Compatibility of Superplasticizers with Limestone-Metakaolin Blended Cementitious System

Behnaz H. Zaribaf, Burak Uzal and Kimberley Kurtis

Abstract This study investigates the performance of polycarboxylate ether (PCE), polymelamine sulfonate (PMS), sodium lignosulfonate and naphthalene formaldehyde condensate (PNS) superplasticizers (SPs) with ASTM C595 Type IL cement (with up to 15% calcium carbonate) combined with 10 and 30 % metakaolin (MK) substitutions by mass. The required dosage of each SP for 10 % and 30 % MK substitutions were determined based on mini slump test to establish equivalent paste flow. At these dosage rates, the effects of SPs on setting time, hydration kinetics, and strength development were measured. Life cycle assessment (LCA) was carried out on different cement compositions used in this study to evaluate the greenhouse gas emissions and embodied energy of limestone-metakaolin blended cement with SP addition. While MK substitution decreases the workability of samples and shortens the setting time, this study shows that adequate dosages of a compatible type of SP can be used to compensate for these effects. Of the SPs examined, PCE and PMS are found to be more compatible, compared to PNS and sodium lignosulfonate, with limestone-metakaolin blended cements.

1 Introduction

Replacing a fraction of portland cement with of metakaolin (MK) helps to reduce the clinker fraction and consequently decreases the associated greenhouse gas emissions and embodied energy of concrete [1]. Metakaolin replacement can improve compressive strength at earlier ages than other supplementary cementitious

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B.H. Zaribaf (✉) · K. Kurtis
School of Civil and Environmental Engineering, Georgia Institute of Technology,
790 Atlantic Dr., Atlanta, GA 30332-0355, USA
e-mail: Behnaz@gatech.edu

B. Uzal
Department of Civil Engineering, Abdullah Gul University, Sumer Campus,
38080 Kayseri, Turkey

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materials (SCMs). Additionally, permeability of concrete decreased with metakaolin substitution that can improve the concrete durability [2].

Extending the use of MK and using it combined with ASTM C595 Type IL cement (Type IL-MK cement) can potentially further contribute to sustainability, by reducing the clinker fraction in concrete [3]. However, decreases in concrete workability can be problematic, as the fraction of metakaolin increased, particularly with limestone cements that have greater fineness.

In practice, several different types of superplasticizers can be used to improve concrete mixture workability. However, the compatibility and dosing of the various types of commercially available superplasticizers (SP) with Type IL-MK cement has not been well examined. This study examined four common superplasticizer types—polycarboxylate ether (PCE), polynaphthalene sulfonate (PNS), lignosulfonate (LS) and polymelamine sulfonate (PMS)—in Type IL-MK cement. After establishing dosage rates, which produce equivalent flow characteristics, time to set, hydration kinetics and strength development are assessed. Finally, life cycle analysis is performed to better understand the influence of binder composition and superplasticizer use on sustainability.

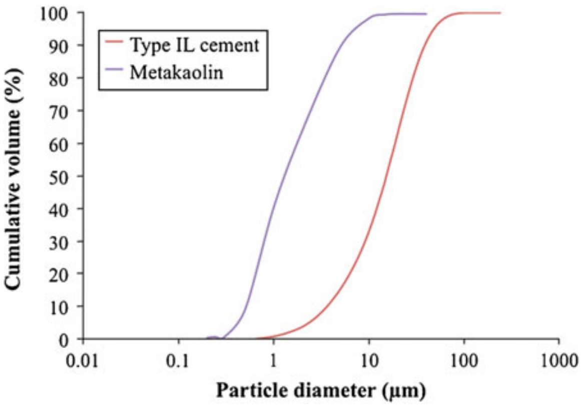
2 Materials and Methods

Pastes were produced from ASTM C595 Type IL hydraulic cement (Argos, Calera, AL) and metakaolin (OPTIPOZZ, Burgess Pigment Company, Sandersville, GA); compositional data and particle size distributions are given in Table 1 and Fig. 1, respectively. For mortars, natural sand (Vulcan Materials, Lithia Springs, GA) with fineness modulus of 3.04 and absorption capacity of 0.42 % was used. Four commercially available superplasticizers (SPs), polycarboxylate ether (PCE),

Table 1 Chemical composition of the cementious materials

Component (%)	Type IL cement	MK
SiO_2	17.13	51.4
Al_2O_3	4.16	44.8
Fe_2O_3	2.86	0.42
CaO	62.05	–
MgO	3.12	–
Na_2O	0.07	–
K_2O	0.48	–
Na_2O_e	0.38	–
TiO_2	0.26	1.46
SO_3	3.31	–
S/A ratio	0.8	–
LOI	6.33	1.05
Free CaO	0.56	–

Fig. 1 Particle size distributions of type IL cement and metakaolin



sodium lignosulfonate and naphthalene formaldehyde condensates (PNS) and polymelamine sulfonate (PMS) were obtained from two different producers (Grace, BASF). All the SPs are liquid, except PMS that was received and used as powder.

