Influence of MK-Based Admixtures on the Early Hydration, Pore Structure and Compressive Strength of Steam Curing Mortars

Jinlong Han, Zhonghe Shui, Guiming Wang, Jiancong Shao and Yun Huang

Abstract Prestressed high-strength concrete (PHC) pipe piles are one of the most widely used concrete elements in building foundation construction. In this study, the effects of material composition on the compressive strength development, early hydration and pore structure of PHC were investigated by a series of analytical techniques. Supplementary cementitious materials, namely metakaolin (MK), granulated ground blast-furnace slag (GGBFS) and limestone powder (L.S) were used to prepare cement pastes and mortars under steam curing condition to improve early compressive strength. Finally the mortar containing 10 % MK and 10 % L.S was prepared, with the compressive strength up to 89 MPa at 1 day and 93 MPa at 7 days. The effects of the blended mineral admixtures on the early hydration and microstructure of steam cured pastes and mortars were investigated by XRD, TG-DTC and MIP. The results showed that the mineral admixtures could consume Ca $(OH)_2$ owing to pozzolanic reaction and promote concrete hydration, which led to the improvement of the properties of hydration products and optimization of pore structure and pore size distribution.

J. Han (✉) · Z. Shui · G. Wang · Y. Huang
State Key Laboratory of Silicate Materials for Architectures,
Wuhan University of Technology, Wuhan, China
e-mail: hhjjllhjl@163.com

J. Han · G. Wang
School of Materials Science and Technology, Wuhan University of Technology,
Wuhan, China

J. Shao
Maoming Kaolin Science and Technology Company, Maoming, China

K. Scrivener and A. Favier (eds.), *Calcined Clays for Sustainable Concrete*,
RILEM Bookseries 10, DOI 10.1007/978-94-017-9939-3_27

1 Introduction

Prestressed high-strength concrete (PHC) pipe piles are widely used in all kinds of engineering projects, such as industry and civil buildings, highway and railway, port and wharf constructions, due to the advantages of high strength, high density and high bearing capacity and reductions in building time. To improve economic efficiency, increasing the utilization efficiency of the moulds to improve production efficiency is a key way. Shortening the cycle of the mould application means the PHC pipe piles should gain a high strength as soon as possible especially at early age.

Without altering productive process, changing the composition binding material such as utilizing mineral admixtures as supplementary cementitious material to replace part of cement is a normal way to gain a high strength at early age [1–3]. Liu reported that the addition of UFA and ground slag can increase the compressive strengths of concrete containing supplementary cementing materials [1]. Metakaolin (MK), because of its high pozzolanic properties due to its amorphous structure and high surface area, has been used as a highly active and effective pozzolan for the partial replacement of cement in concrete. Unlike other pozzolans, it is a kind of primary products, not a by-product or secondary product. The capability of metakaolin used as a mineral addition to improve mechanical and durability properties of cement and concrete is well noted in concrete science, not only under normal maintenance [4–7] but also steam curing [8–10].

In this paper, firstly, the cement pastes and mortars under steam curing were prepared. Then its mechanical property was tested, the early hydration products were studied by X-ray diffraction (XRD) and thermal gravity and Differential Scanning Calorimeter (TG-DSC) analysis, the changes of porous characteristics were evaluated by mercury intrusion porosimeter (MIP) test. Finally, the relationship among mechanical property, hydration products and porous characteristics were discussed.

