

Effect of Limestone Powder on Microstructure of Ternary Cementitious System

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ABSTRACT: The pressure to reach sustainability favours the development of ternary composite cement. The synergistic effect on mechanical behaviour at 28 days between limestone powder (LP) and pozzolanic additives, i.e. fly ash (FA) and blast furnace slag (BFS), has been documented. In order to better understand the synergistic effect, this article investigated the effect of LP on the microstructure of PC-FA and PC-BFS cementitious system. The mineralogy and pore structure were determined after 28 days of curing at 20°C and 95% relative humidity. The mineralogy in pastes was identified by means of X-Ray diffraction (XRD) and thermogravimetry (TG). The pore structure was evaluated by Mercury intrusion porosimetry (MIP). The results showed that neither monosulfoaluminate nor ettringite was found in any of the XRD patterns, instead carboaluminate was observed. Hemicarboaluminate produced in FA-PC or BFS-PC system transformed into monocarboaluminate with the addition of LP. The porosity was enlarged compared with LP-free paste system. It seems that both the physical and chemical effect of LP contribute to the synergistic effect on mechanical behaviour of cementitious system hydrated up to 28 days.

INTRODUCTION

CO₂ emissions from concrete production accounts for around 8% man-made CO₂ (Karen, 2012). The blending of cement clinker with supplementary cementitious materials (SCMs), such as blast furnace slag (BFS), fly ash (FA) and limestone powder (LP), has been the most promising route to increase the sustainability of construction engineering. Nowadays, Portland cement (PC) is still the essential component in cementitious system and blended cements are most often binary, e.g. FA-PC and BFS-PC. While at high replacement levels, the early age mechanical behaviour of binary cementitious system becomes an issue. An possible approach to improve early age mechanical behaviour is to develop ternary cement system, in which different SCMs can interact with each other and may enhance the performance of concrete. LP is a particularly interesting SCM, it can decrease the cost due to the less demand of gypsum content (Weerdt, 2011a) and produce almost zero associate

CO₂ emissions. Therefore, development of LP-filled ternary composite cement is meaningful.

Several series of experiments on mechanical behaviour of LP-filled ternary cementitious system have been performed. Replacing 5% of PC with LP in FA-blended ternary cement system resulted in no strength loss at the age of 28 days (Weerdt, 2011b). Katsioti (2009) also proved the compatible mechanical behaviour of 5% LP addition in pozzolanic mortar system at 28 days. While the effect of 5% LP addition on strength development of binary PC-LP samples appeared to be less pronounced than ternary PC-FA-LP and PC-BFS-LP samples (Seichi 2006; Weerdt 2011a). In some cases, replacing PC by 5% LP in binary LP-PC concrete resulted in a reduction in both compressive strength and flexure strength at 28 days (Weerdt 2011b). It seems there is a synergistic effect on strength development when small amount of LP is combined with pozzolanic additives, i.e. FA and BFS.

Previous studies have documented the influence of LP on the hydration process of pozzolana-contained cement system. It is known that LP interacts with alumina-contained phases and leads to the formation of carboaluminate instead of monosulfoaluminate and thereby stabilizing the ettringite (Hoshino 2006; Kakali 2000; Lothenbach, 2008; Weerdt, 2011a). Especially in high-alumina pozzolanic cement system, the effect of LP in stabilizing the ettringite would be more obvious, which is confirmed by Weerdt (2011b). However, the underlying reasons for the aforementioned synergistic effect on mechanical properties of hydrating cementitious system have not been investigated, except one assumption that the synergistic effect is most likely related to the interaction of LP with AFm and AFt phases (Weerdt 2010).

In order to better understand the synergistic effect, this paper investigated and compared the microstructure formed by pozzolana contained cementitious system with and without LP. To this end, experiments were carried out on a series of mixtures. In this study, 10% PC was replaced by LP. Two different pozzolanic additives were used, i.e. FA and BFS. The replacement level was 30%-50% for FA and 30%-70% for BFS. The mineralogy and associated pore structure were determined after hydration of 28 days. The synergistic effect on better mechanical behaviour of ternary cementitious system was eventually discussed.

