



Montréal, Québec
May 29 to June 1, 2013 / 29 mai au 1 juin 2013

Early Age Properties of Steam Cured High Early Strength Cement Mortars Containing Limestone

M. A. Aqel and D. K. Panesar

Department of Civil Engineering, University of Toronto, 35 St. George Street, Toronto, ON M5S 1A4, Canada

Abstract: Since the introduction of Portland limestone cement (PLC) to the CSA A3000 2008 edition many efforts were made to evaluate the effects of Limestone Filler (LF) on the early and later age strengths of PLC concrete cured under ambient temperature. However, little attention has been given to evaluate the effect of steam curing. This paper aims to investigate the effects of LF content and size on the early age properties of steam cured high early strength cement mortars. CSA High Early Strength Cement "Type HE" was used with water to cement ratio of 0.37. The limestone filler contents were 0, 5, 10, and 15% with particle size of 3, 12 and 17 microns. Mortar and paste specimens were steam cured at 55°C for 12 and 16 hours. Compressive strength was evaluated at 12 and 16 hrs; 3 and 7 days. Heat of hydration was evaluated using Isothermal Calorimetry. Calcium hydroxide Ca(OH)_2 and calcium carbonate CaCO_3 contents were measured using Thermal Gravimetric Analysis and Differential Thermal Analysis (TG/DTA). The results showed increase in the heat of hydration and Ca(OH)_2 content with the increase in LF content and decrease in LF size. The early age compressive strength was increased with the increase in LF content and decrease in size. In general, mix designs containing LF showed better early age hydration and strength compared to control mix without LF.

1 Introduction

In recent years, Portland limestone cement (PLC) has gained interest in the cement manufacturing and construction industries. However the implementation of this type of cement is still limited owing to the understanding of the role of limestone on hydration kinetics and the evolution of hardened properties (Surabhi et al. 2009, Beixing et al. 2011 and Ghomari et al. 2011). This could be attributed to the variations in chemical compositions, content and particle size of LF (Hawkins et al. 2003 and Hooton et al. 2007) Although reports have studied the effects of Limestone Filler (LF) on cement mortars and concrete made of GU cement, little attention was given to evaluate these effects when HE cement is used. The aim of this paper is to evaluate the effects of limestone content and size on the early age hydration of HE cement including compressive strength, heat of hydration and phase composition using Thermal Gravimetric Analysis and Differential Thermal Analysis (TG/DTA).

2 Materials

High early cement was supplied by Holcim Canada, Ontario, Canada. The physical and chemical compositions are presented in Table 1. Limestone filler was supplied by Omya, Canada. The physical and chemical compositions are presented in Table 2. The fine aggregate was natural sand from Dufferin Aggregates Mill Creek Quarry, Cambridge, Canada.

3 Mix Design

The ten mix designs examined in this study are presented in Table 3. For each mortar mix design mortar and corresponding paste were made. The water-to-cement ratio was kept constant at 0.37. For mortars, 5kg of mortar was prepared for each mix design. The content of sand was kept constant at 2967g. Cement, sand and LF were blended initially for 2 minutes in 10 liters mortar mixer. Once water was added the materials were mixed for 4 minutes. Similar procedures were followed for the corresponding paste mixes.

Table 1: HE Cement Composition:

HE Cement (%)	
LOI (1050)	2.78
SiO ₂	19.11
Al ₂ O ₃	5.18
Fe ₂ O ₃	2.35
CaO	61.58
MgO	2.35
SO ₃	4.26
Total Alkali	1.01
Free Lime	1.03
Limestone	3.5

Table 2: Limestone Composition:

Limestone (%)			
Size	17 μ m	12 μ m	3 μ m
LOI (1050)	42.8	42.3	42.4
CaCO ₃	96	96	99
Silica and quartz	4	2	1

Table 3: Mortar Mix Designs:

#	Mix ID	HE (%)	LF (%)	LF Size (μ m)	w/c ratio	HE (g)	Sand (g)	Water (g)	LF (g)
1	HE	100	---	---	0.37	1484	2967	549	0
2	HE-5-17	95	5	17		1409	2967	522	74
3	HE-10-17	90	10			1335	2967	494	148
4	HE-15-17	85	15			1261	2967	467	223
5	HE-5-12	95	5			12	1409	2967	522
6	HE-10-12	90	10	1335			2967	494	148
7	HE-15-12	85	15	1261			2967	467	223
8	HE-5-3	95	5	3			1409	2967	522
9	HE-10-3	90	10			1335	2967	494	148
10	HE-15-3	85	15			1261	2967	467	223