Pastes were produced at water-to-binder (w/b) of 0.40 with 10 % (MK10) and 30 % (MK30) cement substitutions by mass. For similar workability as paste, mortars were produced at w/b of 0.50 and sand-to-cement ratio of 2.75, at the same MK rates of use as the pastes.

Mini slump tests were carried out on pastes containing MK10 or MK30 and each type of superplasticizer, where dosages were adjusted to achieve 12 cm flow as a target [4]. Flow tests were performed on a broader range of paste compositions—with 10, 20, 30, and 40 % MK substitutions—to assess the trend between metakaolin substations and each superplasticizer dosage.

After establishing dosage rates required producing equivalent flow in each binder system with each SP type, isothermal calorimetry (TAM Air calorimeter, TA Instruments) was conducted on fresh paste samples at 25 °C, according to ASTM C1679 [5]. Time to set of mortar samples with Type IL-MK cement cement was measured by the Vicat test, ASTM C191 [6]. Compressive strength, ASTM C109 [7], was measured at 1, 3, 7, and 28 days on 2 inch (50 mm) mortar cubes prepared at w/b of 0.50. Mortar cubes were cured in limewater at 23 ºC. Life cycle assessment (LCA) was conducted using SimaPro 7.1 software (USLCI and BUWAL 250 database) [8].

3 Results and Discussion

3.1 Flowability

Flowability of paste samples was measured using mini slump cone with Type IL-MK cement to assess the effect of metakaolin on flowability of Type IL-MK cement pastes [9]. Four superplasticizer chemistries—PCE, PMS, sodium lignosulfonate and

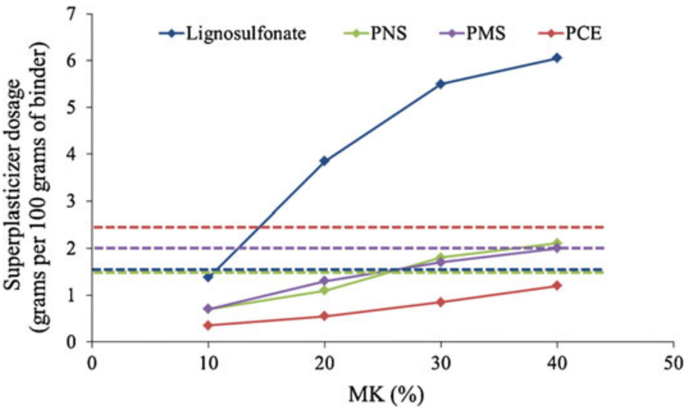


Fig. 2 Superplasticizer dosage required for pastes containing varying metakaolin levels in order to achieve flow comparable to control paste (no metakaolin)

PNS—were tested and the required dosage of each superplasticizer determined for pastes containing 10, 20, 30 to 40% metakaolin substitutions to achieve flow comparable to the control Type IL cement (no metakaolin). (These pastes denote MK10, MK20, etc.) All the superplasticizers used were in liquid form except PMS that was in powder form and dissolved in water before mixing. Figure 2 shows the required dosages of each superplasticizer expressed as the solid content of each superplasticizer for 100 g of binder (cement + metakaolin). The dashed lines show the maximum allowable level of each superplasticizer provided by the manufacturers. The results indicate that several types of superplasticizers, specifically the lignosulfonate and PNS, required significantly higher dosage than the maximum recommended dosage to achieve flow values comparable to the control samples. Use of superplasticizers at such high dosage rates may produce undesirable behavior including set retardation or false set; the latter is primarily found with lignosulfonate.

3.2 Cement Hydration

The early hydration behavior up to 40 h after mixing of Type IL-MK blended cement with water was studied with isothermal calorimetry. Paste samples with 30 % metakaolin were tested with different types of SPs at the dosages determined by the mini slump test to compare the effect of superplasticizers on the hydration of the paste mixtures. Paste samples with 30 % MK and lignosulfonate were not workable enough for testing.