EXPERIMENTS

Materials

Materials used for this work are Portland cement (PC), Fly ash (FA), ground granulated blast furnace slag (BFS), Limestone powder (LP). 10 mixtures were designed. The details of mixtures and chemical composition of each material are shown in Table 1. The CO₂ content in each mixture was obtained by thermogravimetric analysis. The mainly crystal phases in pozzolanic additives are quartz and mullite in FA, melilite and merwinite in BFS.

Sample preparation

For XRD, TGA and MIP measurements, the pastes were cast with constant water to binder ratio (W/B) 0.4. Each paste mixed with water in a HOBART mixer at low

speed for 1 minute and at high speed for 2 minutes. Then the fresh paste was poured into plastic bottles and shaken on the vibration table to remove big bubbles and then sealed with lids. In order to avoid bleeding, the samples were rotated almost one day and then placed in standard curing room with the condition of temperature 20°C and 95% RH. After 28 days curing, the samples were spitted into small pieces. Liquid nitrogen was used to stop the further hydration of the specimens (Ye, 2003). Then these small pieces were moved into a freeze-dryer with temperature of -24 °C and under vacuum at 0.1 Pa. Until the water loss was below 0.01% per day, the specimen then can be used for the XRD, TGA, MIP measurements.

Table 1 Mixture proportions (left) and chemical composition % (right)

	PC	FA	BFS	LP	W/B
M ₁	100%				0.4
M ₂	90%			10%	0.4
M ₃	70%	30%			0.4
M ₄	50%	50%			0.4
M ₅	70%		30%		0.4
M ₆	30%		70%		0.4
M ₇	60%	30%		10%	0.4
M ₈	40%	50%		10%	0.4
M ₉	60%		30%	10%	0.4
M ₁₀	20%		70%	10%	0.4

	PC	BFS	FA	LP
CaO	64	42	5.8	-
SiO ₂	19.9	33	54	0.34
Al ₂ O ₃	4.5	12	23	0.2
SO ₃	2.55	2.3	1.7	0.046
K ₂ O	0.42	0.46	1.9	0.011
Na ₂ O	0.4	0.28	1	0.017
MgO	2.2	7.5	1.4	0.27
Fe ₂ O ₃	3.3	0.63	7.3	0.067
CO ₂	0.52	0.07	0.66	99
Others	2.21	2.54	3.24	0.093

Measurements and methods

(1) Thermogravimetric analysis (TGA)

A STA(TG-DTA-DSC) 449 F3 Jupiter was used to measure the quantity of calcium hydroxide (CH) and assess the pozzolanic behaviour of additives in LP-filled cementitious system. The amount of CH is calculated from weight loss curve during thermal analysis (Bryan, 1988). The mass of sample was about 30-50 mg. The maximum heating temperature was 1100°C with the heating rate 10 °C/min. Argon was used for the protective gas.

(2) X-ray Powder diffraction (XRD)

XRD used in this work was mainly to study the mineralogy of cementitious system with and without LP. For mineralogical investigations, the powders were firstly mixed with standard crystal Al₂O₃ powders and then pulverized to an average particle size of less than 10 micros with no particle feeling. After that, the pulverized powders were evaluated by X-Ray diffraction, operating at 40kV, 30mA, 2 θ angle is from 5° to 70° with step size of 0.03°. A diffractometer was used to identify the crystalline phases. Cu $K\alpha$ radiation was used. The crystalline components of the powdered sample were identified by comparing with the standards established by the International Centre for Diffraction Data.

(3) Mercury intrusion porosimetry (MIP)

MIP was used to assess the influence of LP on pore structure of ternary cementitious paste system. With the assumption that pores are cylindrical and entirely and equally accessible to mercury, the applied pressure can be converted into the pore diameter by using the Washburn equation (Washburn, 1921)

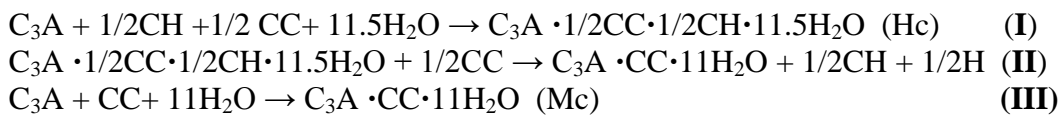
$$D = \frac{-4\gamma \cos \theta}{p} \quad (1)$$

where, D is the equivalent pore diameter, P is the applied pressure, γ is the surface tension of mercury (485 dynes/cm) and θ is the contact angle between mercury and solids, in this study $\theta = 139^\circ$ was used.

