Cement and Concrete Research 64 (2014) 63–72

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Effect of cement type on metakaolin efficiency

Martin Cyr [a,*], Minh Trinh [a,b], Bernard Husson [a], Géraldine Casaux-Ginestet [a]

[a] Université de Toulouse, UPS, INSA, LMDC (Laboratoire Matériaux et Durabilité des Constructions), 135, avenue de Rangueil, F-31 077 Toulouse cedex 4, France
[b] GTS (Travaux Géotechniques et Sécurisation), 29 rue des Tâches, 69800 Saint Priest, France

ARTICLE INFO

Article history:
Received 31 October 2013
Accepted 19 June 2014
Available online 11 July 2014

Keywords:
Metakaolin (D)
Pozzolanic reaction
Alkali content (D)
Portlandite consumption
Cement composition (D)

ABSTRACT

It is acknowledged in the literature that the performance of supplementary cementing materials such as fly ash or silica fume often depends on the characteristics of the cement used. This work aims to show that this dependence also concerns metakaolin. Compressive strength tests were carried out between 2 days and 2 years using one flash metakaolin and a panel of 11 cements having a wide range of characteristics. At 28 days of age, the difference in terms of strength activity index could reach 0.4 between the most and the least efficient cements. The hydration of MK pastes followed by XRD and thermal analysis showed that the pozzolanic reaction involving MK was postponed with low-C_3A cements, as characterized by a delay of portlandite consumption and stratlingite formation. Several mechanisms are reviewed and discussed with the aim of explaining the role of cement in the development of the pozzolanic activity of MK.

1. Introduction

It has long been known that supplementary cementing materials (SCMs) have an influence on the hydration of cement compounds, by either physical (e.g. heterogeneous nucleation) or chemical (e.g. early pozzolanic activity, and/or interaction of soluble minerals such as alkalis, sulfates or heavy metals with cement compounds) effects [1]. The literature also suggests that the type and origin of cements have significant effects on the reactivity of SCMs. Experimental research has shown that the efficiency of SCM in terms of strength development can be influenced by the clinker composition and reactivity [2–9].

For instance, studies on fly ash have shown that the efficiency factor (k) can take a wide range of values, between 0.10 and 0.85 for a given fly ash tested with 20 different cements, and without any apparent correlation with the cement compositions [6]. According to Fraay et al. [2], the reactivity of fly ash is mainly influenced by the pH of the pore water. Popovics [5] compared the effect of regular (type I) and high early strength (type III) cements on the strength of 30% fly ash mortars. The two cements differed primarily by their fineness (mean diameters 18 and 12 μm for types I and III respectively). He found that the latter led systematically to higher performance, with 11–39% higher strengths at 28 days. Sybertz [3] studied the effect of four different Portland cements, with low, medium and high alkali contents, on the strength activity index (SAI) of fly ash mortars. On mixtures with high fly ash content (50%), it seemed that the fineness and, above all, the alkali content of the cement were significant influencing parameters: SAI varied from 0.85 (0.61% of Na_2O_{eq} in the cement) to 1.04 (1.31% of Na_2O_{eq} in the cement). Gu et al. [9] also found a fair correlation of SAI with the alkali content in the cement/fly ash system. In another study, Meng et al. [4] concluded from their tests that high levels of alkalis in cement did not appear to induce an increase in the reaction rate of fly ash, whereas it did induce such an increase for silica fume. Moreover, they found that the supply of $Ca(OH)_2$ had a decisive influence on the capacity and rate of reaction of silica fume. Frigione and Sersale [7] examined the effect of the chemical composition of the clinker on the compressive strength of blast furnace slag cements. By means of linear regression analysis, they showed that no correlation existed between the strength of the slag and the main constituents of the clinker (C_3S, C_2S, C_3A, C_4AF), but they found a fair relationship with the total and the soluble alkali contents (Pearson's r values around 0.5).