4 Curing Regime

Steam curing was conducted in an environmental chamber for 12 and 16 hours. The maximum holding temperature was 55°C and 98% relative humidity (RH). After mixing, the mortars and pastes were kept in the chamber at 23°C and 98% RH for 2 hours to ensure that specimens have gained enough strength to resist thermal stresses (Hwang 2012). A sample curing regime is presented in Figure 1. The curing regime consists of:

- heating the specimens to 55°C in 2 hours
- holding the temperature for 10 hours
- cooling down to 23°C in 2 hours

The chamber was controlled by the internal temperature of the samples using Type T thermocouples. For 12 hours steam curing cycle, the specimens were steam cured in an open plastic container in the chamber for 12 hours then the container was sealed with its lid and removed from the chamber to cool down in room temperature. The specimens were stored in limewater until tested.

5 Testing

The mortar was used for the compressive strength evaluation and the paste was used for evaluating the heat of hydration and TG/DTA tests. Compressive strength was evaluated according to ASTM C109 at 12 hrs., 16 hrs., 3 and 7 days. The heat of hydration was evaluated using Tam Air Isothermal Calorimeter over a period of 72 hours. The calcium hydroxide ($\text{Ca}(\text{OH})_2$) and calcium carbonate (CaCO_3) contents and degree of Hydration (DOH) were measured using TG/DTA heated to 1145°C at heating rate of $10^\circ\text{C}/\text{min}$. The specimens were freeze/dried until a constant mass (less than 0.1% in 24 hours period) was achieved. The mass of the tested samples were $100 \pm 0.4\text{mg}$ and were tested after 16 hours of steam curing.

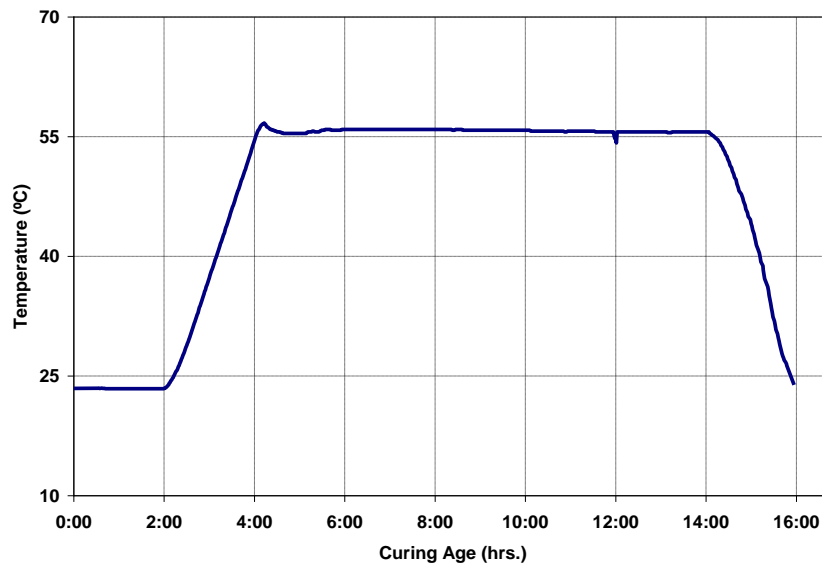


Figure 1: Typical Steam Curing Regime

6 Results and Discussion:

6.1 Heat of Hydration:

Figure 2 presents the effect of LF size and content on the heat of hydration. Each curve represents an average of three specimens. In general, the addition of LF caused an increase in the heat of hydration regardless of the LF size or content compared to control specimen without LF. From Figure 2 (a, b and c), it can be observed that increase in LF content caused increased in the heat of hydration compared to control mix which indicates acceleration in the hydration process. Similar behavior was also observed with the reduction in the LF size as shown in Figure 2 (d, e and f).

To further explain these effects, the value of the maximum hydration peaks and the occurrence time for each peak were compared for each mix as presented in Figure 3. The maximum peak was found to increase and occur earlier with the increase of LF content and decrease in size except for Mix HE-3-15 where the maximum peak occurred in a second peak after sulfate depletion. It was observed that hydration peak increased by 3, 7 and 10% in mix designs made with 5%, 10% and 15% LF of $17\mu\text{m}$, respectively compared to control mix. In mix designs made with $12\mu\text{m}$ LF the increase in the peaks were 7, 11 and 17% for replacement levels of 5, 10 and 15%, respectively compared to control mix. Increases

of 10, 13 and 20% were observed in mix designs made with 3 μ m for the same replacement levels. Second hydration peaks following sulfate depletion point were observed in mix designs made with LF of 12 and 3 μ m only. However, these peaks were more pronounced in mix designs made with LF of 3 μ m. On the other hand, the reductions in the time at which the hydration peaks occurred were 6, 8 and 7% for LF of 17 μ m, 8, 12 and 15% for 12 μ m LF and 12, 19 and 14% for 3 μ m LF at replacement levels of 5, 10 and 15%, respectively. The increase in heat of hydration can be attributed to the increase in surface area and reduction in the energy barrier and thus accelerate the Ca(OH)₂ and C-S-H precipitation from solution. The formation of carboaluminate that fills the pores between cement particles can also be a contributing factor (Shi et al. 2004, Heikal et al. 2000).