RESULTS

Mineralogy

The phases determined by XRD for the samples with and without LP were compared and shown in Fig. 1. The crystal phases were somewhat similar as expected, except the peaks at the low angles, where the hemicarboaluminate [$C_3A \cdot 0.5CaCO_3 \cdot 0.5Ca(OH)_2 \cdot 11.5H_2O$] produced in PC-FA and PC-BFS samples disappeared (2Θ peak at 10.8°), and transformed into monocarboaluminate [$C_3A \cdot CaCO_3 \cdot 11H_2O$] (2Θ peak at 11.7°) in PC-FA-LP and PC-BFS-LP samples. This proved that LP did influence the chemical constitution of alumina-contained phase (AFm) in cementitious system. In addition, the products of carboaluminate would fill the capillary pores and the mechanical behaviour could be therefore enhanced. According to Kuzel (1991),



As shown in Fig.1, there was neither monosulfoaluminate (2Θ peak at 9.89° and 19.8°) nor ettringite (2Θ peak at 9.1° and 15.8°) in any of the cementitious systems including pure PC system at 28 days, instead carboaluminate was observed. The absent of monosulfoaluminate was also found in literature (Ogawa, 2012). It can be ascribed to the presence of CO_3^{2-} in PC clinkers (from Table 1). Very small amount of CO_3^{2-} content could lead to the rapid consumption and decrease in the amount of monosulfoaluminate (Matschei, 2007). At $22^\circ C$ and $pH > 12$, the SO_4^{2-} groups in the interlayer region of monosulfoaluminate are easily substituted by CO_3^{2-} , therefore the crystallisation of Hc or Mc is observed (Kuzel, 1991). However, the sulfate released from monosulfoaluminate did not lead to the formation of gypsum ($2\Theta = 20.7^\circ$) or anhydrite ($2\Theta = 25.4^\circ$) or bassanite ($2\Theta = 29.7^\circ$). Then it can be concluded that the absent 2Θ peak of ettringite was most probably due to its poorly crystalline and lower amount ($< 5\%$) in cementitious system.

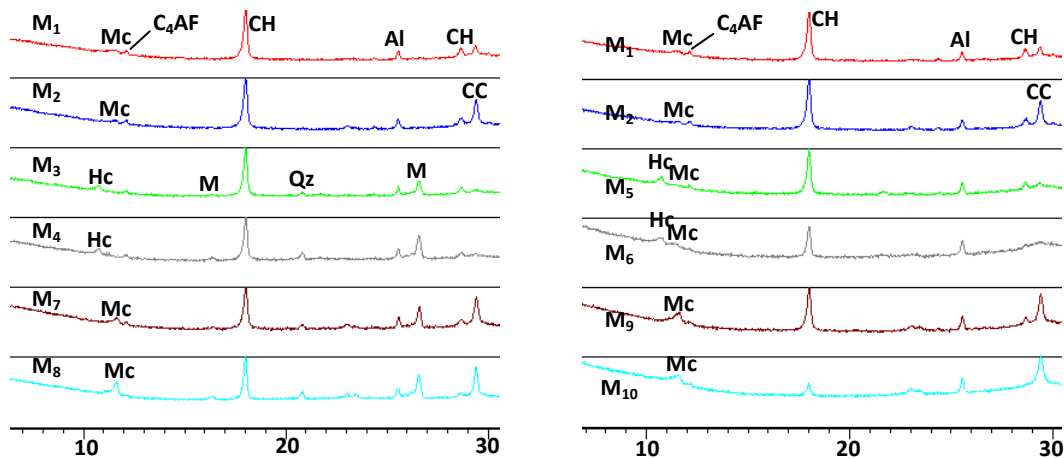


FIG. 1 XRD patterns (5° - 30°) for pastes hydrated up to 28 days (Hc-hemicarboaluminate, Mc-monocarboaluminate, Qz-quartz, M-mullite, CH-calcium hydroxide, CC- CaCO_3 , Al- Al_2O_3).

