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Mechanical properties and microstructure of high strength LC3 pastes with varying limestone/calcined clay ratios and different curing conditions

Yemin Dong[1], Chuanlin Hu[1*]
[1]State Key Laboratory of Silicate Materials Architectures, Wuhan University of Technology, Wuhan, China
[*]Corresponding author: chuanlin@whut.edu.cn

Bin Wang[2]
[2]Sinoma International Engineering Co., Ltd., China

Asad Hanif[3]
[3]Institute of Applied Physics and Materials Engineering, University of Macau, Taipa, Macau S.A.R China

ABSTRACT

The effects of calcined clay and limestone on early hydration, microstructure and compressive strength of low water to binder ratio (0.19) pastes under two curing systems (i.e., standard curing and steam curing) were studied. The relevant properties of the high strength cement-based materials were investigated by compressive strength test, X-ray diffraction, Hydration calorimeter and Scanning electron microscope-Electron back scattered diffraction. The experimental results show that with the decrease of calcined clay/limestone ratio (2, 1.25, 0.67 and 0.25), the compressive strength of the system first decreases and then increases. The decrease of calcined clay content makes the content of hydrated ettringite decrease. Steam curing improves the early compressive strength and hydration degree of the system as a whole, but the content of carboaluminate in the system decreases due to accelerating the hydration of early cement. Therefore, it is necessary to adopt appropriate calcined clay/limestone ratio and curing system to improve the performance of the system.

1. INTRODUCTION

Sustainability is an important direction of the current concrete industry. Among them, the greenhouse gas produced by cement industry accounts for a considerable part of the total global greenhouse gas emissions [1]. To achieve sustainable development, on the one hand, high strength concrete (HSC) can be used to reduce the amount of cement clinker and improve the utilization efficiency of concrete materials. On the other hand, the use of auxiliary cementitious materials instead of cement clinker can reduce greenhouse gas emissions from the perspective of raw material production [2]. Common auxiliary cementing materials include limestone (LS), fly ash (FA), slag and calcined clay (CC). Among them, limestone and calcined clay are rich in reserves, and the production and firing process is similar to Portland cement, which means that cement production equipment can be used for large-scale production, and the calcination temperature is low, and the calcination process does not emit greenhouse gas CO_2, which demonstrates great advantages [3-5]. Limestone calcined clay cement (LC^3) has a good development prospect, which is attributed to the formation of aluminosilicate phase with pozzolanic activity after calcination of kaolinite [6]. The research shows that metakaolin reacts with silicate, water and sulfate to form C-A-S-H, AFt and AFm [7]. After limestone is added to Portland cement, $CaCO_3$ could react with C_3A in cement clinker to form semi-carbonaluminate (Hc) and single carbon aluminate phase. With the synergistic effect of higher territory, the formation of carboaluminate is enhanced, and the strength source of the system is produced [8].

Under the condition of fixed cement clinker content, four kinds of mix proportion of limestone and calcined clay were designed to prepare high strength cement-based materials with low water binder ratio. The standard curing and the steam curing were carried out respectively. The compressive strengths of the specimens were tested at the ages of 1d and 3d. Meanwhile, the systems were determined by X-Ray diffraction (XRD), Scanning electron microscope-

Electron back scattered diffraction (SEM-BSE) and Hydration calorimeter. Through this study, the understanding on the evolution of phase composition of high strength cement-based materials in limestone calcined clay system under low water binder ratio and its influence on the strength development of the system has been improved.

2. MATERIALS AND METHODS

2.1. RAW MATERIALS

The raw materials include P.I.52.5 cement, calcined clay, limestone powder and fly ash were used and their particle size distributions are shown in as shown in Figure 1 Polycarboxylate superplasticizer (50wt.% solid content) is used as additive to keep all mixtures with similar fluidity.