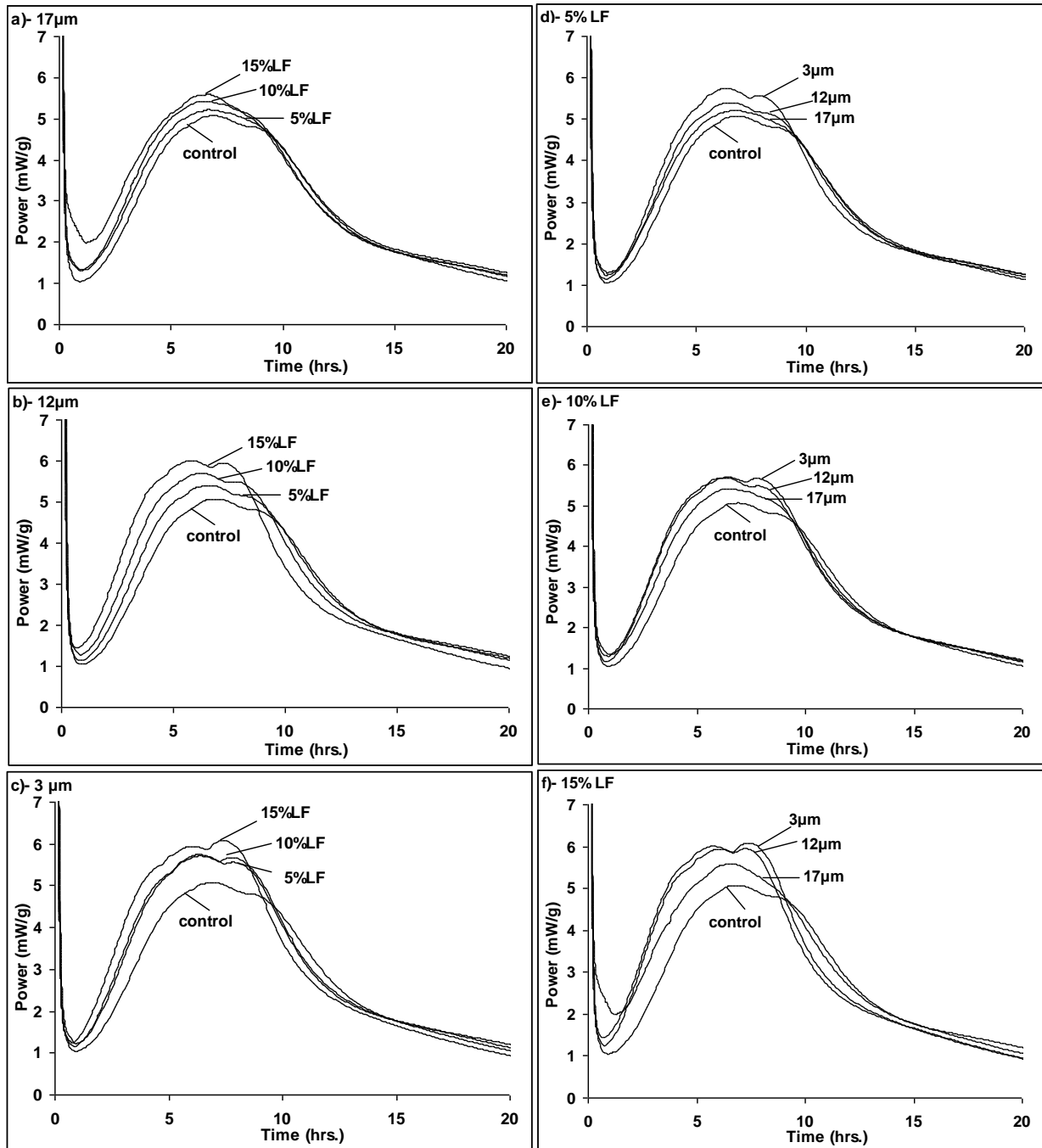


Figure 2: Effect of Limestone Particle Size on Heat of Hydration

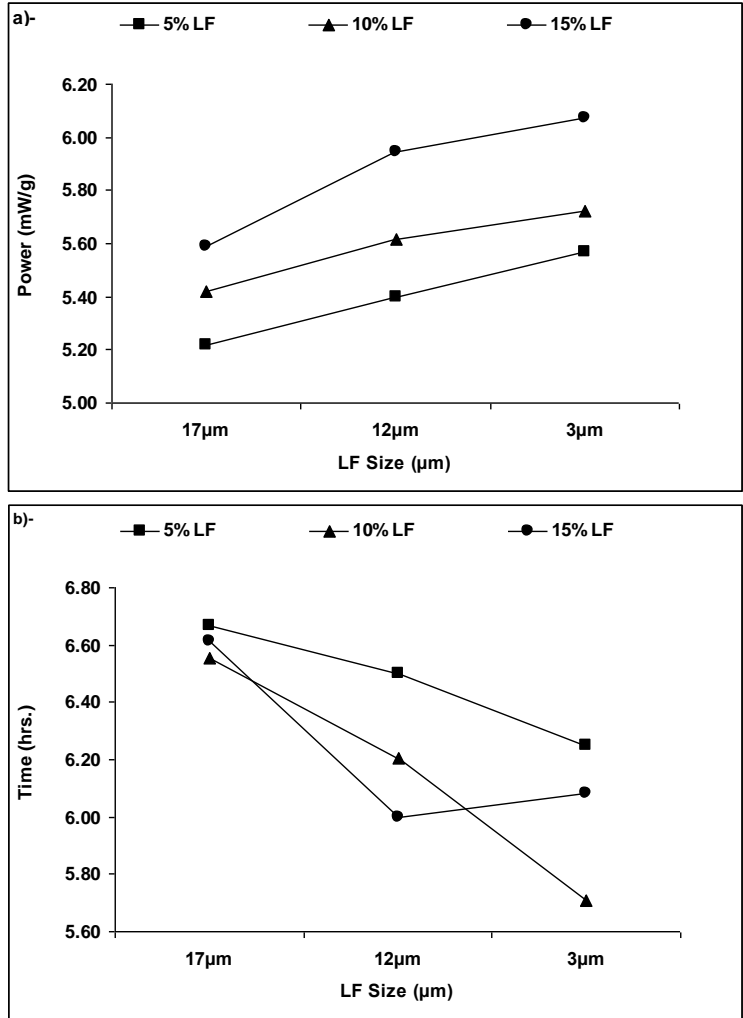


Figure 3: Effect of Content and Size of LF on: a) Value of Hydration Peaks and b) Occurrence Time

6.2 Compressive Strength:

The results of the compressive strength are presented in Figure 4 (a, b and c) for the effect of LF content and Figure 4 (d, e and f) for the effect of LF size.

At 12 hours, the increase in the compressive strength was 5, 8 and 9% in mix designs made with 17μm and LF contents of 5, 10 and 15%, respectively. For mix designs made with LF of 12μm, the increase in the compressive strength was 6, 8 and 10% at the same replacement levels, respectively. Further improvement in the compressive strength was observed with 3μm as the strength increased by 6, 9 and 14% for LF contents of 5, 10 and 15%, respectively, compared to control mix.

At 16 hours, the relative gain in compressive strength was lower compared to 12 hours. The increase in compressive strength was 3, 5 and 1% for 17μm at replacement level of 5, 10 and 15%, respectively, compared to control mix. However, the increase in compressive strength was enhanced with the reduction in LF size. The increase in strength was 5% for mix designs made with 12μm regardless of the LF content while 4, 5 and 11% improvement in the strength was observed in mix designs made with 3μm at replacement level of 5, 10 and 15%, respectively, compared to control mix.

At 7 days, the strength of mix designs made with 17μm was similar to control mix regardless of the LF content. Similar observation was obtained from mix designs made with 12μm at replacement levels of 5 and 10%. However, 6% increase in the compressive strength was observed at 15% LF content. Finally,

the increase in the compressive strength was 6, 10 and 12% for 3 μ m LF at replacement level of 5, 10 and 15%, respectively, compared to control mix.

The increase in the early age compressive strength can be explained by the acceleration effect in hydration with the increase of LF content and decrease in size. This acceleration effect was observed in the heat of hydration results (section 6.1).