2 Experimental Procedure

2.1 Materials

The cement used was 52.5 type I Portland cement (PC) complying with Chinese National standard GB175-2007. Blast furnace slag (GGBS), metakaolin (MK) and

Table 1 Chemical composition of binders (%)

Chemical composition	SiO_2	Al_2O_3	CaO	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	LOI
PC	19.37	3.92	68.3	3.69	0.81	1.61	0.13	0.59	1.09
MK	53.15	44.43	0.02	0.7	0.21	0.13	0.34	0.53	0.12
GGBFS	33.64	15.27	35.46	0.45	2.05	10.2	0.51	0.52	0.15
L.S	8.27	2.64	45.11	0.9	2.01	0.11	–	4.29	35.43

Table 2 Mix design of cement pastes and mortars/g

Blended	Mixes	PC	MK	GGBFS	L.S	Sand	Water	HRWRA
Cement pastes	P0	800	–	–	–	1350	200	8
	P1	720	80	–	–			
	P2	640	80	80	–			
	P3	640	80	–	80			
Mortars	M0	500	–	–	–	–	125	5
	M1	450	50	–	–			
	M2	400	50	50	–			
	M3	400	50	–	50			

limestone powder (L.S) were also used as mineral admixtures. The chemical composition and physical properties of PC, GGBS, MK and L.S were listed in Table 1. Natural sand with a fineness modulus of 2.8 was used as fine aggregates. A polycarboxylate type High-Range Water Reducer Admixture (HRWRA) with a solid content of 40 % was used to achieve the required workability for the mixtures.

2.2 *Specimen Preparation and Steam Curing Regimes*

The details of mix design are given in Table 2. After mixing and vibration, the mortar mixture was placed in 40 × 40 × 160 mm moulds for compressive strength test and MIP test, and the cement paste mixture was placed in 40 × 40 × 40 mm moulds for XRD, TG-DSC analysis.

2.3 *Thermal Treatment*

Immediately after moulding, the pastes and the mortars were exposed to a steam curing cycle with a total duration of 17 h. The cycle included 4 h of presetting at 25 °C, followed by 3 h of heating at 15 °C temperature increase per hour up to 70 °C, 7 h of exposure at 70 °C and a 3 h cooling down period. Then removed from their moulds and stored at 20 ± 2 °C for testing ages.

2.4 *Methods*

2.4.1 Mechanical Tests

The compressive strength test was carried out at the ages of 1 and 7 days using a 2000 kN capacity compression testing machine.

2.4.2 Mineralogical Analysis: XRD

The measuring instrument used for XRD worked with Co-Kα radiation ($\lambda_{K\alpha}$ = 1789) at 40 kV and 30 mA. The 2-Theta values ranged from −10° to 168° and were recorded in 0.04° steps with a counting time of 10 s per step. The measurement was carried out on powder passing through a 40 μm sieve. The XRD technique identifies crystallized hydrated and anhydrous phases in a paste.

2.4.3 Thermal Analysis: TG-DSC

Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TG) were used to qualitatively and quantitatively analyze the hydration reactions. DSC locates the temperature ranges corresponding to the thermal decomposition of different phases in a paste.

2.4.4 Porosity and Pore Size Distribution by MIP

Total pore volume and pore size distribution measurements were carried out by mercury intrusion porosimeter (MIP). High-pressure Porosimeter Micrometrics Auto Pore IV 9510 (with sufficiently large pressure range up to 414 MPa) was used to measure pores ranging from 3 nm to 400 μm. Before testing, the samples were immersed in alcohol immediately for 48 h, then dried up at 105 °C for 24 h in vacuum oven.

3 Results and Discussion

3.1 Mechanical Performance

The compressive strength test was conducted on 40 × 40 × 160 mm specimens immediately after steam curing at the ages of 1 and 7 days. The final strength was an average calculated from six measurements on half parts of the specimens. The results are presented in Fig. 1.

As shown in Fig. 1, the compressive strength of the mortars at 1 and 7 days are in the sequence of M3, M1, M2, and M0. The mortar M3 containing 10 % MK and 10 % L.S gains 89 MPa at 1 day and 93 MPa at 7 days, which are 17 % and 14 % higher than the control mortar M0 respectively.

The strength results of mortars show that using MK, GGBS or L.S to replace part of cement can lead to better performances at early and later ages when steam curing is adopted.