The 2θ peak at 11.7° is not so strong in mixture of pure PC and PC-LP system, which indicates that the chemical interaction (III) is not pronounced due to the limited aluminate content in anhydrous clinkers. Therefore, LP is often considered as inert filler in PC-LP cement system (Weerdt, 2011b). While pozzolanic additives (FA, BFS etc.) usually contain high amount of aluminate phases, thus additional calcium aluminate hydrates (Hc or Mc) may be produced, which is confirmed by the XRD patterns in this study. The strong chemical interaction between alumina phases of FA/BFS and LP may further account for the synergistic effect on strength development of cementitious system.

If looking into the patterns in detail, Mc is observed in PC system, both Mc and Hc are produced in BFS-PC system, while only Hc appears in FA-PC system. From chemical composition (as shown in Table 1), more aluminate phases contained in FA, followed by BFS and PC, the gradual transformation from Mc into Hc could indicate the reactivity of carbonate is highly dependent on the content of aluminate phases in cementitious system. While when 10% of LP is filled in FA-PC and BFS-PC system, all the Hc is transformed into Mc phase. Then it could be concluded that the occurrence of reaction (I) or (II) or (III) is determined by the ratio of weight percentage of $\text{CO}_3^{2-}/\text{Al}_2\text{O}_3$ in cementitious system. Due to the reaction between LP and alumina phases, the phases assemblage and stability in cementitious system were influenced with the addition of LP, which was confirmed by the patterns M_1 - M_{10} . In addition, LP could react with CH (reaction I), with the hydration process, pozzolanic reaction would be significantly influenced. Hence, the chemical effect of LP is of great importance in high aluminate containing pozzolanic cement system and cannot be neglected. Nevertheless, its chemical benefit needs to be investigated in the long term standpoint and systematic studies are worthy to be carried out.

The CH content of each paste tested by TG was shown in Fig. 2. As expected the CH content was decreased with the increase of replacement level of pozzolanic materials. This was mainly due to less amount of Portland cement in the mixture

meanwhile the CH was consumed by the pozzolanic reaction. It can be found that the CH content is less in BFS-filled system than that in FA-filled system when the same amount (30%) of PC is replaced. This proves that the pozzolanic behaviour of BFS is higher than that in FA at the early age. The presence of LP further reduced the CH content in all the ternary cementitious system and interestingly the reduction (1.74%-2.57%) is more than the dilution effect of 10% LP substitution (1.61%). The same phenomenon was also discovered in (Weerdt, 2010). As the formation of hemicarboaluminate (Hc) in both FA-PC and BFS-PC requires the consumption of CH, while the monocarboaluminate (Mc) produced in LP-FA-PC and LP-BFS-PC does not consume CH. Therefore the extra decrease of CH amount is most probably due to the enhancement of pozzolanic reaction, assuming the Ca/Si in C-S-H do not increase with the addition of LP (Locher, 1966; Stucke, 1976). It is well known in the presence of LP, cement hydration was highly accelerated in the first 7 hydration days, which involves a higher production rate of CH (Mounanga, 2011), and thus an increase in the pozzolanic behaviour at early age. In addition, the better phases assemblage with the addition of LP may also contribute to the progress of pozzolanic reaction. It should be noted that due to enhanced pozzolanic reaction CH ($32.9 \text{ cm}^3/\text{mol}$) transformed into C-S-H (almost $350 \text{ cm}^3/\text{mol}$) (Taylor, 1997) and the mechanical behaviour of cementitious system would be also enhanced.