To the authors' knowledge, very few data exist on the effect of the cement type on the reactivity of metakaolin (MK). Lagier and Kurtis [10], who studied the heat of hydration of blended cements, stated that the dissolution of MK could be promoted by the abundance of alkalis in high-alkali Portland cements. However, no mechanical tests revealed whether this could lead to an enhancement of the MK efficiency. Given the divergent conclusions found in the literature, it seems difficult to have any advance knowledge of the characteristics of the cement that will influence the efficiency of MK in blended cements.

The aim of this paper is to study the dependence of the pozzolanic reactivity of flash-MK on the type of cement used. Measurements of compressive strength, evolution of hydration followed by XRD and

---

* Corresponding author. Tel.: +33 5 61 55 67 07; fax: +33 5 61 55 99 49.
E-mail address: martin.cyr@insa-toulouse.fr (M. Cyr).

http://dx.doi.org/10.1016/j.cemconres.2014.06.007
0008-8846/© 2014 Elsevier Ltd. All rights reserved.

thermal analysis, pH and alkalinity of the pore solution of MK-cement pastes were carried out (1) to help understand the role of the cement in the development of the pozzolanic activity of MK, and (2) to improve the choice of a cement suited to the use of a given MK.

2. Materials and methods

2.1. Materials

The metakaolin was obtained by an industrial flash calcination process [11], which consisted of heating the kaolinite in a calciner (flame at a temperature between 1000 and 1200 °C) for a few tenths of a second, just long enough for it to reach 700 °C and be transformed into metakaolin, before sending it to air cooling cyclones. This process and its consequences on the properties of the metakaolin obtained are discussed by San Nicolas et al. [11]. The sample of MK used in this study was composed of an amorphous phase (~50%) containing mainly silica and alumina and coming from the dehydroxylation of kaolinite. The crystallized phases were quartz–SiO_2 (~44%), anatase–TiO_2 (~1%) and mullite–$3Al_2O_3, 2SiO_2$ (~5%). The production of mullite was due to particles being over-calcined when passing around the flame. The chemical composition is given in Table 1. The density of MK was 2.54 g/cm^3 and its specific surface area (BET) was 12.5 m^2/g.

A large selection of cements (11, labeled C1 to C11) conforming to the European cement standard EN 197-1 were used in order to cover a wide range of characteristics (Table 2), especially in terms of fineness (3000–4600 cm^2/g) and C_3A (0–12%), C_3S (53–70%) and alkali contents (Na_2O_{eq} 0.32–0.85%). The cement types included 10 CEM I and 1 CEM II, with normal (N) and rapid (R) strength development. The medium and low-C_3A cements complied with French standards NF P 15-317 [12] and NF P 15-319 [13] (in France, medium and low-C_3A cements are named "PM" and "ES or PM-ES," respectively; EN 197-1 uses the term "SR-cements").

2.2. Sample preparation and test methods

This project was started in the context of the optimization of injecting grouts, and a previous paper [14] justified the use of 40–60% of MK, a range of replacement rates for which MK showed high pozzolanic efficiency. All the tests in the present study were carried out on pastes containing cement, metakaolin and water. No superplasticizer was needed in regard to the flow behavior. The replacement rates of cement by metakaolin were set at 40 and 60%. The volumetric solid concentration (Γ = volume of solid/total volume) was kept at a constant value of 0.39, meaning that the mass water/binder ratios were 0.50, 0.54 and 0.57 for 0, 40 and 60% MK, respectively.