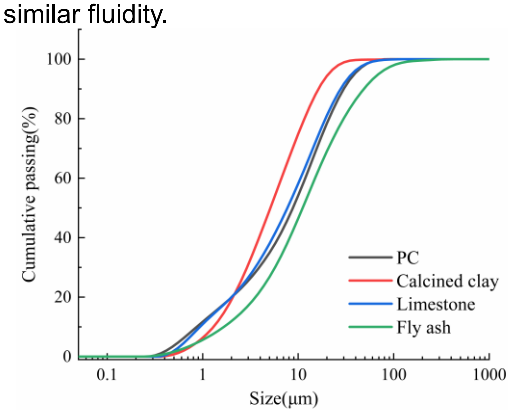


Figure 1. Particle size distribution of raw materials

2.2. MIX DESIGN AND MAINTENANCE SYSTEM

Table 1 shows the system mix proportion design of compressive strength and microstructure measurement. Four mix proportions are chosen, in which the cement clinker content is fixed at 50wt.%, and the calcined clay content is set at 30wt.%, 25wt.%, 20wt.% and 10wt.%. According to the content of calcined clay, $LC^3$50-30, $LC^3$50-25, $LC^3$50-20 and $LC^3$50-10 are respectively marked, in which 5% fly ash is added to 30% and 25% groups respectively. The content of superplasticizer in each group was adjusted according to the slurry fluidity of different systems. The samples were placed in 40 × 40 × 40 m^3 abrasive tools at room temperature. The steam curing group was placed in the steam curing box for 4 h in advance. The steam curing system is shown in Figure 2. After curing for 1d and 3d, the samples were broken and sampled, and soaked in isopropanol to stop hydration. All samples were pre dried in a vacuum drying oven at 40 ℃ for 24 hours before testing.

Table 1. Mix proportion(g)

Sample	PC	MK	LS	FA	B	W	W/B
$LC^3$50-30	500	300	150	50	1000	190	0.19
$LC^3$50-25		250	200	50	1000	190	
$LC^3$50-20		200	300	/	1000	190	
$LC^3$50-10		100	400	/	1000	190	

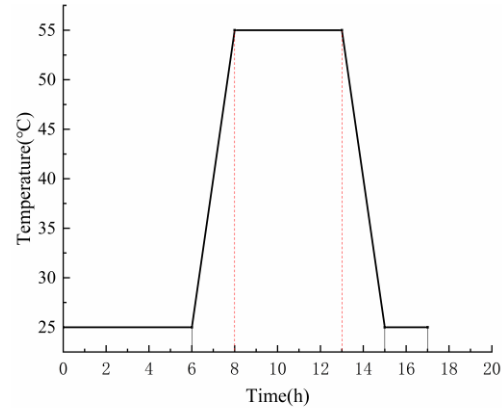


Figure 2. Steam curing system

2.3. TESTING METHODS

According to Chinese standard GB/T 501 07-2010 [9], the compressive strengths of cubic samples with size of 40×40×40 mm^3 at the ages of 1 d and 3 d were tested by a compression machine, and the loading rate was set at 2.4 kN/s.

The powder samples were tested by empyrean / empyrean X-ray diffractometer. The samples were ground with quartz mortar and sieved with 200 mesh sieves. About 10 g powder samples were tested by XRD. The detection method was 5-70 ° conventional scanning.

The hydration heat release was tested by tamair type hydration calorimeter. Each group weighed 15 g paste sample and placed it in the hydration calorimeter. The steam curing group set the instrument to heat up to 55 ℃ in advance, and observed the hydration heat release rate and cumulative heat release from 1d to 3d.

SEM-BSE images were pre polished with 400, 800, 1200, 1500 and 4000 mesh sandpaper, and then polished with diamond polishing solution. After polishing, the samples were photographed at 20.00 kv voltage and 500 × magnification.

3. RESULTS AND DISCUSSION

3.1. COMPRESSIVE STRENGTH

Figure 3 shows the 1d and 3d compressive strength of four mix design pastes under different curing systems. It can be seen from the results that the compressive strength of sample in the steam curing system is higher than that in the standard curing system at 1d. The compressive strength of the sample under standard curing has been greatly improved, while under steam curing, due to the improvement of hydration degree at the early age, the improvement of 3d compressive strength is less obvious than that of standard curing.

