

Properties of the Cement-Based Composites with High Content of Metakaolin

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Abstract. Environmental concerns and sustainable development require increased replacement of cement. Most of previous studies have shown that the compressive strength of cement-based composites is maximized with a 20% content of metakaolin. We investigated composites prepared by replacing ordinary Portland Cement (OPC) with 30 to 50% of metakaolin (MK) and addition of appropriate amount of hydrated lime, which were ordinary cured for 2, 28 or 90 days. Hydration products and microstructure of the pastes were determined by X-ray diffraction (XRD), differential thermal analysis/thermal gravimetry (DTA/TG) and mercury intrusion porosimetry (MIP). MK was produced by calcination of kaolin from a Serbian deposit, which contained a high level of impurities.

Replacement of OPC with 30% of MK achieved 28 days compressive strength equivalent to that of the control mix. Higher replacement levels, 40% and 50%, combined with the addition of hydrated lime, achieved satisfactory relative strengths of 94% and 87%, respectively. The positive contribution was particularly pronounced after 90 days for a composite containing 50% of MK. The results clearly showed a possibility of obtaining composites having acceptable compressive strength with reduced cement content in accordance with environmental and sustained development requirements.

Keywords: Metakaolin · Hydrated lime · Cement-based composites · Compressive strength

1 Introduction

The advantages of use of supplementary cementitious materials (SCMs), such as fly ash, granulated blastfurnace slag, silica fume and natural pozzolana are well known, but their supplies are quite limited compared to the worldwide production of cement. Thus, the main goal of recent studies is to develop new SCMs, such as metakaolin (MK).

The effects of MK addition on the strength of mortar and concrete has been reported by many investigators. It was shown that better performance of cement-based composites is achieved with addition of 10% to 25% of MK, compared to the reference.

In most of these studies cement was replaced with up to 30% MK, due to the limiting quantity of available calcium hydroxide (CH) that could participate in the pozzolanic reaction and thus contribute to the strength. Properties of the composites with MK content over 30%, which are of particular interest with respect to environmental benefits, are rarely reported [1]. In this study, we investigated strength of composites prepared by replacing OPC with 30% to 50% of MK. Influence of hydrated lime addition was also determined. Factors affecting strength were studied by examining the microstructure of pastes by different analytical methods.

2 Materials and Methods

OPC (Lafarge CEM I 42.5R), MK (produced in the laboratory furnace by thermal treatment of Serbian kaolin) [2], sand, distilled water, hydrated lime and superplasticizer were used. The OPC and MK chemical composition and main physical properties are given previously [3].

Composite mixtures, with 0%, 30%, 40% and 50% of MK, were prepared. The mix proportions, with hydrated lime (designation CH) or without, are shown in Table 1. For estimation of the hydrated lime quantity it was assumed that 20% of CH was released during the cement hydration, and that the best mechanical properties could be achieved when MK was reacted with CH in the ratio $MK/CH = 2$ [4, 5].

Table 1. Composite mixture proportions (in g)

Designation	Cement	MK	Sand	Water	CH
CTRL	450	–	1350	225	
MK 30	315	135	1350	225	–
MK 30 CH	315	135	1350	225	5
MK 40	270	180	1350	225	–
MK 40 CH	270	180	1350	225	36
MK 50	225	225	1350	225	–
MK 50 CH	225	225	1350	225	68

The workability was adjusted using superplasticizer. The samples were cured in water under standard curing condition until testing periods (2, 28 and 90 days). Compressive strength measurements were carried out according to EN 196-1.

For microstructure analyses, selected pastes with 30 and 50% of MK, with the addition of appropriate hydrated lime quantity, were prepared. Paste without MK was prepared as the control (CTRL P). Blends of cement and MK were mixed with distilled water at a water-to-binder ratio (w/b) of 0.4. Pastes were cured under standard curing condition for 28 days. Microstructure was determined using XRD, DTA/TG and MIP analyses. The preparation of paste samples and analytical methods are thoroughly described in work [3].

3 Results and Discussion

3.1 Compressive Strength

The compressive strength of composites ordinary cured for 2, 28 and 90 days are presented in Fig. 1.