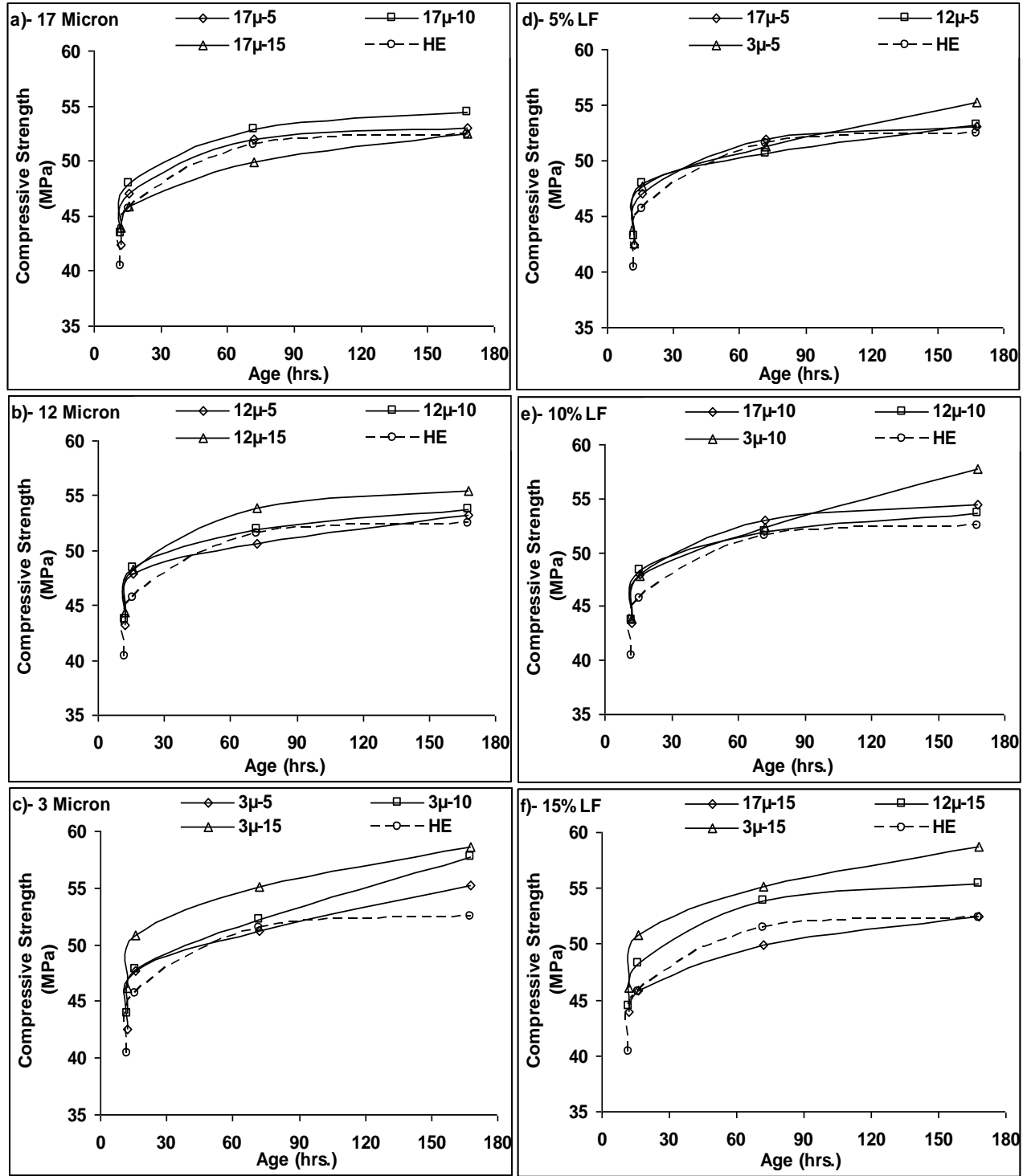


Figure 4: Effect of Limestone Content and Limestone Size on Early Age Compressive Strength: a) 17 μ m, b) 12 μ m, c) 17 μ m, d) 5%LF, e) 10%LF and f) 15%LF

6.3 TG/DTA Results:

The results of TG/DTA are presented in Figure 5 for the effect of LF content (a, b, and c) and size (d, e and f). The mass losses at approximately 450 to 500°C and 680 to 800°C were used to calculate the $\text{Ca}(\text{OH})_2$ and CaCO_3 using stoichiometry. To provide explanations of Figure 5, the contents of $\text{Ca}(\text{OH})_2$ and CaCO_3 were presented in Figures 6 and 7. The results showed an increase in the $\text{Ca}(\text{OH})_2$ content with decrease in LF size as shown in Figure 6(a). A similar effect was observed with the increase in the LF content up to 10%. Mix designs made with 15% replacement level of LF showed similar contents of $\text{Ca}(\text{OH})_2$ compared to counterparts made with 10% LF. However, all mix designs made with LF showed higher $\text{Ca}(\text{OH})_2$ compared to the control mix without LF. This could be attributed to the increase in rate of hydration with the increase in LF content and decrease in LF size as observed in Section 6.1.

