Construction and Building Materials 159 (2018) 18–26

Contents lists available at ScienceDirect

Construction and Building Materials

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

Chemical and mechanical characterization of ternary cement pastes containing metakaolin and nanosilica

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HIGHLIGHTS

- Chemical and mechanical properties of ternary cement pastes were evaluated.
- A synergistic effect of nanosilica and metakaolin was observed.
- Nanosilica and metakaolin increased the compressive strength and refined the pore structure of the matrix.
- Ternary mixes presented a high potential for the production of high performance cementitious materials.

ARTICLE INFO

Article history:
Received 5 April 2017
Received in revised form 14 October 2017
Accepted 28 October 2017

Keywords:
Nanosilica
Metakaolin
Activity
Ternary cement
Properties

ABSTRACT

This paper, for the first time, focuses on the characterization of the chemical and mechanical properties of ternary cement pastes with the addition of up to 18% of metakaolin and colloidal nanosilica. The paste containing 15% of metakaolin and 3% of nanosilica presented an increase of 44% on the compressive strength and a reduction of 66% on the average pore diameter at the age of 91 days, in comparison with the reference paste. Results obtained remark the high potential of ternary cement mixes produced with the combination of metakaolin and nanosilica for the production of high performance cementitious materials.

1. Introduction

The recent development in nanotechnology has caused positive impacts on construction materials. Some authors [1–5] stated that the better comprehension of the micro and nanostructure of cementitious materials may lead to a new generation of concretes, which are more resistant and durable than the cementitious matrices commonly employed nowadays. The improvement in these properties may increase the field of application of construction materials.

Hou et al. [4] considers that one of the most important steps in the development of cementitious materials in the past decades was the employment of mineral additions to partial replacement of ordinary Portland cement (OPC). These additions significantly improve the economic, energetic and technical characteristics of concretes and play an important role to obtain materials that are more sustainable and environmentally friendly. The cement industry is responsible for approximately 5–7% of the total CO_2 emissions in the world, while in Brazil, that amount is reduced to around 2.6%. This reduction is based on the use of materials with a low clinker/cement ratio (0.70), which is achieved by the employment of mineral additions in cements [6].

Nowadays, silica fume, metakaolin and rice husk ash are used for the production of high performance concrete. These mineral additions are highly reactive due to their pozzolanic activity [5,7]. The main beneficious effects observed in blended cement matrices are the improvement in the mechanical properties and durability with respect to reference ones. Their pozzolanic activity develops between non-crystalline SiO_2 particles and portlandite present in the cementitious matrix, which results in the formation of secondary C—S—H gels with a lower Ca/Si ratio and a higher degree of polymerization of C—S—H chains. In addition, their

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https://doi.org/10.1016/j.conbuildmat.2017.10.123
0950-0618/

physical action (filler effect) is also relevant because their elevated fineness contributes to pore refinement, which decreases the final porosity and improves the cohesion of the matrix in the fresh state [7].

Some previous studies [7,8] presented the scientific and technical advantages when adding metakaolin to the cement matrix. This addition has a high alumina content in its composition, which makes it different from the other additions based only on amorphous silica. When metakaolin is employed, the formation of C—A—S—H that occurs by the replacement of Si by Al on the C—S—H chains is observed [9]. This substitution generates gels with a higher degree of polymerization and with longer chains [10].

The incorporation of nanoparticles in cementitious systems alters the microstructure of the matrix and influences their chemical, physical and mechanical properties. Silica nanoparticles (nanosilica) have a higher reactivity and pozzolanic activity than silica powders with similar composition due to their smaller particle size. The use of nanosilica contributes to form a denser and more compact matrix than the use of silica fume [11] and accelerates cement hydration reactions. Moon et al. [12] noticed the presence of additional C—S—H during the early age hydration of cement containing nanosilica. Some authors state that it is still necessary to improve the knowledge on nanosilica [1–4,13–15].

A few works deal with the characterization of the microstructure and the mechanical properties of ternary cementitious systems composed by Portland cement, colloidal nanosilica and reactive mineral additions. Although these additions are beneficious to improve the performance of cementitious matrices [16–21], no studies regarding the evaluation of the synergistic effect of metakaolin and nanosilica have been found, so it represents an important gap for the scientific community today.

