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Pore structure analysis of hardened cement mortars containing silica fume and different nano-powders

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HIGHLIGHTS

- Effect of nano-SiO_2, nano-Al_2O_3 and nano-Fe_2O_3 powders on mortars was investigated.
- The pore-size distribution of the mortars becoming finer with the addition of nano-powders.
- Nano-powders affected the pore structures, compressive strengths and capillary absorption coefficients of cement mortars.

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ABSTRACT

In this article, the 56-day pore structures of the cement mortars produced by the addition of silica fume and nano-SiO_2 (NS), nano-Al_2O_3 (NA) and nano-Fe_2O_3 (NF) powders in singular, binary or ternary combinations at 3 different proportions (0.5%, 1.25% and 2.5%) of the binder content were investigated through MIP and BET analyses. The compressive strengths and capillary water absorptions of produced mortars were also determined in order to investigate the effects of changes in pore structure on these properties.

As a result, it was found that pore structures of the mortars determined by MIP and BET were influenced by the choice of singular, binary or ternary uses as well as the content of nano-powder(s) added into the mortar. The highest reductions in porosity of mortars and the total volume of mercury intruded were obtained by the use of NA powder at 1.25% for singular, NS + NA powders at 0.5% for binary, and all three powders at 1.25% for the ternary combination. On the other hand, the specific surface area of the mortars were increased the most by the addition of 1.25% of NA, 0.5% of NS + NA and 0.5% of NS + NA + NF. Among the 22 mortar groups produced within the scope of this study, NA content of 1.25% yielded the best results on the properties measured by MIP and BET (total volume of mercury intruded, porosity and specific surface area) as well as the pore-size distributions. The reduction in pore volume, the pore-size distribution becoming finer and the improvement in physico-mechanical properties of the mortars after the addition of nano-powders could be explained by the filler effect or amount of hydration products of cement. However, the addition of the powders at proportions in excess of 1.25% resulted in an increase in the pore volume of some mortars because of agglomeration.

1. Introduction

In the early 2000s with the developments in nano-science can also have a great impact on construction materials. The use of nanotechnology products especially nano-powder have increased. Nano-powder not only improve of mechanical properties due to accelerate hydration and the formation of small-sized crystals (such as $Ca(OH)_2$ and AFm) and uniform clusters of CSH but also improve durability of cement-based composites due to filling very small pores and have beneficial action on the pore structure depend on type of powder [1–5].

The pore structure of cement based composites, whose pore sizes vary between nm and μm, plays a major role on the mechanical and durability properties [6–13]. The pore structure, which also affects the permeability, depends on many factors such as the water to cement ratio, pore volume, pore-size distribution, the interconnections of capillary pores and the aggregate–cement paste interface [6,10,14]. It is known that low permeability composites exhibit high resistance against chemical interactions [15].

The various methods are used to determine the pore structure of cementitious materials (such as Mercury Intrusion Porosimetry (MIP), Gas Adsorption (BET), Wood's metal intrusion test, X-Ray microtomography, Thermoporometer, NMR (Nuclear Magnetic Resonance) and SAS (Small Angle Scattering) methods) [6,13]. Among these techniques, the most widely used are MIP and BET methods [11,15,16]. Mindess et al. [17] and Abell et al. [15] reported that MIP method yields the better results for capillary pore structure, while BET should be preferred in the analyses of meso- and micro-pores as well gel pore systems. Moon et al. [18] noted

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that pore distributions between 1–3 nm, 3–30 μm and 30–1 mm can be determined by BET, MIP and SEM (Scanning Electron Microscope), respectively. It is inferred that multiple methods should be employed in combination in case the pore-size distribution in a porous material is to be fully evaluated.

1.1. Research significance

Numerous studies were conducted in which mineral admixtures were added into the composites to enhance their pore structures [19–22]. Pores in the composite can be partially filled with these admixtures. However, in order to fill in the smallest pores and thereby obtain a more compact composite, smaller sized materials are required. It is expected that the use of nano-particle emerging in parallel with the developing nanotechnology will cause in improvement of the composite's pore structure, and hence its physico-mechanical behavior [23–26].

The increasing number of recently conducted studies analyzing the addition of nano-powders into cement based composites to improve their compactness and ameliorate their microstructure, as well as the results obtained from these studies, are worthy of attention. However, the previously conducted studies on the pore structure of cement mortars containing nano-powder utilized a single type of nano-powder rather than a combination of multiple types [27–29]. For this reason, the fact that the combined effects likely to be observed in case of using different types of powders could not be investigated creates a notable void in the literature. Likewise, no study was conducted that investigated the pore structures of mortars containing different types of nano-powders in combination with silica fume, which is currently a widely utilized as mineral admixture. In this study, it was intended to analyze the singular, binary and ternary combinations of nano-powders of the three main cement oxides (nano-SiO_2, nano-Al_2O_3 and nano-Fe_2O_3) on the pore structure of cementitious mortars containing silica fume. It is envisaged that the findings of this study will be guidance towards the production of more compact cement based composites.