The content of CaCO_3 increased with the increase in LF content. However, the CaCO_3 content was found to slightly decrease with the decrease in LF size as shown in Figure 6(b). It is important to understand that HE cement used in this study has 3.5% interground LF. Therefore, the total LF content has to be corrected as shown in Table 4. The theoretical and measured content of CaCO_3 from TG were also compared in Table 4. Total materials, represents the total mass of all materials used for each mix design including all cementing, filler and liquid constituents. From the comparison, it was observed that the difference between theoretical and measured CaCO_3 increases with the increase in LF content and decrease in LF size. This difference is assumed to be the portion of LF that reacted with the aluminate phases in hydrated cement to form carboaluminate.

The DOH was calculated using non-evaporable water measured between 30 to 550°C and ultimate non-evaporable water of 0.23 (Powers and Brownyard 1948, Taylor 1990). The results of DOH are presented in Figure 7. In general, all mix design containing LF exhibited higher DOH compared to the control mix without LF regardless of the LF content or size.

Table 4: Comparison between Theoretical and Measured CaCO_3 :

Mix ID	Theoretical LF (%)				Measured LF/Total Materials (%)	Difference (%)
	Interground	Blended	Total	LF/Total Materials (%)		
HE	3.5	0.0	3.5	2.6	1.6	1.0
HE-5-17		5.0	8.5	6.2	5.8	0.2
HE-10-17		10.0	13.5	9.9	8.6	0.6
HE-15-17		15.0	18.5	13.5	11.9	0.3
HE-5-12		5.0	8.5	6.2	5.5	0.5
HE-10-12		10.0	13.5	9.9	7.8	1.4
HE-15-12		15.0	18.5	13.5	11.2	1.0
HE-5-3		5.0	8.5	6.2	5.2	0.8
HE-10-3		10.0	13.5	9.9	7.1	2.1
HE-15-3		15.0	18.5	13.5	10.4	1.8