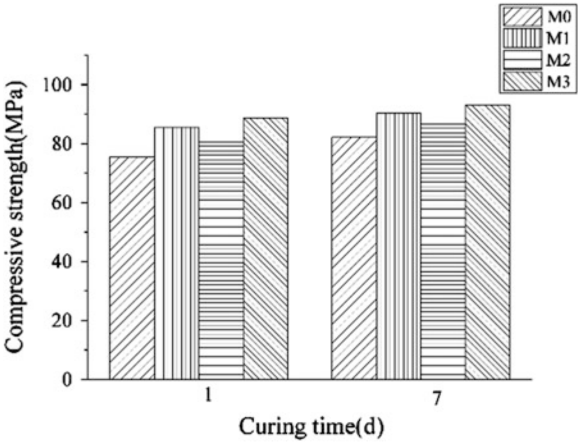


Fig. 1 Compressive strength *X-axis* 2θ (°) *Y-axis* intensity (arbitrary units) of mortars M0, M1, M2 and M3

The XRD technique identifies crystallized hydration products and unhydrated clinker. Figure 2 shows the X-ray diffraction patterns for the reference paste (P0) and the pastes incorporating MK (P1, P2 and P3) at 1 day.

Several observations and comments can be made according to the analysis of the XRD patterns. The main peaks in the patterns are $Ca(OH)_2$, ettringite and unhydrated C_3S. Observing the diffraction peaks at about 2θ = 18.1° (4.9 Å) and 2θ = 34.1° (2.63 Å), the peak height of $Ca(OH)_2$ decreased obviously for pastes P1, P2 and P3 relative to the reference paste P0. This issue is related to a reaction

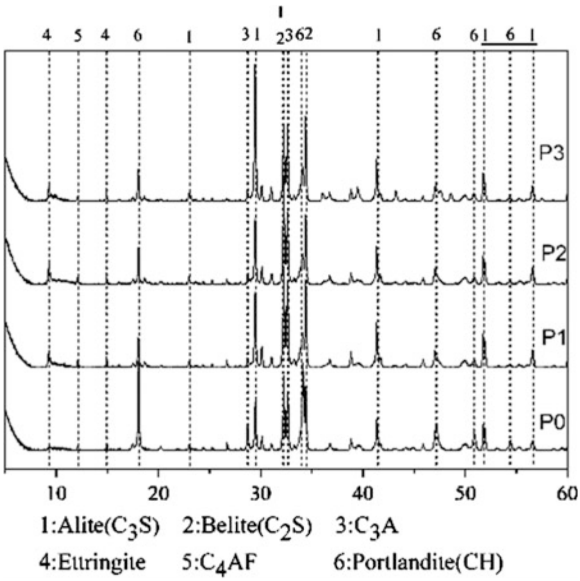


Fig. 2 XRD patterns for pastes P0, P1, P2 and P3 at 1 day 3.2. X-ray Diffraction (*XRD*) analysis

between active ingredients like activated alumina in MK and calcium hydroxide (CH), transforming calcium hydroxide (CH) into secondary C–S–H or C-A-H gel.

According to the diffraction peak at about 2θ = 9.1°, ettringite is visible for P1, P2 and P3, except for P0, indicating that MK, MK and GGBFS, MK and L.S all can promote the formation of ettringite.

3.2 Thermal Analysis

Figure 3 shows the DSC curves of steam cured reference cement pastes (P1) and paste incorporating MK (P1-10MK%, P2-10 %MK and 10 % GGBFS, P3-10 % MK and 10 % LS). Specific hydrated phases resulting from pozzolanic reaction could be distinguished by DSC analysis has been reported in several studies. The amount of C-S-H and CH are considerable concerned (Fig. 4).

