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Influence of organoclay structural characteristics on properties and hydration of cement pastes

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HIGHLIGHTS

- Hydration of cement pastes with the addition of organoclay (1 wt%) was studied.
- Organomontmorillonites (OMT) with different cation exchange degree were used.
- Pozzolanic behaviour of OMT depends on the cation exchange degree of nanoclay.
- Considerable decrease of water sorptivity was achieved for cement pastes with OMT.

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ABSTRACT

In this study the effect of small amount (1 wt%) of organically modified montmorillonite (OMT) on the hydration peculiarities, strength and water sorptivity of cement pastes was investigated. Three types of OMT with cation exchange degrees 0.6, 0.8 and 1.0 were selected for cement substitution in the paste. Cement hydration was analysed by XRD/Rietveld method, SEM/EDS and thermogravimetric analysis. OMT of lower cation exchange degree (0.6) displayed pozzolanic behaviour after 14 days while the activity of OMT with higher cation exchange degree (0.8–1.0) was observed only after 28 days. The use of OMT with higher cation exchange degree resulted in the extra formation of aluminohydrates in cement pastes. The capillary sorption of the samples decreased with the increase of the cation exchange degree of OMT.

1. Introduction

Nowadays, the application of nanomaterials has received great attention to enhance the properties of conventional concrete [1–4]. The main hydrate phases in OPC pastes are calcium silicate hydrate (C-S-H) and portlandite (CH) [5,6]. In the case of pozzolanic additives, the pozzolan reacts with portlandite, producing supplementary C-S-H or C-A-H or calcium alumina silicate hydrates responsible for the mechanical strength [7,8]. Through the combination of filler and additional chemical reaction in the hydration system, new nanoconcrete with durable and enhanced performance can be developed [1].

Different amount of various materials was added to OPC in order to improve some properties or obtain special characteristics of cement-based materials [1–4]. Fly ash, silica fume (SF) and slag are thoroughly explored among the most widely investigated silica rich additives [3,4,6,7]. In the review on the existing literature about the application of nanomaterials in concrete, the potential use of nanoclays and their modified organic derivatives was particularly highlighted [1]. Several researchers showed [9–15] that moderate addition of nanoclays into cementitious composites effectively improves the mechanical properties of the mixtures. Moreover, it was denoted the possibility to use organically modified clay of small percentage as cement substitute for the fabrication of cement-based materials with better mechanical performance [10–12,14–16]. In the critical overview Nehdi M. L. [10] outlined the possibility to use organically modified nanoclays in cementitiuos materials instead of un-modified clays. Papatzani S. [11] also noted that organomodification of

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montmorillonite (MT) clay at nanoscale can hinder the swelling of MT particles in the hydrating cement environment. Pique T. M. and Vazquez A. [15] studied cements with organically modified montmorillonite (Cloisite 30B) and revealed that modified clay has influence mainly on the behaviour of PVA without significant impact on cement hydration, perhaps due to insufficient amount of modified clay (0.07 wt%). A. Hakamy et al. [12] found that the addition of 1 wt% of nanoclay Cloisite 30B as partial replacement of cement in hemp fabric reinforced composites improved the mechanical strength by about 26%. However, essential accent in that study was assigned to hemp fabric. Later A. Hakamy et al. [17] concluded that the addition of 1 wt% of calcined nanoclay enhances the microstructure of cement nanocomposite due to the filler and pozzolanic reaction effects. It was also noticed [18,19] that optimum content of nanoclay which ensures good dispersion of nanoclay in cement matrix and enhances the microstructure of the composite is less than 2 wt%.

However, most of those works were focused on the properties of nanoclay/cement materials while little attention has been paid on the understanding of the behaviour of organically modified nanoclay particles in a hydrating alkaline cement environment. For example, J. Calabria-Holley et al. [20] investigated the behaviour of modified (OMT) and nonmodified montmorillonite (MT) nanoparticles in cement environment and found that OMT nanoparticles have the same potential as inorganic MT with regards to nucleation of C-S-H, but the dispersion stability of OMT in cement matrix is lower. On the other hand, the properties of nanoclay, such as cation exchange capacity, the type of organomodifier, modification extent and even the purity of the clay can affect the final properties of nanocomposite [1]. For example, our previous study [21] showed that the type of organic modifier used for modification of nanoclay had different impact on the properties of organoclay/cement paste even though the interlayer (or basal) spacing of organoclay was similar. In general, the expansion of the interlayer or increase in basal spacing proceeds through cation exchange process when molecules of organic cationic surfactant (or modifier) replace Na^{2+} and Ca^{2+} in basal planes of the clay [22]. Thus, the basal spacing varies according to the content of modifier, its type, chain length, etc. Based on findings presented in [21] the enhancement in mechanical strength can be achieved through cement substitution by OMT of different basal spacing, however, the effect of modifier content (hereinafter cation exchange degree) on the properties of OMT/cement paste remains unstudied. Therefore, in this research, three OMT with different structural characteristics (different cation exchange degree) were selected for cement substitution. The impact of OMT on the microstructure and functional properties, such as mechanical strength and water sorptivity of cement paste was investigated.