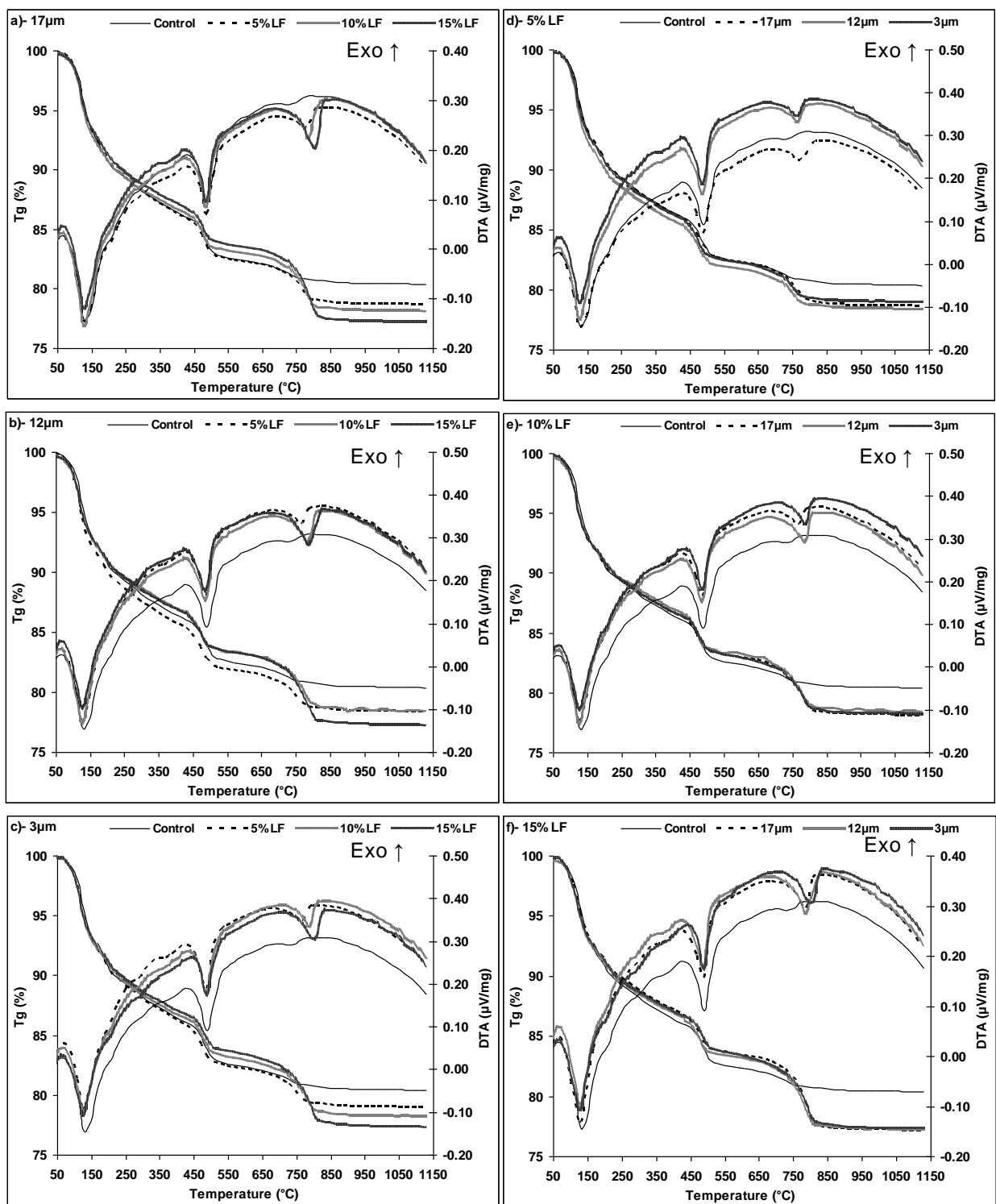


Figure 5: Effect of Limestone Content and Size on TG/DTA Results

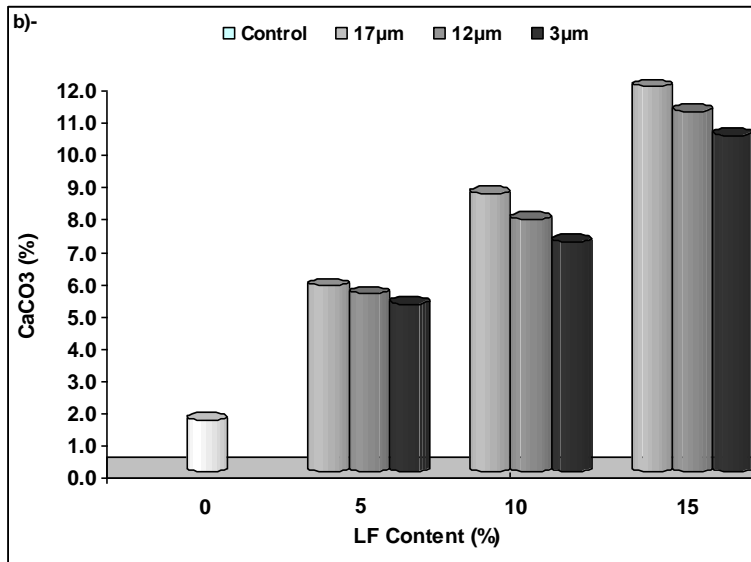
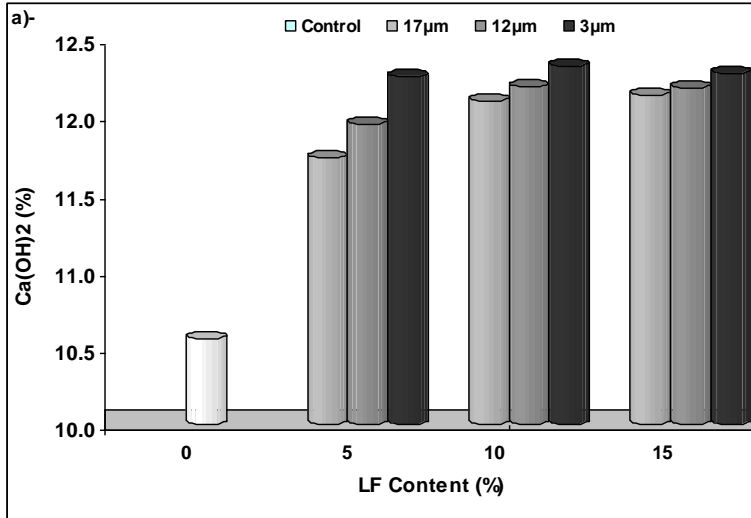


Figure 6: Effect of Limestone Size and Content on Ca(OH)₂ (Right) and CaCO₃ (Left)