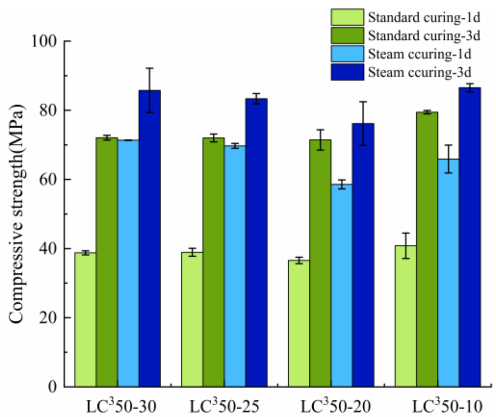


Figure 3. 1d and 3d compressive strength

Figure 4 shows the influence of different calcined clay/limestone ratios on the compressive strength of cement-based materials. For both curing conditions, it can be found that the compressive strength first decreases and then increases with the decrease of calcined clay/limestone ratio. Considering the high content of calcined clay, the content of metakaolin with pozzolanic activity in the system is relatively high, and with the decrease of the proportion, the limestone only plays the role of filler. When the content of limestone increases, the reaction activity of the system decreases, so the strength of the system decreases. When the content of limestone is large, the calcined clay has a relatively small particle size, and more part of it plays a dense filling role, which makes the whole system accumulate more intensively, which leads to the increase of the system strength. Previous studies have shown that the compressive strength of matrix containing 20wt.% CC is lower than that of matrix with 10wt.% CC at each age. When the content of CC is higher than 15wt.%, steam curing cannot slow down the decreasing trend of compressive strength [10]. The reason is that when 20% or more calcined clay is added, the mixing degree of matrix particles is relatively poor. At the same time, because of the high water absorption of calcined clay, more water reducing agents are needed, resulting in the decrease of compressive strength of matrix [11]. At a lower content of calcined clay, due to the use of less water-reducing agent, the hydration of calcined clay is less inhibited. At a content of 20wt.% calcined clay, due to the use of water-reducing agent, the water content of calcined clay the compressive strength of the matrix is significantly reduced, but as the content of calcined clay increases, the synergistic effect of cement, limestone, and calcined clay in the system begins to become prominent, and the compressive strength of the system is improved.

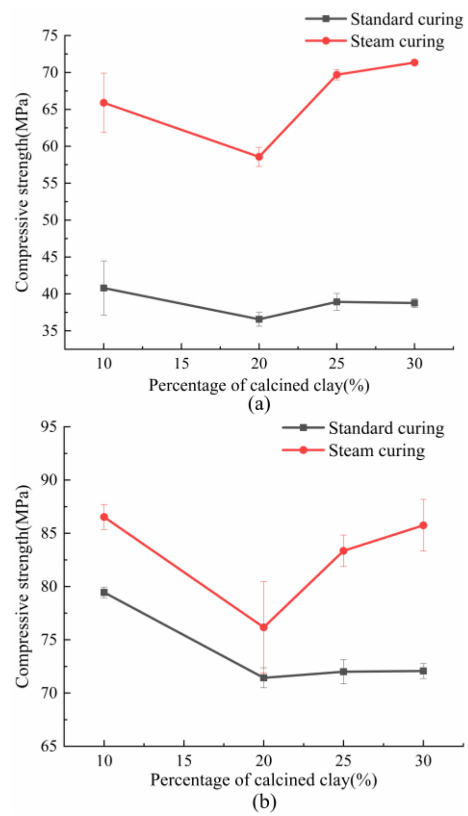


Figure 4. The 1d and 3d compressive strength changes with the ratio of calcined clay / limestone, (a) curing age of 1 d; (b) curing age of 3 d.

3.2. HYDRATION

Figure 5 and Figure 6 show the XRD patterns under different curing conditions for 1d and 3d, respectively. More contents of $CaCO_3$ and C_2S and C_3S phases in unhydrated cement clinker are observed after 1d and 3d of curing, which proves that part of cement does not undergo hydration reaction under low water binder ratio, and limestone is mainly used to replace cement clinker for physical filling; for hydration products, under two curing conditions, the hydration products of cement clinker are not subject to hydration reaction The results show that the peak of AFm phase decreases with the decrease of calcined clay content under standard curing. At higher calcined clay content, the aluminates involved in the reaction increase, which is conducive to the formation of carboaluminate phase. The more favorable formation is semicarbon aluminate. The higher calcined clay enriches the hydration products, resulting in the decrease of CH [12,13], However, under the steam curing condition, the carboaluminate phase formed in the limestone calcined clay system is not obvious. Considering that under the steam curing condition, the cement clinker consumes more water in the system due to the acceleration of early hydration degree, which results in the formation of carboaluminate or the content of formed calcium aluminate is less than that of standard curing. It can be seen from the figure that the hydration products change with the increase of hydration degree, the change of calcined clay/limestone ratio has no obvious change, which is also attributed to the low hydration degree caused by low water binder ratio.