2. Experimental program

2.1. Material

Nano-SiO_2 (NS), nano-Al_2O_3 (NA), and nano-Fe_2O_3 (NF) powders were used in the mixtures. Maximum powder size of NS used in the study was 12 nm, while its Blaine value was 200 m^2/g and purity was 99.8%. Maximum particle size, Blaine value and purity of NA were 13 nm, 100 ± 15 m^2/g and 99.8%, while those of NF were 20–60 nm, 60 m^2/g and 98%, respectively. SEM images of the nano-powders are given in Fig. 1.

CEM I 42.5 R type of cement and CEN reference sand conforming to TS EN 196-1 [30] and TS EN-197-1 [31], respectively, were used in all mixtures. The chemical properties and physical characteristics of the cement are presented in Table 1. The sand was in a regular spherical structure, with a maximum grain size of 2 mm and a relative density of 2.6. SiO_2 content of the sand was 98% at minimum. The mineral additive material used in the experiments was silica fume (SF) with a maximum grain size of 0.1 μm, whose chemical properties is also given in Table 1.

High range water reducing agent (HRWRA) (commercially available as Visco-Crete-PC 15, a product of SIKA) and defoamer (anti-foam agent) were used in the mixtures as chemical additives. HRWRA was a modified policarboxilate based polymer with a relative density of 1.09 ± 0.02 and amount of the additive corresponded to 0.75% of the binder by weight. The defoamer include propylene glycol was added to the mixture as in Refs. [24,32] for the purpose of preventing foam formation which may likely cause additional pores. The relative density of the defoamer was 1.35 and was used at a ratio of 1% of the binder material. Marsh Funnel Method [33] was used in order to determine the cement's harmony with HRWRA and optimum proportion of the chemical admixture.

2.2. Mix proportions

A total of 22 groups of cement mortar with different mixtures were produced in the study. Cement:sand ratio was selected as 1:3 (by weight) [34–36]. SF was added to the mixtures at a ratio of 5% of the cement amount and the water/binder ratio of all mixtures was 0.4.

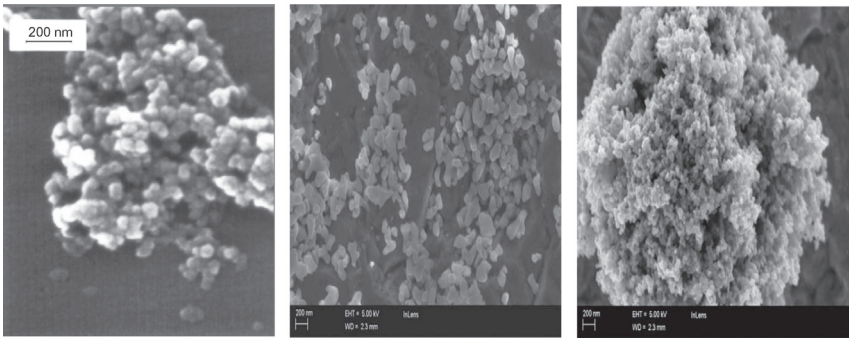
The literature does not offer precise information about the optimum ratio of nano-powders. As exemplified in the Ref. [37], some researchers used NS up to 10% of the cement amount, whereas others reported that using the powder at proportions higher than 5% would lead to an adverse impact on the properties of the cement based materials. In this study, the proportions of nano-powders were determined based on preliminary experiments performed on the mortars produced with NS. Depending on results of the fresh and hardened properties of preliminary experiment mortars NS powder at seven different proportions, it was decided to use powder amounts at ratios corresponding to 0.5%, 1.25%, and 2.5% of the binder by weight for all mixtures. The total proportions of the powders were the same in all single, binary and ternary uses. For example, in specimens containing the three powders at a ratio of 2.5%, each nano-powder is present at a proportion of 0.83% (=2.5%/3).

2.3. Specimen production procedure and hardened mortar experiments

Due to their large surface area [32,38], nano-powders may not exhibit a uniform distribution in the mixture. As the failure to achieve uniform distribution could directly affect the physical-mechanical properties of the mortars, the specimen production procedure used in this study was finalized after several preliminary experiments. Specimen production steps were detailed in Ref. [37].

The resulting final mixture was poured into moulds of 5 × 5 × 5 cm, which were placed after shaking them in the vibrating table for 10 s. 1 day later, the demoulded mortar specimens were stored in curing containers containing lime-saturated water at a temperature of 20 ± 2 °C until they were tested. The mechanical and physical properties of the mortars were determined using compressive strength tests according to the Turkish standard (TS EN 12390-3) [39] performed at 56 days, the pore structure of mortars was investigated through MIP and BET methods conducted on the 56-day specimens and capillary water absorption tests according to the Turkish standard (TS EN 772/11) [40] carried out at 180 days, respectively. The later age strength on the day (56 days) selected for the analysis of the micro-structure of specimens. To find a later age strength of the specimens, the compressive test was performed on 180th day rather than on 90th day specimens.

For capillary water absorption tests, specimens were taken from the water curing medium, and kept in the drying oven for 24 h. Specimens taken out of the drying oven were cooled down and immersed in water such that their cut surfaces would be submerged in water at a depth of 0.5 cm. Other surfaces were covered with



(a) Nano-SiO_2 (b) Nano-Al_2O_3 (c) Nano-Fe_2O_3

Fig. 1. SEM images of the nano-powders obtained from manufacturer companies.