsum without limestone shows the peak of the dissociation of CSH with sulfoaluminate hydrate. Sample containing 3 wt.% limestone and 2 wt.% gypsum illustrates two endothermic peaks at 153 and 199 °C due to the decomposition of CSH as well as the carboaluminate hydrate. The peak of calcium carboaluminate hydrate at 200 °C increases with the increase in limestone content (5 wt.%).

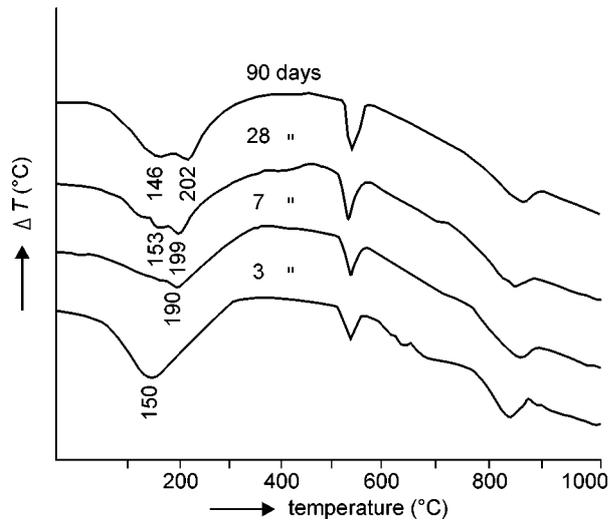


Figure 5. DTA thermograms of the low heat Portland cement with 5 % limestone curing up to 90 days.

Figure 5 illustrates the DTA analysis of the low heat Portland cement pastes containing 5 wt.% limestone ( $M_5$ ) hydrated up to 90 days. It is clear that the endothermic peak of the dissociation of  $\text{Ca(OH)}_2$  slightly increases with curing time as revealed by the chemical analysis. In addition, the formation of carboaluminate hydrate increases with curing time; this peak is overlapped by the peak of calcium aluminate hydrate and CSH at 3-days. From 7 up to 90 days, the formation of carboaluminate hydrate increases on the expense of calcium sulfo-aluminate hydrate.

The total porosity of the hardened cement pastes cured for 3, 7, 28 and 90 days is plotted in figure 6. It is clear that the total porosity for all hardened cement pastes decreases with curing time due to the filling up of a part of the available pore volume with the hydration products. In addition, as the amount of limestone

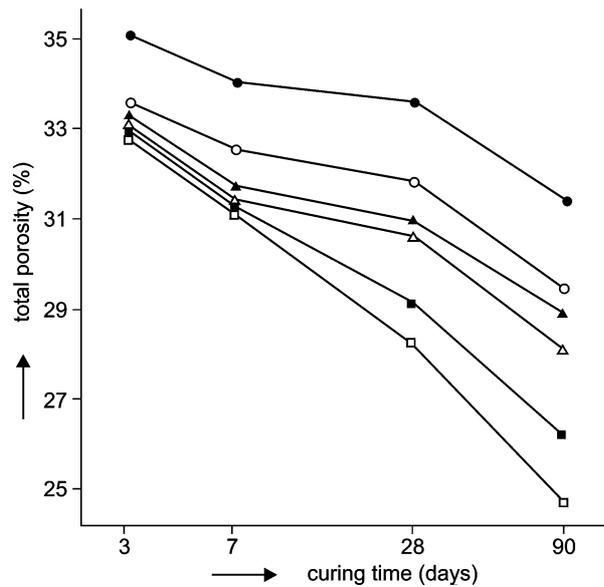


Figure 6. Total porosity of the low heat Portland cement pastes. ● -  $M_0$ , ○ -  $M_1$ , ▲ -  $M_2$ , △ -  $M_3$ , ■ -  $M_4$ , □ -  $M_5$

