Construction and Building Materials 95 (2015) 257–268

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effect of metakaolin substitution on physical, mechanical and hydration process of White Portland cement

Azime Subaşı [a], Mehmet Emiroğlu [b,*]

[a] Duzce University, Gümüşova Vocational School, Department of Metallurgy, Turkey
[b] Duzce University, Technology Faculty, Department of Civil Engineering, Turkey

HIGHLIGHTS

- Effect of metakaolin on physical and mechanical properties of cementitious composites was studied.
- Metakaolin was substituted with White Portland cement in different proportions.
- Hydration properties of the cement paste were evaluated by spectroscopic methods.
- C-S-H layers were formed on the hydrate particles of all metakaolin replaced with cement pastes.

ARTICLE INFO

Article history:
Received 30 March 2015
Received in revised form 28 June 2015
Accepted 14 July 2015
Available online 21 July 2015

Keywords:
Metakaolin
White Portland cement
Hydration process
Spectroscopic methods

ABSTRACT

In this study characterizations of cementitious composites containing metakaolin were examined via spectroscopic methods (XRD, DTA, TGA, FT-IR and SEM). Hybrid binders were obtained by replacing cement with metakaolin (5, 10, 15, 20, 25 and 30% by weight). In addition to spectroscopic methods, the bending and compressive strengths of the prepared samples were measured at the 2nd, 7th, 28th, 56th and 90th days. In conclusion it was determined that while the metakaolin replacement ratio increases the strength values on the 28th day decrease, yet due to the pozzolanic effect significant increases in strength are obtained on the 56th and 90th days.

1. Introduction

In the presence of water, metakaolin (MT) (AS_2), which is obtained as a consequence of the calcination of kaolinite-rich clays or soils, goes into reaction with CH and forms calcium alumina hydrate and alumina silicate hydrate crystal structured products (such as C_2ASH_8-stratlingite, C_4AH_{13} and C_3ASH_6-hydrogarnet) [1–3]. White Portland cement, considered indispensable particularly in terms of architectural concrete applications, has a minimum whiteness of 85% since it is produced from raw material of high purity. It allows for the preparation of successful mixtures with colorant pigments. Besides, with the use of suitable forms desired concrete surfaces with high levels of fineness can be obtained [4,5].

Positive effects of the use in metakaolin in the production of concrete and mortar such as its superior mechanical properties at early ages, reduction of the high hydration heat of cement, improvement of compressive, tensile and flexural strengths, reduction of shrinkage, increase in the freezing and thaw resistance, reduction of permeability, resistance against chemical effects, decrease of alkali silica reactivity and allowing for denser concretes were reported by several researchers [6–12]. Some researchers have also reported that metakaolin enhances workability, allows for obtaining a smoother surface and decreases efflorescence [9,11]. Samples that contain metakaolin at various rates up to 15%, pozzolanic reaction develops rather rapidly until 14 days, and therefore strength is increased and improvements in the porous structure of cement paste are observed. In curing periods longer than 14 days, on the other hand, it is reported by several researchers that the puzzolonic reaction rate decreases significantly and accordingly also the increase in compressive strength slows down [6,8,13–17].

Metakaoline's positive contributions to strength and durability in concrete and mortar depend on three separate mechanisms.

* Corresponding author at: Duzce University, Technology Faculty, Department of Civil Engineering, Düzce, Turkey.
E-mail addresses: azimesubasi@duzce.edu.tr (A. Subaşı), mehmetemiroglu@duzce.edu.tr (M. Emiroğlu).

http://dx.doi.org/10.1016/j.conbuildmat.2015.07.125
0950-0618/

These are the acceleration of the hydration of cement, the puzzolonic reaction created and the increase of compactness by filling the voids by means of a filler effect [10,18,19]. Wild and Khatib examined CH consumption and strength development in paste and mortar samples produced by using MT instead of Portland cement in the standard water cure condition. CH amounts were determined through TG analysis until a curing period up to one year. In conclusion, it was reported that CH amount decreases significantly with the use of MT. They are reported that CH consumption in samples containing MT is at its lowest values in the 14th day, in other words the pozzolanic activity is at the highest rate. Besides, as it is expected relative strength is not at the highest value at 14th day [16]. Frias and Cabrera examined hydration degree and pore size distribution in paste samples having 0.55 water/cement ratio and varying rates of MT replacements. While the CH amounts in the MT substituted samples increased between 3 and 7 days, later on the CH amount decreased depending on the MT amount [20]. Poon et al. on the other hand determined that the pozzolanic reaction was higher in pastes that contained 10% and 20% MT, in comparison with samples with 5% MT replacement. This high pozzolanic activity was explained with the observation that the CH amounts were higher in pastes that had more PC amount [15]. Brooks et al. reported that setting delays as the amount of MT increases, yet at 15% MT replacement a significant decrease in setting time takes place. The authors explained this significant decrease particularly in initial setting time with the acceleration of setting due to the formation of a denser binding phase due to the increasing need of water [21]. Moulin et al. found out that the setting time of pastes containing MT with 0.40 water/binder ratio are shorter than the setting time of control samples (as per ASTM C 191). They reported that mixtures that contain MT have a high need of water and MT causes thixotropic behavior, which the authors explained it to be a result of the accelerating effect of MT on PC hydration [22].