Therefore, this paper intends to complement the researches carried out on the topic, focusing on the chemical and mechanical characterization of Portland cement pastes produced with metakaolin and nanosilica. Pastes were characterized by X-ray diffraction (XRD), thermogravimetry (TGA), Fourier transform infrared spectroscopy (FT-IR), compressive strength and mercury intrusion porosimetry (MIP). Results showed the potential of the combined use of metakaolin and nanosilica for the production of high performance cementitious materials.

2. Experimental program

2.1. Materials

The following materials have been used in this experimental campaign:

- Cement type I (CPI), following the requirements of Brasilian standard [22], supplied by Votorantim Cimentos;
- Nanosilica (NS), based on an aqueous suspension of SiO_2 nanoparticles (30% of solid content), supplied by Akzonobel;
- Metakaolin (MK), supplied by Metacaulim do Brasil;
- Potable water;
- Superplasticizer based on a polycarboxylate solution (40% of solid content), supplied by Sika.

Table 1 presents the properties and characteristics of the cement used in this study. Table 2 shows the chemical composition of cement, metakaolin and nanosilica, determined by X-ray fluorescence spectrometry. As observed in Table 2, metakaolin contains 57% of silica and 32% of alumina, whereas nanosilica is composed mainly by silica (89%). It is important to note that the loss on ignition was determined with the solid residue of the nanosilica, previously dried at 100 °C.

Fig. 1 presents the X-ray patterns obtained with metakaolin and nanosilica. The peaks observed in the diffractogram from metakaolin (Fig. 1a) indicate that the kaolinite is present in the calcined product (MK), which may indicate that the temperature reached during calcination and/or retention time were not sufficient for the complete transformation into metakaolin. Apart from the kaolinite, quartz, goethite and illite are also present as crystalline phases. The amorphous halo observed between 15° and 30° (2<theta>) indicates the presence of metakaolin, mineralogical phase well known for its non-crystalline nature. The X-ray pattern from nanosilica (Fig. 1.b) shows that this compound does not contain crystalline phases, that is, it is totally composed by an amorphous nature.

Fig. 2 presents the particle size distribution of metakaolin, determined according to [23], which showed d_{10}, d_{50} and d_{90} equal to 2.27, 29.07 and 59.01 μm, respectively. Fig. 3 shows TEM images of nanosilica, where spherical SiO_2 nanoparticles, measuring around 27 nm in diameter, may be observed. Due to their high surface energy, interparticle distance and molecular configuration, these nanoparticles tend to form clusters, which were also observed by [24].

2.2. Composition and preparation of cement pastes

Six different pastes were produced with Portland cement, nanosilica and/or metakaolin and their compositions are presented in Table 3. The objective was to evaluate the effect of these ternary cementitious systems on high performance concretes. Thus, all the pastes were produced with a fixed water/binder ratio equal to 0.35. In order to do that, the water contents from nanosilica (NS) and superplasticizer (SP) were deducted from the total amount of water used to prepare the pastes.

Nanosilica was dosed considering its solid content (30% by mass). The dosage of superplasticizer varied according to the composition of each paste, to maintain a fixed consistency equal to (260 ± 10) mm, which was considered the most favorable for the molding process. The consistency was measured in a flow table, according to [25].

Pastes were produced in a climatic room at the temperature of (23 ± 1) °C, using a universal mortar mixing machine following the requirements of [25]. The procedure to prepare the pastes consisted in adding the water/SP/NS mix to the MK blended cement and homogenizing the resulting paste for 60 s at 140 rpm and, then, for 90 s at 280 rpm. The pastes obtained were used to mold cylindrical specimens, measuring 50 mm in diameter and 100 mm in height. After preparation, the molds were kept in a 100% humid chamber for 24 h. Then specimens were demolded and kept at the same chamber until the date of testing.

Samples employed for the XRD, TGA and FTIR tests were obtained from the centre of the specimen used for the compression

Table 1
Properties and characteristics of the cement used in this study.

Setting Time		Blaine (cm^2/g)	Residue on sieve #200 (%)	Specific mass (g/cm^3)	Compressive strength (MPa)		
Initial (h:min)	Final (h:min)				1 day	7 days	28 days
02:10	03:30	4678	0.97	3.15	28.30	35.76	44.08