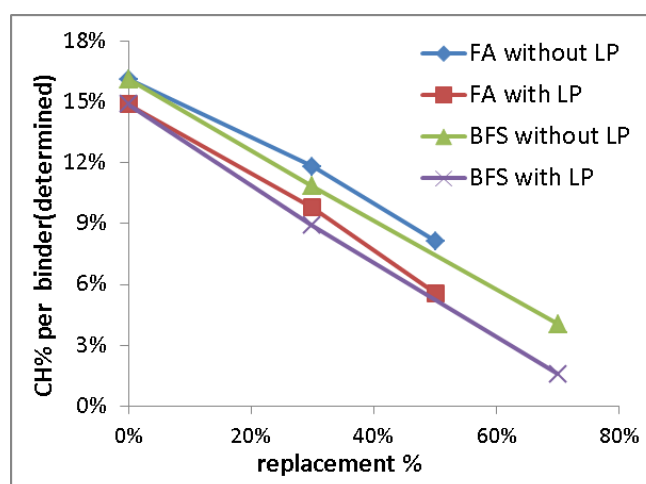


FIG. 2 CH content in pastes with and without LP at 28 days.

Pore structure

From Fig. 3, as expected the porosity of FA-filled system increases with the increase of replacement levels (30% and 50%) at curing age of 28 days. However, lower amount of BFS substitution (30%) could decrease the porosity because of the intensive pozzolanic reaction at the early age, as indicated by the lower amount of CH in hydrated system (Fig. 2). While the porosity increased when 70% of PC is replaced by BFS, this may be ascribed to the lower amount of CH content in the blended system that highly influenced the progress of pozzolanic reaction at the age

of 28 days. On the other hand, the rate of reaction of the slag decreases with the increase of replacement level of the slag (Escalante, 2001).

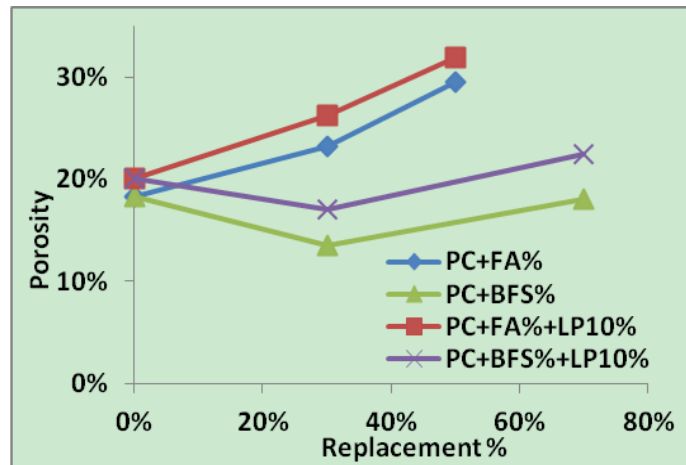


FIG. 3 Porosity of pastes at 28 days with and without LP.

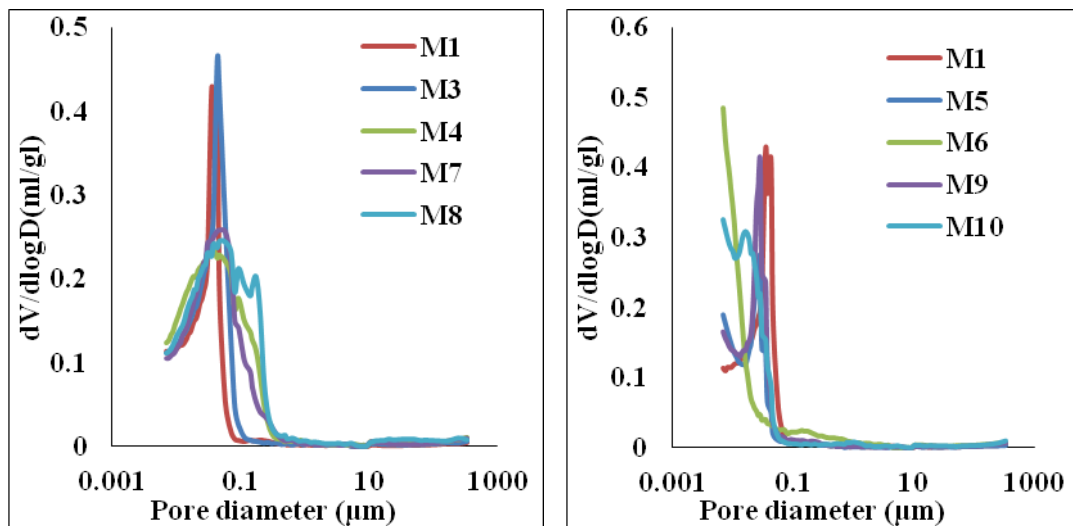


FIG. 4 Pore size distribution of pastes at 28 days with and without LP.