Use of puzzolan, particularly for the purposes of reducing cement consumption and improving durability parameters, causes changes in the molecular and mineralogical structures. It will be possible to better explain the material behavior of cement-containing composites by means of the use of spectroscopic methods which are used for the determination of material characterizations in several disciplines [23,24]. Koçak states that determining the surface characteristics of materials and the interaction between particles would contribute to the comprehension of reactions, particularly for understanding the change caused by puzzolan addition on the hydration process of cements. Therefore, it is suggested that in addition to standard cement tests, modern techniques such as DTA–TG, XRD, FT-IR, DTA, TGA and SEM should be employed with which the structural changes such as zeta potential can be observed [25]. For this reason, within the scope of the present study the effects of the use of metakaolin in cement composites including high-strength white Portland cement with high level of fineness. Metakaolin was used for production of high-strength composites with cement, mechanical and physical properties of cement mortars were examined through spectroscopic methods.

2. Materials and method

In the study, metakaolin (MT), which is a highly reactive puzzolan, obtained from the Microns Company and the CEM I 52.5 R-type White Portland cement (WPC) produced by Cimsa Mersin Cement Factory pursuant to the TS EN 197-1 standards was used as the binder [26]. In the mixtures CEN reference sand with standard distribution produced by SET Trakya Cement Industry pursuant to TS EN 196-1 was used while tap water was used as mixture water [27].

In the preparation of the samples, the standard TS EN 196-1 was followed [28]. Expansion, consistency water and setting time of the cement paste samples were determined as per the standard TS EN 196-3+A1. Consistency water and setting time of each cement paste were determined in a laboratory environment with 20 °C temperature and 65% relative humidity. Within the scope of the study, CEM I 52.5 R White Portland cement (WPC) was replaced with metakaolin (MT) at 6 different rates as 5, 10, 15, 20, 25 and 30%, and thus a total of 7 different cement mixtures were prepared. The data concerning the prepared mixtures are presented in Table 1.

The samples were removed from curing as per their hydration times and kept in a drying oven of 60 °C for 2 h. After the hydration process during 28 days the samples were then turned into dust in agate mortar for FT-IR and DTA–TGA analyses.

All mortar mixtures were prepared in an automated mortar mixer machine with the use of 450 g cement, 1350 g standard sand and 225 ml water. Prepared mortars were poured into three-compartment molds in the form of rectangular prism with the dimensions of 40 × 40 × 160 mm. The samples were then compacted for one minute in a shaking equipment, and thus the mortars were settled in the molds. Prepared samples were kept in laboratory environment during the 24 h and at the end of this period they were removed from the molds and cured in water at 20 ± 2 °C temperature until strength tests. On the 2nd, 7th, 28th, 56th and 90th days, the samples were taken out of the water and subjected to flexural strength and compressive strength tests as per TS EN 196-1.

Material amounts and codes used in the preparation of reference (R) and MT replaced cement mortar samples are presented in Table 2.

Flexural and compressive strength tests were conducted on the samples after the curing periods of 2, 7, 28, 56 and 90 days as per the standard TS EN 196-1 method.

3. Results and discussion

3.1. Physical properties

While the graphic of the particle size distributions of WPC and MT determined by laser particle distribution equipment are presented in Fig. 1, physical properties of the same raw materials and MK replaced cements are presented in Table 3.

Particle size analysis shows that MT has a finer particle in comparison with WPC. It was determined that the particle sizes of WPC and MT are respectively 31 and 41 μm according to 90% sieved rates, 12 and 10 μm according to 50% sieved rates and 2.4 and 4.9 μm according to 20% sieved rates (Fig. 1). It can be seen that MT has smaller particle sizes less than 15 μm, while WPC are smaller within the range of 15–100 μm particle sizes. However, according to Blaine values it is observed that MT has two times larger specific surface area than WPC (Table 3). With a specific gravity of 3.08 g/cm^3, it is observed that WPC has a higher specific gravity than MT.

3.2. Chemical properties

Results of the chemical analyses conducted on WPC and MT are presented in Table 4.

According to the chemical compositions, WPC contains a high rate of CaO, and of low rates of Al_2O_3, Fe_2O_3 and MgO. The primary compound of MT, on the other hand, is SiO_2. The fact that potassium oxide (K_2O) in MT is higher than sodium oxide (Na_2O) shows that it is rich in terms of K^+ ions. Also from the fact that the FeO content of metakaolin is very close of that of WPC it is understood that due to its near-white color, it is a puzzolan that can be used in combination with WPC particularly in architectural concrete applications.

Table 1
Cement compositions and sample codes.

Sample code	Compositions	WPC (%)	MT (%)
R	CEM I 52.5 R (WPC)	100	0
K1	CEM I 52.5 R + %5 MT	95	5
K2	CEM I 52.5 R + %10 MT	90	10
K3	CEM I 52.5 R + %15 MT	85	15
K4	CEM I 52.5 R + %20 MT	80	20
K5	CEM I 52.5 R + %25 MT	75	25
K6	CEM I 52.5 R + %30 MT	70	30