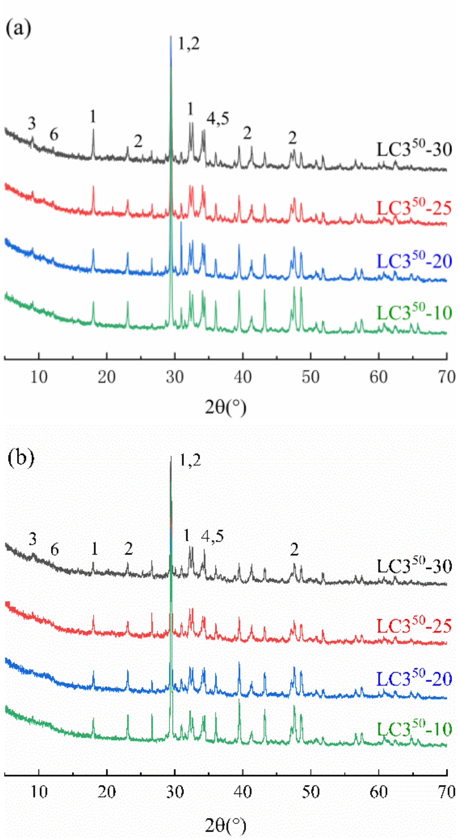
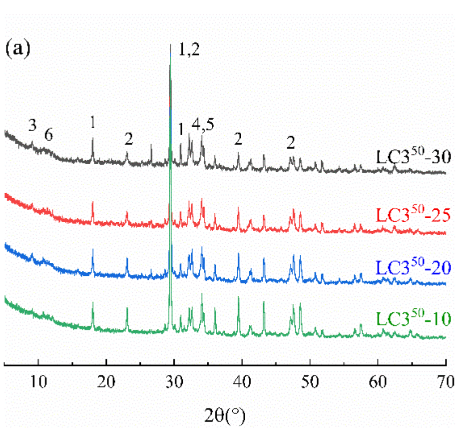


Figure 5. XRD patterns of curing age of 1d, (a) standard curing, (b) steam curing (1-calcium carbonate, 2-calcium hydroxide, 3-Ettringite, 4-Dicalcium silicate, 5-Tricalcium silicate, 6-Carboaluminate)



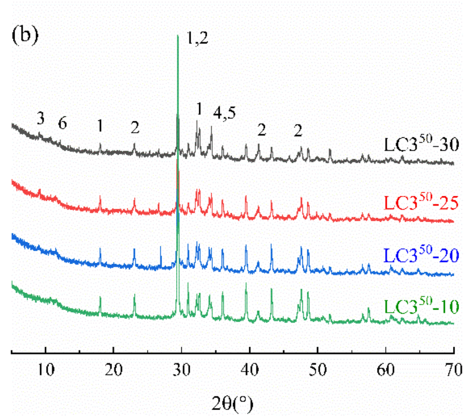


Figure 6. XRD patterns of curing age of 3d, (a) standard curing, (b) steam curing (1-calcium carbonate, 2-calcium hydroxide, 3-Ettringite, 4-Dicalcium silicate, 5-Tricalcium silicate, 6-Carboaluminate.)

Figure 7 and Figure 8 show the heat release rate and cumulative heat release under standard curing and steam curing respectively. According to the heat flow rate, the hydration process can be divided into four stages: initial reaction, induction, acceleration and deceleration [14,15]. There is only one exothermic peak under standard curing.

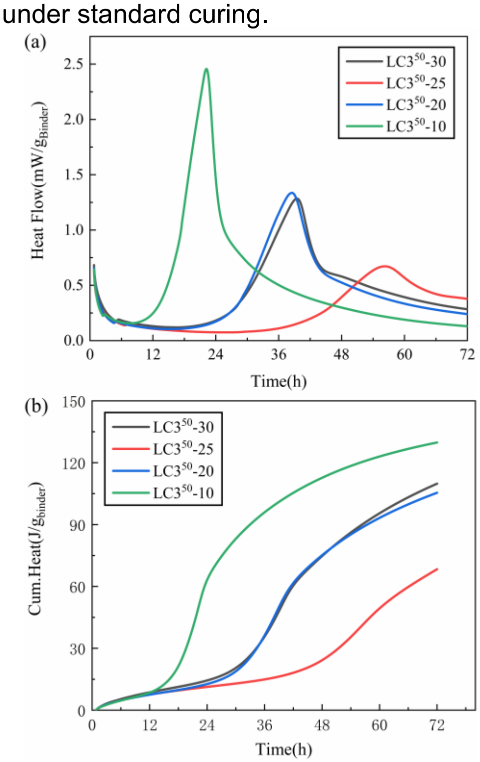


Figure 7. The hydration heat of standard curing, (a) hydration heat release rate, (b) cumulative heat release.