In addition, from Fig. 4 the critical pore size of reference Portland cement system is smaller than all the FA-filled cementitious system, while larger than all the BFS-filled cementitious system. The critical pore size in M_6 paste was even smaller than $0.01\mu\text{m}$, which revealed that the pore size was highly refined by BFS additives, this was also discovered by (Song, 2006). The denser microstructure in cement paste with BFS may also partly due to the optimal proportion match and particle size match. However, the data in Fig. 4 should be treated with caution, as MIP is insufficient in determination of pore size distribution due to its accessibility problems (Sidney, 2000).

With the addition of LP, the porosity of all pozzolanic cement pastes increased and the pore size was also enlarged. When LP is introduced into pozzolanic cement system, the main phase change is the transformation of Hc ($280 \text{ cm}^3/\text{mol}$) to Mc ($262 \text{ cm}^3/\text{mol}$) (Taylor, 1997), which means there is a little bit increase of the pore volume percentage when this reaction happens. In addition, the stronger peak of pattern M₇-M₁₀ in Fig. 1 at 29.4° and relatively weaker peak at 11.7° seemingly revealed that most of LP is still in the presence of unreacted calcium carbonate. Then it could be concluded that the dilution effect, combined with the chemical transformation, could account for the increment of porosity.

CONCLUSIONS AND DISCUSSIONS

This article investigated the effect of LP on the mineralogy and pore structure of PC-FA-LP and PC-BFS-LP system hydrated up to 28 days with cement substitution rates from 40%-80%. The results proved that LP reacts with aluminate contained phases and leads to the formation of carboaluminate in cementitious system, and monosulfoaluminate was not found as expected. The porosity and pore size of hydrated cement pastes were enlarged compared with LP-free cement pastes. In addition, the experimental results obtained also lead to the following conclusions:

- (1) The reactivity of carbonate is highly dependent on the content of alumina phases in cementitious system and the phases assemblage of hydrated AFm (Hc or Mc) is determined by the weight ratio $\text{CO}_3^{2-}/\text{Al}_2\text{O}_3$ in cementitious system.
- (2) The addition of LP may enhance pozzolanic reaction of additives due to the accelerated production of CH at early age and may also due to the better hydrates assemblage in ternary cementitious system.

Compared to FA-PC and BFS-PC system, the total porosity is increased with the addition of LP. Therefore, the better mechanical behaviour in the presence of LP at 28 days could be ascribed more to the filling effect of unreacted LP and reaction products of carboaluminate that fulfilled the big capillary pores of cementitious system, whereby the possibility of strength failure by big pores was reduced. Additionally, it seems due to filler effect, the addition of LP could enhance pozzolanic reaction at 28 days that contributes to the better mechanical behaviour. Thus, both the physical and chemical effect of LP could contribute to the synergistic effect on the mechanical behaviour of hydrating ternary cementitious system. Nevertheless, the chemical effect of LP needs to be investigated in the long term standpoint due to the probable transformation of carboaluminate into ettringite.

It is believed the phases assemblage in hydrating cementitious system is of paramount importance in mechanical behaviour of hydrating cement-based system. Therefore better understand the influence of LP on nucleation and formation of microstructure of hydrating ternary cementitious system would be helpful in better understanding of the synergistic effect. To this respect, further studies regarding to surface energy of unhydrated particles and hydrated particles should be performed.

ACKNOWLEDGEMENT

The authors would like to appreciate the financial support from China Scholarship Council (CSC). In addition, gratefully acknowledgment should be given to technicians in Microlab of Delft University of Technology.

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