Fig. 3 DSC pattern for pastes P1, P2, P3 and P4 at 1 day of age

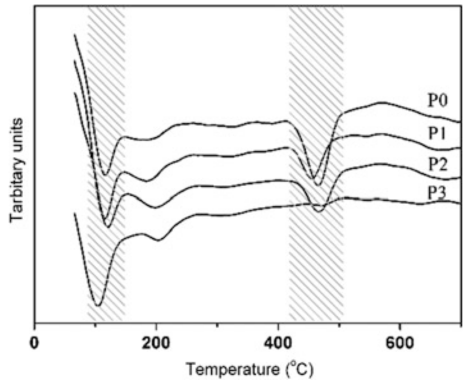
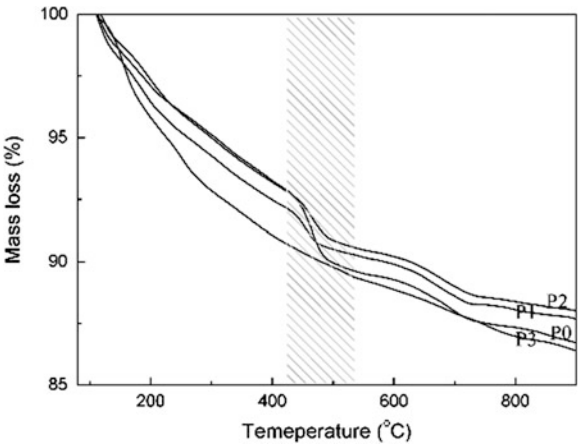


Fig. 4 TG pattern for pastes P1, P2, P3 and P4 at 1 day of age



The pozzolanic reaction can be observed by the decomposition of hydration products at about 100 °C. P3 presents a marked endothermic peak. This observation can be explained by the development of a large amount of C–S–H phases.

As expected from the XRD results, a smaller amount of CH is visible at the temperature about 450 °C in pastes with MK (P1, P2 and P3) than in reference pastes(P0), especially the amount of CH of P3 is smallest, indicating the consumption of CH by the pozzolanic reaction at the age of 1d.

3.3 Porosity and Pore Size Distribution by Mip

Effects of MK, GGBFS and L.S on pore structure of mortars are shown in Figs. 5 and 6 at 1 day under steam curing.

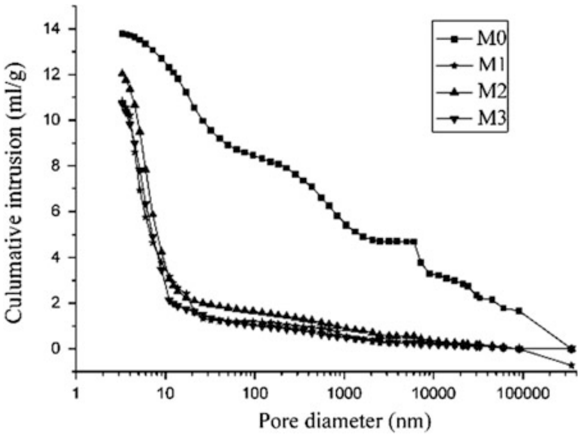


Fig. 5 Cumulative intrusion volume of mortars M0, M1, M2 and M3 at 1 day

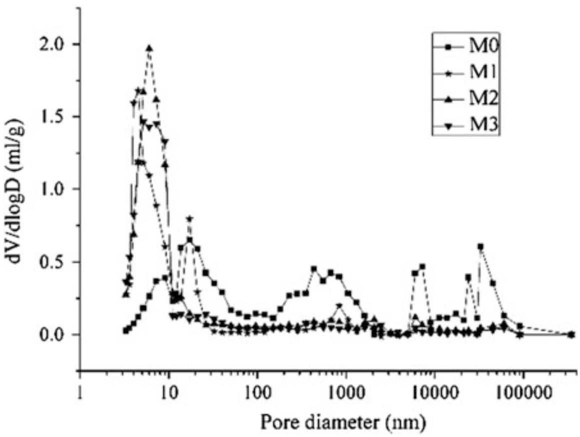


Fig. 6 Pore size distribution of Mortars M0, M1, M2 and M3 at 1 day

Due to micro aggregate filling and the pozzolanic effect of mineral admixtures, the total pore volume of mortar decreases significantly .Accumulative intrusion volume of mortar can be calculated in Fig. 5, 14.44 % for M0, which is higher than 11.27 % for M1, 12.46 % for M2, 10.97 % for M3. This is consistent with the strength test results of the mortars for the less total pore volume make mortar denser.