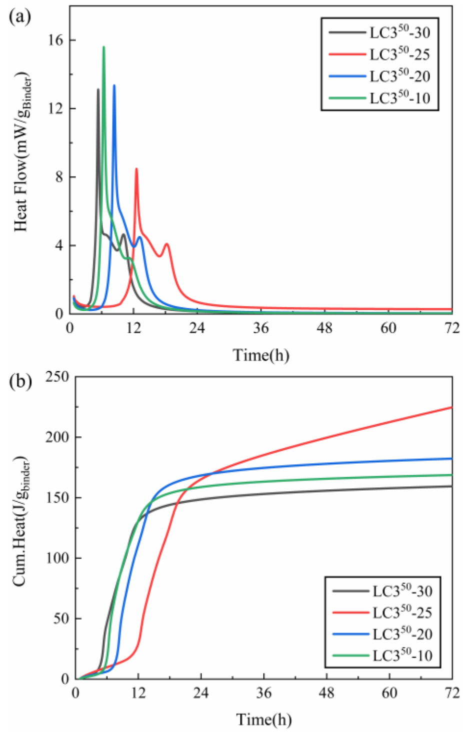


Figure 8. The hydration heat of steam curing, (a) hydration heat release rate, (b) cumulative heat release.

3.3. SEM-BSE

Figure 9 shows a group of SEM-BSE images of LC^{3}50-30 in one day and three days under different curing conditions. From the images, it can be seen that the system presents a relatively close stacking mode due to the low water binder ratio, and more unhydrated cement clinker can be observed. When the cement clinker is replaced by a large amount of limestone, the unhydrated cement clinker is relatively reduced, and at the same time, it is around the cement particles Some hydration products can be observed. When steam curing is adopted, it can be observed that the amount of unhydrated cement clinker is reduced and the content of hydration products in the early system is higher than that of standard curing.

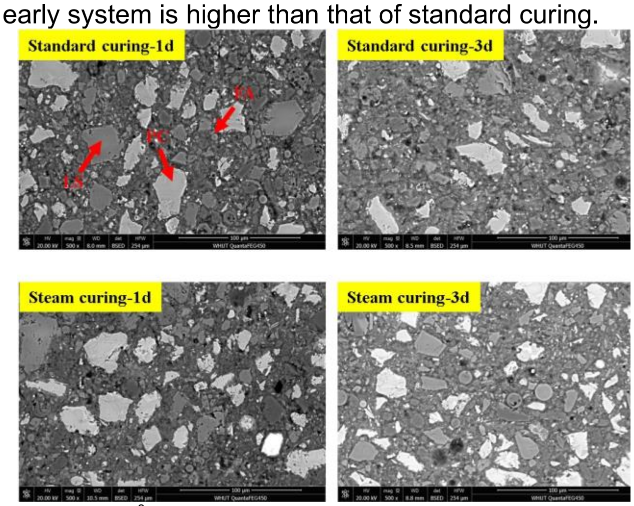


Figure 9. LC^{3}50-30 standard curing and steam curing 1d and 3d SEM-BSE images

4. CONCLUSIONS

By analyzing and comparing the early experimental data of each group, the following conclusions can be drawn:

(1) Steam curing at 55℃ for 5h significantly increased the compressive strength at 1d, but after curing, the increase of compressive strength decreased significantly with the increase of age, and the 3d compressive strength of standard curing increased nearly twice.

(2) The ratio of calcined clay / limestone has obvious influence on the compressive strength. With the increase of the ratio, the compressive strength first decreases and then increases, and the compressive strength is the lowest when the content of calcined clay is about 20wt.%.

(3) Steam curing can significantly improve the degree of hydration reaction of the system, shorten the induction period and enhance the early hydration rate. Meanwhile, it is observed by BSE that the amount of unhydrated cement clinker after steam curing is less than that of standard curing, and the hydration degree of the system is improved.

(4) The addition of calcined clay contributes to the formation of AFm phase in the system, but steam curing improves the hydration degree of cement, resulting in insufficient water in the system to provide reaction conditions for the formation of AFm phase, so relatively less AFM phase is observed under steam curing.

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