Figure 3 shows that MK30 samples with no SP exhibit a lower cumulative heat of hydration and a slightly accelerated hydration compared to the control sample (no MK), while adding any of the SPs adjusted the rate of heat evolution and increased the cumulative heat released. Samples with PCE showed the highest peak

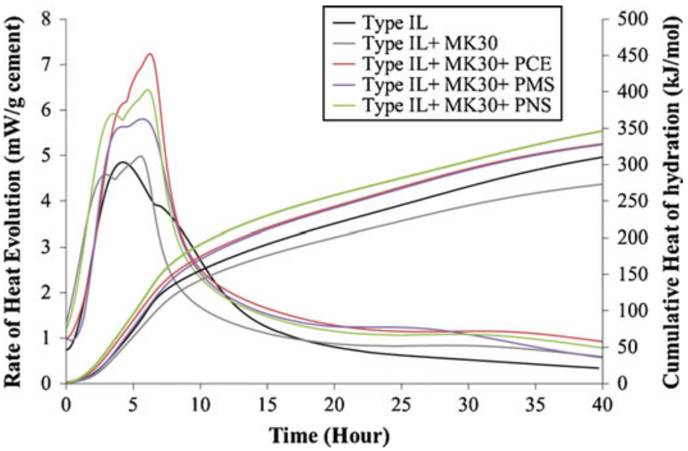


Fig. 3 Isothermal calorimetry results for type IL cement and 30 % MK and each of the four types of superplasticizers

rate of heat evolution while the cumulative heats of hydration were similar for all three types of SPs, and still higher than control sample with no MK.

3.3 Time to Set

The effect of metakaolin substitution on initial and final setting times of mortar samples was assessed by Vicat test. The initial and final setting time of mortar samples (w/b = 0.5) MK10 and MK30 are shown in Fig. 3. In general, metakaolin substitution shortens the initial and final setting time of samples; however, with appropriate dosage of superplasticizer, setting time can be adjusted to be similar to the control cement (i.e., no metakaolin).

The initial and final setting time of MK10 and MK30 mortar samples with each type of superplasticizer with the dosage determined by the mini slump test, is shown in Fig. 4. The results show that metakaolin mortars with no SP has a shorter final set while PMS, PNS and PCE increased the final set time of samples to be similar to the control samples. Lignosulfonate slightly lengthen the setting time of MK10 sample but MK30 sample with lignosulfonate was not sufficiently workable to measure the setting time. The retardation effect of PCE was observed for samples with MK30.

In addition to varying the chemistry of SP used, two procedures of adding PMS powder to cement (PMS (S)) and adding PMS to water (PMS (L)) were tested. It can be seen that the setting time results are very consistent. Based on setting time and calorimetry data, PCE was determined to be an effective SP and was chosen for further testing with MK10 and MK30.

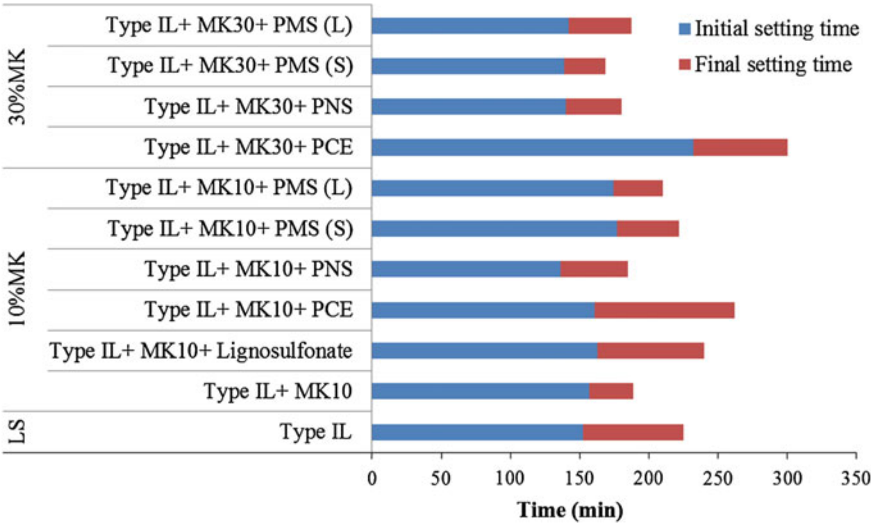


Fig. 4 Setting time data for limestone cement mortar samples with metakaolin substitution of 30 % and each type of superplasticizers

3.4 Compressive Strength

The compressive strength of samples with 10 and 30 % metakaolin with PCE was measured at 1, 3, 7, and 28 days of age. Figure 5 show that mortar samples with 10 and 30 % metakaolin have 40 and 20 % higher compressive strength at early age (1 day) compared to control sample (no MK). Higher compressive strength (30–40 %) was also observed for 7 day and 21 day samples.