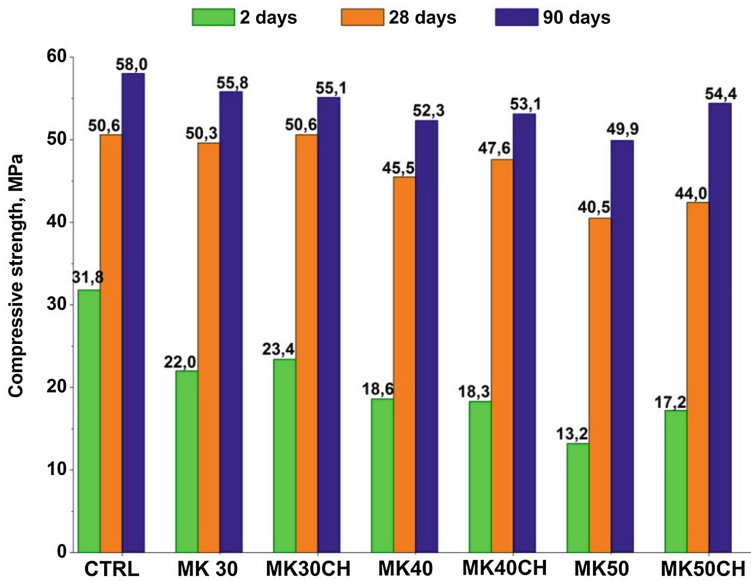


Fig. 1. Compressive strength of MK composites

At 2 days increased content of MK, either with or without hydrated lime, caused significant compressive strength decrease, compared to the control sample, which could be explained by a low degree of pozzolanic reaction and high dilution effect. The hydrated lime addition resulted in a small increase of compressive strength.

At 28 days composite MK 30 achieved the strength equivalent to that of the control. Higher MK content reduced the strength compared to the control. For composites containing hydrated lime this strength reduction was lower. Very good results, in terms of relative strengths of 94% and 87%, were obtained for MK 40 CH and MK 50 CH, respectively. At 28 days pozzolanic reaction significantly contributed to the strengths, but together with the MK filler effect, it was not sufficient to overcome the dilution effect [6].

At 90 days compressive strengths were lower than control. The positive contribution of hydrated lime addition was particularly pronounced for the composite MK 50 CH, where the relative strength was 94%.

It is evident that for all ages hydrated lime addition increases compressive strengths, and that further investigations are needed to optimize its quantity.

3.2 Microstructure

3.2.1 XRD Analysis

Figure 2 shows the XRD patterns of pastes.

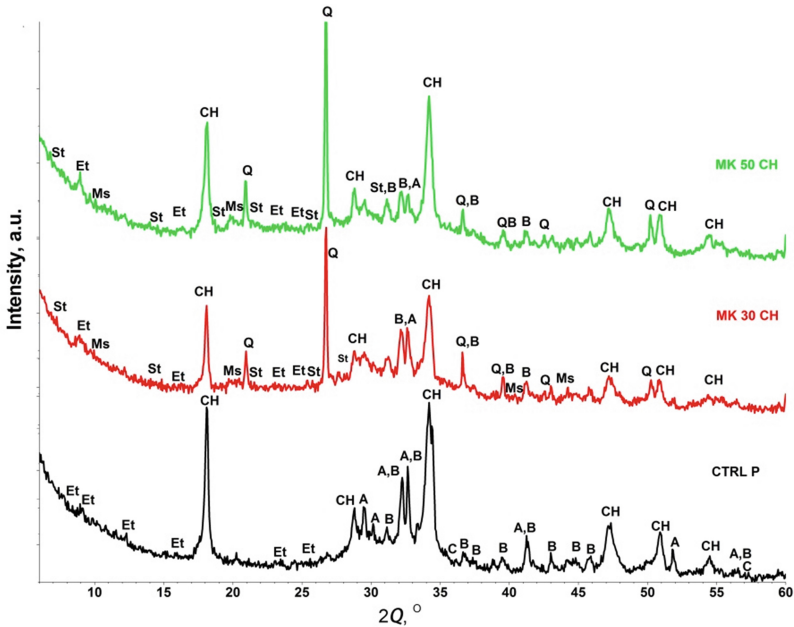


Fig. 2. XRD patterns of the pastes

The major crystalline minerals (hydrated phases) detected on the control paste were portlandite (CH), alite (A) and belite (B). As minor phases, ettringite (Et) and small content of calcite (C) were detected.

A significant reduction of the portlandite (CH) peaks for MK pastes can be observed compared to the control paste. It was less pronounced at composite MK 50 CH due to the higher hydrated lime addition.

New phases identified in MK pastes, which have positive effect on compressive strength, were strätlingite (St) and hardly noticeable monosulfoaluminate (Ms). Intensity of strätlingite and ettringite reflections increases with higher MK content and they are most pronounced in the paste MK 50 CH. Quartz (Q) reflections arise from impurities present in MK. Detected hydrated phases in MK pastes are similar to the findings reported previously [7, 8].

3.2.2 Thermal Analysis (DTA/TG)

DTA/TG curves corresponding to thermal decompositions of different phases in MK pastes are given in Fig. 3.