2. Materials and methods

2.1. Materials

Ordinary Portland cement type CEM II/A-LL 42.5 N (OPC), with specific gravity 2.95 g/cm^{3}was used for preparation of the cement-based composites. The chemical composition analysis of raw materials (OPC and MT) was performed by X-ray fluorescence spectroscopy (XRF) on a Bruker X-ray S8 Tiger WD spectrometer equipped with a Rh tube with energy of up to 60 keV. Powder samples were measured in Helium atmosphere, data were analysed with SPECTRA^{Plus} QUANT EXPRESS standardless software and summarised in Table 1.

Sodium montmorillonite (cation exchange capacity (CEC) 105 meq/100 g), was used for OMT synthesis in the laboratory by applying the ion exchange method. Quaternary ammonium salt (QAS) methylbenzyl di-hydrogenated tallow ammonium chloride (Noramium MB2HT = 640 g/mol) (Fig. 1a) was selected as a modifier to produce three OMT denoted as 06 M, 08 M and 1 M, respectively. The concentration of modifier in OMT was equivalent to 0.6, 0.8 and 1.0 CEC of MT and consequently, cation exchange degrees of OMT were equal to 0.6, 0.8 and 1.0. The preparation procedure of OMT was not the focus of this study, therefore is not presented in detail. However, schematic illustrations of MT modification reaction and produced OMT are presented in Figs. 1b and 2, respectively.

It should be noted that the substitution of inorganic cations with the organic ones results in the increment of hydrophobicity of organically modified clays [14,23]. The structural parameters of organoclays 06 M, 08 M and 1 M and their pore structure characteristics obtained through N_2 physisorption are presented in Table 2. The average particle size of all OMT was in the range of (7–9) μm and was independent on the modification level of OMT.

2.2. Preparation of test samples

Portland cement was mixed with water and a set of reference samples was prepared at water to solid ratio (w/s) equal 0.27. Reference samples were denoted as pc. Another batch of samples was prepared with OMT, where 1% of cement was replaced by three different OMT. These samples were entitled as pc-06 M, pc-08 M and pc-1 M. At least six samples were prepared for each composition and each hydration period (7, 28 and 56 days). No plasticizing additives were used.

Primarily, each OMT was mixed with distilled water and stirred rigorously for one day at 20 °C, to ensure the formation of well-dispersed suspension. After stirring time terminated, the OMT-water suspension was mixed with the required amount of cement. The prepared paste was cast into steel moulds and placed in climatic chamber CTC 256 at (20 ± 1) °C temperature and (95 ± 5)% relative humidity. The samples were demoulded after 24 h and left to cure in a chamber for a certain curing period prior to further tests.

2.3. Testing

The pozzolanic activity of the modified clays was determined by a widely used Frattini test, according to EN 196-5 [24]. A mixture of 20 g OPC to 100 ml distilled water was used as a reference. A part of dry cement (4 g) was substituted by each OMT for the preparation of test samples. The samples were conditioned in a climatic chamber at (40 ± 2) °C and RH = 60% for 7, 14 and 28 days. The tests were replicated three times. For all sets a typical standard error in the average of three samples was less than 0.009. The theoretical maximum concentration of [CaO] was calculated by formula

$$[\mathrm{CaO}]_{\max} = 350/([\mathrm{OH}] - 15).$$

Compressive strength measurements were performed on 20 mm cubic samples following the procedure described in EN 196-1 [25]. The tests were carried out on a universal testing machine Zwick Roell (capacity up to 50 kN), with a constant crosshead speed of 0.5 mm/min. Each result was reported as an average value of the measurements on six test samples. Strength activity index (SAI) was calculated as a percentage ratio of strength of cement paste with OMT to the reference.

Water absorption due to capillary action was performed following the test procedure described in the standard EN 1015-18 [26]. Five specimens from each set of the samples were tested after their conditioning at a temperature (60 ± 5) °C up to the constant mass in a ventilated oven. The absorption test involved monitoring of