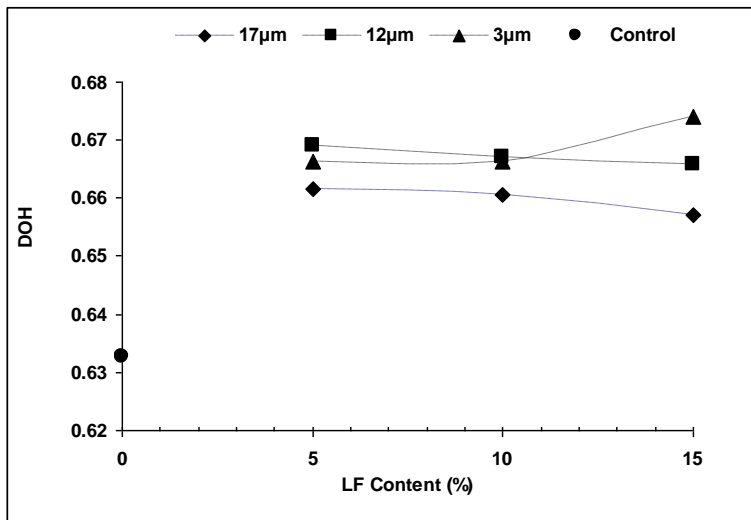


Figure 7: Effect of LF on the Degree of Hydration at 16hours

7 Conclusions

- The particle size of LF was found to have more influence on early age hydration and strength of HE cement mortars/pastes compared to LF content.
- At 15% LF of 12 and 3 μ m, improve in the early age compressive strength up to 6 and 12%, respectively, was observed at all ages compared to control mix without LF. However, for of 17 μ m LF, 4% improve in the compressive strength of was observed up to 10% replacement level followed by decrease in strength with the increase of LF content.
- The addition of 15% LF of 17, 12 and 3 μ m caused increases of 15, 17 and 20% in the heat of hydration compared to control mix without LF.
- The Ca(OH)₂ content increased with the increase in LF content and decrease in LF size which can be explained by the acceleration effect on the hydration by LF.
- The results of the TG/DTA indicate decrease in the CaCO₃ content at 16 hours with the decrease of LF size which is assumed to be consumed in the reaction with aluminate phases in hydrated cement.
- In general, the results of isothermal calorimetry, TG/DTA and compressive strength indicate an improved early age hydration and strength with the addition of LF.
- Due to the various factors (such as chemical compositions and particle size distribution of limestone filler and other parameters related to mix design) that affect the influence of LF, the results are valuable for the LF and mix designs tested in this study.

8 References

1. Surabhi S., Soman M. and Prakash S. 2009. Influence of Limestone Powder on Properties of Self-Compacting Concrete. *10th National Conference on Technological Trends (NCTT09)*, Trivandrum, India. 1: 159-164.
2. Beixing L., Mingkai Z., Yanwei F., Putao S. and Guoj K. 2011. Self-compacting Concrete-filled Steel Tubes Prepared from Manufactured Sand with a High Content of Limestone Fine, *Journal of Wuhan*. University of Technology-Mater. 1: 325-328.
3. Ghomari F., Hacene S. and Taleb O. 2011. Study of Limestone Addition on the Mechanical and Rheological Characteristics in the SCC. *Jordan Journal of Civil Engineering*. 5: 412-423.
4. Hawkins, P, Tennis, P.D. and Detwiler, R.J. 2003. The Use of Limestone in Portland Cement: A State-of-the-art Review. Report EB227. Portland Cement Association, Skokie, Illinois, USA.
5. Hooton, D., Nokken M. and Thomas M. 2007. Portland-Limestone Cements: State of the art Report and Gap Analysis for CSA A3000, Report prepared for St. Lawrence Cement. 2-48.
6. ASTM C109 (2008) Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 50mm Cube Specimens). American Society for Testing and Materials. Annual Book of ASTM Standards, Philadelphia, USA.
7. Hwang, S., Khatib, R., Lee, H., Lee, S. and Khayat K. 2012. Optimization of Steam-curing Regime for High-strength, Self-consolidating Concrete for Precast, Prestressed Concrete Applications. *PCI Summer Journal*, 1: 48-62.
8. Shi C., Wu Y. and Riefler C. 2004. The Use of Crushed Limestone Dust in Production of Self-Consolidating Concrete (SCC). *ACI Materials Journal*, 219: 115-130.
9. Heikal M., El-Didamony H., and Morsy, M. 2000. Limestone-filled Pozzolan Cement, *Cement and Concrete Research*, 30:1827-1834.
10. Weerdt, K., Sellevold, E, Kjellsen, Sellevold, E. and Justnes, H. 2011. Fly Ash-Limestone Ternary Cements: Effect of Component Fineness. *Advances in Cement Research*. 23: 203-214.
11. Powers, T. and Brownyard, L. 1948. Studies of the Physical Properties of Hardened Portland Cement Paste: Bulletin 22 of the Research Laboratories of the Portland Cement Association. The Portland Cement Association, Chicago.
12. Taylor, H. 1990. Cement Chemistry, 1ST ed. Academic Press Limited, San Diego, CA, USA. 240-248.