3.5 Environmental Impacts

Life cycle assessment (LCA) was conducted to compare the embodied energy and greenhouse gas (GHG) emissions associated with ordinary (ASTM C150 Type I) and Type IL cement with 0, 10 and 30 % metakaolin substitution rates [8]. Data in Fig. 6 show use of Type IL cement saves up to 15 % in GHG emissions and embodied energy. Moreover, limestone cement with 10 and 30 % MK replacements can save up to 20 and 32 % of the GHG emissions and 17 and 22 % of the embodied energy associated with cement portion in concrete mixtures.

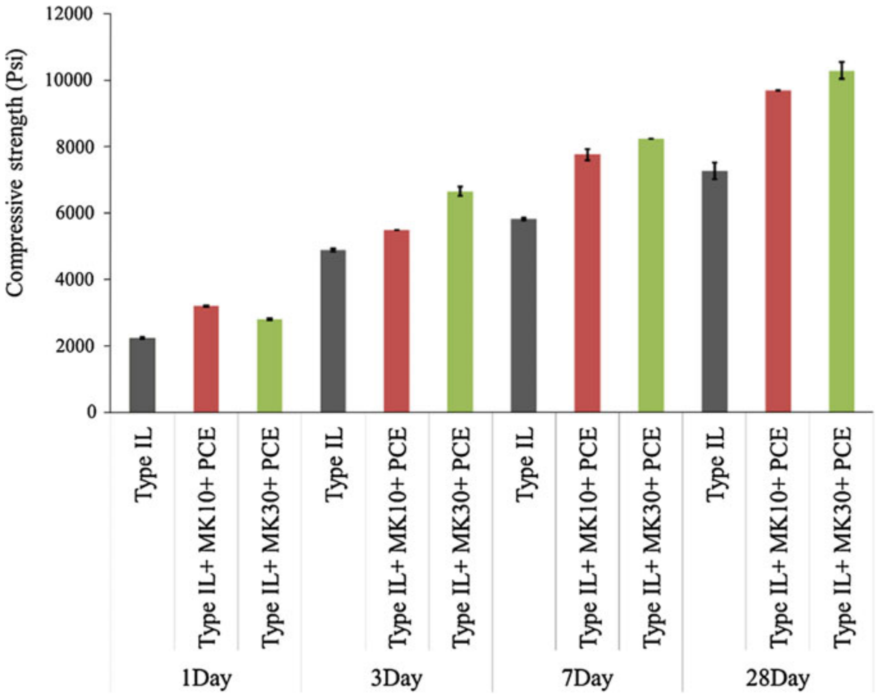


Fig. 5 Compressive strengths of mortars with limestone cement and 10 and 30 % MK and PCE superplasticizer (w/b = 0.50)

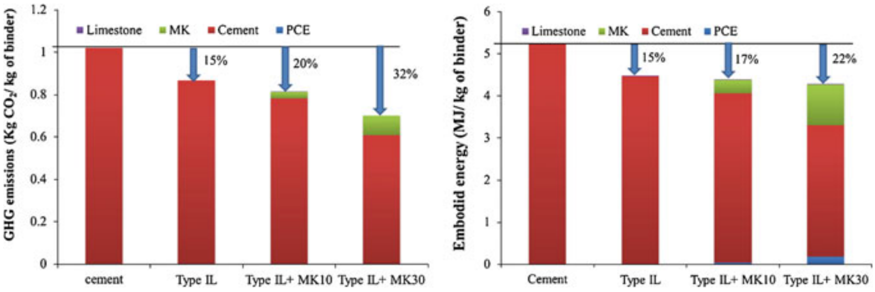


Fig. 6 Life cycle assessment of cements with metakaolin substitutions of 10 and 30 %

4 Conclusions

This study shows that PMS and PCE are the most compatible SPs for Type IL-MK cement. MK inclusion accelerates the hydration of cement and shortens the setting time, while addition of compatible SP can increase the setting time and adjust the hydration rate. Finally, compressive strengths of specimen increased with MK substitutions (10 % and 30 %) and PCE as a superplasticizer. Further, LCA study showed that MK replacements can reduce the GHG emissions and embodied energy associated with cement portion in concrete mixtures, even when increased SP dosages necessary for workability are considered.

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