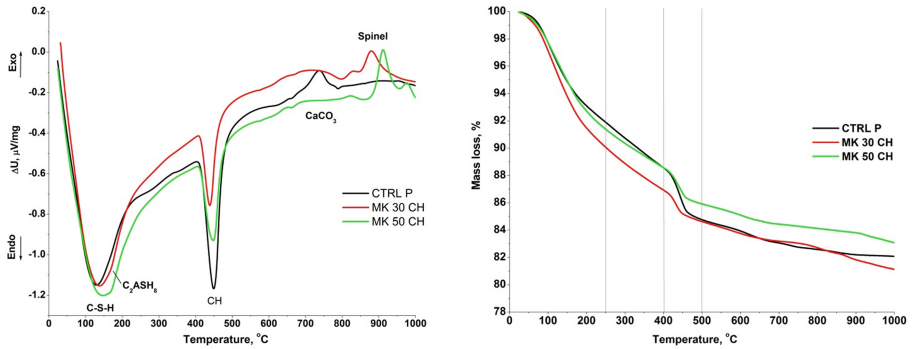


Fig. 3. DTA/TG curves of pastes

The endothermic peak at approximately 120–150 °C is a result of decomposition of amorphous C-S-H phase, as well as the possible presence of calcium sulfoaluminate hydrates (ettringite and monosulfate hydrates) [9, 10]. The peak increases with higher quantity of MK, indicating the formation of additional amounts of C-S-H, which in turns leads to higher strength.

Endotherm between 400 and 500 °C is characteristic for the decomposition of CH. Significant decrease in the CH peak intensity is notable in MK pastes, compared to the control paste, due to the consumption of CH in the pozzolanic reaction. This thermal effect is most pronounced in MK 30 CH.

Exothermic peaks at around 890 °C (respectively ~915 °C) and 975 °C could be attributed to the formation of precursors (alumina or aluminium-silicon spinel) of high temperature phases (mullite and cristobalite) from unreacted MK [7]. This peak is most pronounced in MK 50 CH paste.

TG curves can be divided into four regions. A mass loss in the temperature range up to 250 °C originates from dehydration of the C-S-H phases and possible presence of ettringite and monosulfoaluminate. Between 250 °C and 400 °C a dehydration reaction takes place due to the loss of water from the C-A-S-H phases. Mass loss between 400 °C and 500 °C is a result of dehydroxylation of CH, while decarbonation of calcium carbonate takes place in the region between 600 and 800 °C. The results of TG analysis, showed that content of C-S-H phases, as well as the consumption of CH, is higher in MK pastes (up to 40% in MK CH 30), compared to the control, which positively affects compressive strength of MK composites.

3.2.3 Pore Size Distribution

Figure 4 shows the pore size distribution curve for the studied pastes.

In general, pore radius higher than 0.025 μm influences the compressive strength [11]. MK pastes have a higher volume fraction of pores with radius smaller than 0.032 μm compared to the control paste. This result indicates that the substitution by MK reduces the volume fraction of larger pores. However, almost no pores larger than 0.25 μm are detected in any of the pastes, with the exception of a small fraction of the

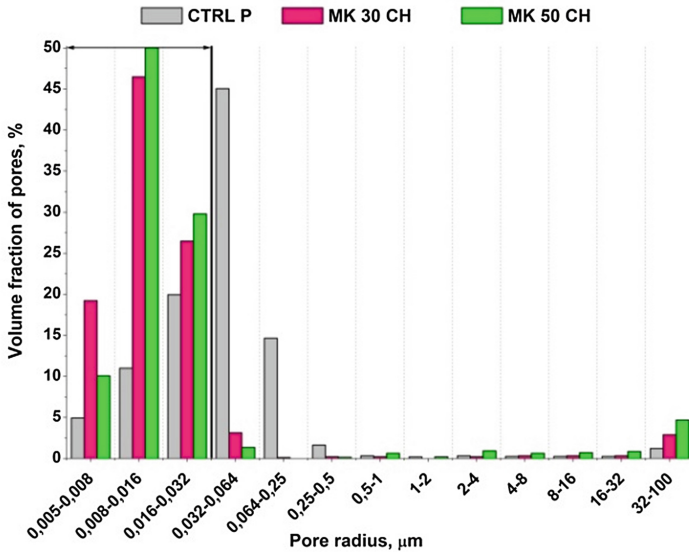


Fig. 4. Pore size distribution of pastes

largest pores (32–100 μm). The results are in accordance with the conclusions that MK is effective in the refinement of pore structure [6, 12].

4 Conclusions

Metakaolin could be used for higher cement substitution level, from 30% to 50%, in order to achieve satisfactory high compressive strengths. The positive contribution was particularly pronounced after 90 days for the composite MK 50 CH where the relative strengths was 94%, which is specially important with respect to environmental protection.

Microstructure analyses showed the pore structure refinement and the presence of C-S-H/C-A-S-H phases, which contributes to the strength, as well as the existence of remained CH, that might be the reason for the strength decrease.

Further improvements of compressive strength could be expected with optimization of quantity of the hydrated lime addition.

Acknowledgments. The work reported in this paper is a part of the investigation within the research projects TR 36017 and 45001, supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia. This support is gratefully acknowledged.

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