Figure 6 shows that pore size distribution shifts to the small pore diameter portion when MK, GGBFS and L.S replace part of cement due to its micro aggregate filling and the pozzolanic effect. It can be calculated that the content of micro pore that less than 10 nm of M0, M1, M2 and M3 account for 9.46 %, 70.8 %, 65.32 % and 80.07 % of the accumulative intrusion volume, respectively. The result is consistent with the strength test results of the mortars. C–S–H gels with higher strength were formed due to reactions between mineral admixtures and cement to optimize the microstructure of concrete.

4 Conclusions

- The compressive strength of mortar can be improved with the incorporation of MK, GGBS and L.S at early age and later age. The mortar M3 containing 10 % MK and 10 % L.S gains 89 MPa at 1 day and 93 MPa at 7 days under the steam curing.
- According to the results of XRD and thermal analysis, the amount of the hydration products (C-S-H and C-A-S-H) is increased with the incorporation of MK, while the amount of $Ca(OH)_2$ is decreased due to the pozzolanic reaction at the age of 1 day. The evolution of hydration observed is in agreement with the strength results on mortars.
- The MIP results show that pore size distribution shifts to the small pore diameter portion when MK, GGBFS and L.S replace part of cement and the total pore volume of mortar decreases significantly, which make the mortar denser and, the compressive strength increase.

Acknowledgments This research is financially supported by YangFan Innovative & Entrepreneurial Research Team Project (No.201312C12).

References

1. Liu, B., Xie, Y., Li, J.: Influence of steam curing on the compressive strength of concrete containing supplementary cementing materials. Cem. Concr. Res. **35**, 994–998 (2005)
2. Ho, D.W.S., Chua, C.W., Tam, C.T.: Steam-cured concrete incorporating mineral admixtures. Cem. Concr. Res. **33**, 595–601 (2003)

3. Baoju, L., Youjun, X., Shiqiong, Z., Jian, L.: Some factors affecting early compressive strength of steam-curing concrete with ultrafine fly ash. Cem. Concr. Res. **31**(2001), 1455–1458 (2001)
4. Frias, M., Cabrera, J.: Pore size distribution and degree of hydration of metakaolin cement pastes. Cem. Concr. Res. **30**(4), 561–569 (2000)
5. Fraire-Luna, P.E., Escalante-Garcia, J.I., Gorokhovsky, A.: Composite systems fluorgypsum blastfurnance slag metakaolin, strength and microstructures. Cem. Concr. Res. **36**, 1048–1055 (2006)
6. Janotka, I., Puertas, F.M., Palacios, M.: Metakaolin sand–blended-cement pastes: rheology, hydration process and mechanical properties. Constr. Build. Mater. **24**, 791–802 (2010)
7. Duan, P., Shui, Z., Chen, W., Shen, C.: Effects of metakaolin, silica fume and slag on pore structure, interfacial transition zone and compressive strength of concrete. Constr. Build. Mater. **44**, 1–6 (2013)
8. Cassagnabère, F., Mouret, M., Escadeillas, G.: Early hydration of clinker-slag-metakaolin combination in steam curing conditions. Cem. Concr. Res. **39**, 1164–1173 (2009)
9. Cassagnabère, F., Escadeillas, G., Mouret, M.: Study of the reactivity of cement/metakaolin binders at early age for specific use in steam cured precast concrete. Constr. Build. Mater. **23**, 775–784 (2009)
10. Ramezanianpour, A.M., Esmaeili, Kh, Ghahari, S.A., Ramezanianpour, A.A.: Influence of initial steam curing and different types of mineral additives on mechanical and durability properties of self-compacting concrete. Constr. Build. Mater. **73**, 187–194 (2014)