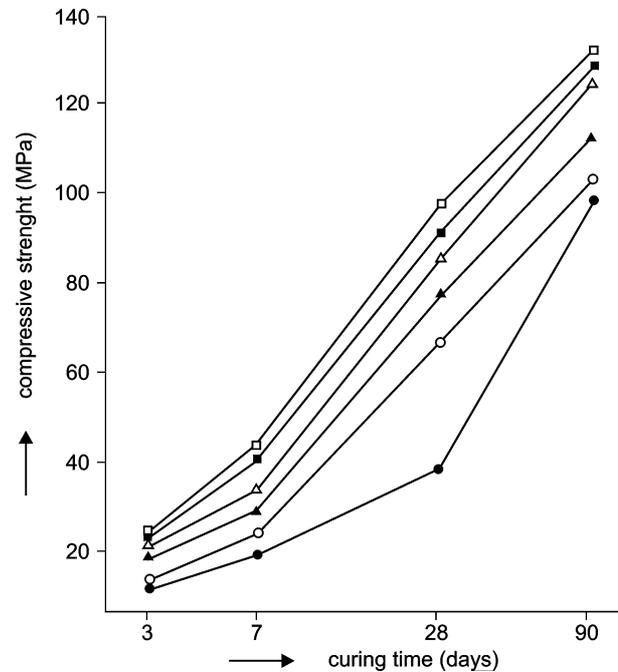


Figure 7. Compressive strength of the low heat Portland cement pastes. ● -  $M_0$ , ○ -  $M_1$ , ▲ -  $M_2$ , △ -  $M_3$ , ■ -  $M_4$ , □ -  $M_5$

increases the porosity decreases, due to the formation of a dense structure and crystallization of a highly polymerized calcium silicate hydrate [7].

The compressive strength of the hardened cement pastes cured for 3, 7, 28 and 90 days is plotted in figure 7. The compressive strength increases with curing time for all cement pastes. This is attributed to the increase of the amount of hydrated products especially tobermorite gel (the main source of compressive strength), so, this leads to a corresponding increase in the compressive strength of the hardened cement pastes. In addition, it can be seen that as the amount of limestone increases the compressive strength enhances. The cement with gypsum alone ( $M_0$ ) gives a lower rate of hardening up to 28-days, then increases at latter ages up to 90 days. On the other side, ( $M_5$ ) with only 5 wt.% limestone gives a maximum rate of hardening at all curing times. These results are in a good agreement with the kinetics of hydration and total porosity, which indicate that the fine limestone plays an important role in the activation of silicate phases of low heat Portland cement at all ages.

#### CONCLUSIONS

The substitution of gypsum by limestone slightly decreases the water of consistency as well as the setting time of cement paste due to the filling of pores by limestone, which accelerates the setting of the cement paste.

The heat of hydration increases with the amount of substituted limestone up to 90 days. The limestone activates the hydration of alite and probably belite.

As the amount of limestone increases, the total porosity decreases and accordingly the compressive strength enhances. The kinetics of hydration is in a good agreement with those of the mechanical properties.

Most of the free lime content ( $\geq 3.5$  wt.%) was liberated at early ages (3 days) while a little increase was obtained at latter ages up to 90 days ( $\geq 4.8$  wt.%) for all cement pastes.

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Submitted in English by the authors.

#### PŘÍDAVEK VÁPENCE K PORTLANDSKÉMU CEMENTU S NÍZKÝM HYDRATAČNÍM TEPLEM - ČÁST 1.

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Náhrada přibližně 50 hmotn.% sádrovce vápencem v Portlandskému cementu ovlivňuje rozdělení velikostí částic, snižuje pórovitost a zvyšuje rychlost hydratace cementové pasty. Byl sledován účinek částečné až úplné náhrady sádrovce na vlastnosti cementové pasty během 90 dnů hydratace. Výsledky ukazují, že náhrada 60 hmotn.% sádrovce zvyšuje rychlost hydratace v počátečních stádiích až do 28 dní. Přídavek vápence zvyšuje dále v počátečních stádiích hydratační teplo a pevnost v tlaku.