Pastes were prepared using a turbo-type mixer with a 65-mm-diameter head. They were mixed for 10 min at a controlled speed of 2000 rpm. The pastes were cast in prismatic molds of dimensions 4 × 4 × 16 cm. After casting, the samples were kept in the molds for 24 h at 95% RH and 20 °C, then were demoulded and immersed in water at 20 °C until the age of testing. Compressive strength tests were performed at 2, 7, 14, 28, 90, 365 and 730 days according to standard EN 196-1. Each result was the mean value of 6 samples. The heat evolved was measured by semi-adiabatic calorimetry using a Langavant calorimeter (NF P15-436), which can handle large amounts of material (1.6 kg). In this apparatus, the mortar was put into a well, but not perfectly, thermally insulated bottle placed in an air-conditioned room at 20 ± 1 °C. The calibration of the bottle allowed us to calculate the heat lost by the tested mortar. The hydration of cement pastes was monitored using X-ray diffraction (XRD) and thermal analysis (thermogravimetric – TG, and differential scanning calorimetry – DSC). Two cements were studied: one CEM I 52,5N (cement C1) and one low-C_3A CEM I 52,5N PM-ES (cement C10). The mixtures with MK contained 40% cement and 60% MK (w/b = 0.57), and two mixtures without MK (w/b = 0.50) were used as references. The pastes were kept in sealed plastic boxes and cured in a room at 20 °C and 95% R.H. until the age of testing. XRD, TGA and DSC tests were carried out at 2, 7, 14 and 28 days. A diffractometer (Siemens D5000) with variable slit opening, CoKα radiation, and a thermoanalyser (Netzsch STA 449F3 with heating rate 10 °C/min – 2 g of sample for TG and 30 mg for DSC, both in an argon atmosphere) were used for the tests. Extractions of pore fluid were carried out at 28 days according to the procedure given by Cyr et al. [15]. The pH of the pore solution was determined as soon as possible after collection using a standard pH-meter. The solution was then stabilized with 1 mL HNO_3 65% (14.4 M). Concentrations of alkalis were measured by inductively coupled plasma optical emission spectrometry (ICP-OES).

3. Results

3.1. Compressive strength dependence on cement type

The compressive strength results of pastes containing 0%, 40% and 60% of MK with cements C1 to C11 are given in Table 3, for curing ages between 2 days and 2 years. The mean interval of confidence on the compressive strength results was 1 MPa ($\alpha = 0.05$). It can be seen that a decrease in strength was systematically observed for mixtures containing MK. This was due to an increase in the water content (w/b = 0.50, 0.54 and 0.57 for 0%, 40% and 60% MK, respectively) and to the dilution effect of the cement by MK. The MK contents were too high to allow the pozzolanic activity to counteract the dilution of the cement. However, most of the pastes conformed to the minimum strength constraint initially fixed for 28 days in grouting application (>20 MPa) [14], except for mixtures with 60% MK used with C9, C10 and C11.

Table 3 and Fig. 1 show significant differences between the performance of pastes made from the different cements. It is noteworthy that, for a given replacement rate and curing time, a relatively large scatter of the SAI was obtained, the differences being in the range 0.2–0.4 between min and max SAI (Fig. 1). These differences were quite significant considering that the mean strength activity indexes ranged from 0.11 (60% MK at 2 days) to 0.77 (40% MK at 730 days).

Fig. 2 gives an example of the scatter on strength and SAI at 28 days for pastes containing 40% and 60% of MK for all types of cement used in the present study. Let us recall that cements C1 to C6 were normal CEM I, C7 was CEM II, C8 was medium-C_3A CEM I, and C9 to C11 were low-C_3A CEM I. For 40% of MK, SAI reached 0.68 in the best case (cement C6), but only 0.44 in the worst case (cement C10). The difference was even worse for 60% of MK (0.58 vs. 0.18 for cements C6 and C10, respectively). It is obvious that the three lowest values were obtained for low C_3A cements (C9, C10 and C11), with strengths decreased by about 30% compared to other cements. These differences were not made up at later ages.

These results show the difficulty of characterizing a given SCM, and it seems impossible to dissociate the SCM from the cement used. The rest of the paper focuses on the factors explaining the differences of efficiency when MK is associated with different types of cement.

Table 1
Chemical composition of flash-metakaolin.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	LOI
Chemical composition (% by mass)	67.1	26.8	2.6	1.1	0.1	0.0	0.1	0.01	0.8
Approximate mineralogical composition (% by mass)	Metakaolinite (~50%), quartz (~44%), anatase (~1%) and mullite (~5%)								