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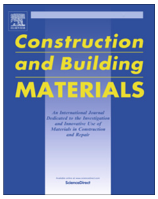

The effects of Fe_3O_4 and Fe_3O_4/SiO_2 nanoparticles on the mechanical properties of cement mortars exposed to elevated temperatures

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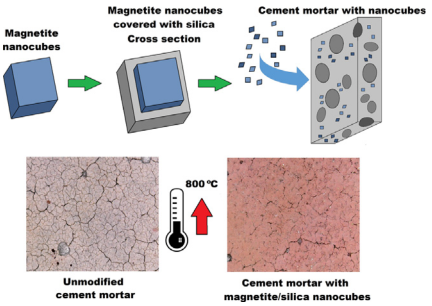
HIGHLIGHTS

- Fe_3O_4 and Fe_3O_4/SiO_2 nanoparticles were incorporated to cement mortar.
- Fe_3O_4 and Fe_3O_4/SiO_2 show no effect on relative residual flexural strength.
- Fe_3O_4/SiO_2 has better performance in cement mortars than pristine Fe_3O_4 nanoparticles.
- Fe_3O_4/SiO_2 improves resistance to elevated temperature of cement mortars.
- Fe_3O_4/SiO_2 diminishes the amount of cracks in cement mortars, up to 800 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates the effects of Fe_3O_4 and Fe_3O_4/SiO_2 nanoparticle admixtures on the behavior of cement mortars exposed to elevated temperatures. Pristine nanoparticles of magnetite (Fe_3O_4) were coated with a solid silica shell (via the Stöber method), to form a core-shell nanostructure (Fe_3O_4/SiO_2). The cement mortars were incorporated with an optimized ratio of 3 wt% Fe_3O_4 and 5 wt% of Fe_3O_4/SiO_2 admixture. The specimens were exposed to elevated temperatures of 200, 300, 450, 600 and 800 °C. After cooling, the mass loss and flexural and compressive strengths of the specimens were determined. The results demonstrated that the presence of magnetite-silica (Fe_3O_4/SiO_2) nanostructures is much more beneficial for improving the thermal resistance of cement mortars than pristine Fe_3O_4 nanoparticles. The silica (SiO_2) shell in the nanoparticles improves residual compressive strength and prevents crack extension in cement mortars exposed to elevated temperatures. The investigations undertaken in this study were supported by optical and scanning electron microscopic studies.

1. Introduction

The resistance of concrete to elevated temperature is one of the key factors, which needs to be taken into account when predicting structural safety. Exposure to high temperatures significantly affects the performance of concrete structures, leading to losses in integrity and stability, which can result in collapse, as increases in temperature result in chemical and physical transformations in cement pastes and aggregates [1]. In engineering practice, it can be assumed that, concrete heated to a temperature of 300 °C does not significantly loose strength and any strength loss can be recovered through re-hydration processes. However, above 300 °C, decomposition of calcium hydroxide – CH and dehydration of calcium-silicate-hydrates (C-S-H) occur, leading to significant strength deterioration in cementitious composites [2]. The thermal resistance of cement-based composites is highly related to the type of aggregate used in production, as well as to the additives

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incorporated [3–5]. Various research directions are being pursued in order to enhance the thermal resistance of cementitious composites, including the addition of certain types of fibers to mixtures, the determination of the proper aggregates to use, as well as the incorporation of supplementary cementitious materials (SCMs). Studies have shown that, concretes exhibit lower strength decrements, as well as a diminished amount of surface cracks, when certain amounts of fly ash (FA) or ground granulated blast-furnace slag (GGFBS) are included in the concrete [6–13]. These effects have been attributed to the pozzolanic activity of SCMs, which contributes to a reduction of disruptive CH re-formation during the cooling process [14]. Nevertheless, certain types of SCMs, namely silica fume (SF), increase the deterioration process of concrete when exposed to high temperatures, as a result of induced explosive spalling [15,16]. This phenomenon has been attributed to a significant compaction of cement matrices and interfacial transition zones (ITZ), as effects of the presence of SF, which contributes to increases in vapour pressure in concrete pores [4,17–19].

In recent years, some nanomaterials (NMs) have been found to be excellent admixtures which suppress the deterioration of cement-based composites [14,20–23], caused by elevated temperatures.

Significant interest has focused on the application of nanosilica (NS), which exhibits superior reactivity compared to that of SF [24–26]. Moreover, it has been widely reported [27–30] that the reduction of particle size to nanoscale can greatly affect cement hydration rates leading to a significant improvement in strength and microstructure.

Studies [14,31–37] have shown that, NS significantly improves the resistance of cement-based composites to elevated temperatures, as a result of the retention of higher residual compressive strength, as compared to plain samples, as well as by reducing crack width. These phenomena are attributed to the improved amount and stability of the C-S-H phase, as well as the filling effect of NS. In addition, Maheswaran et al. [38], have reported that, due to the pore-filling effect of NS and enhanced particle packing in the mortar, NS inclusion in cement mortars helped to prevent the spalling of their samples.

The iron oxides nanoparticles, have also been tested in improving the thermal resistance of cementitious composites. It has been reported that, both micro-Fe_2O_3 and nano-Fe_2O_3, when incorporated to cementitious composites, improve their mechanical and microstructural properties [39–43]. Data regarding the effects of nanomagnetite (Fe_3O_4) are more limited, but, research has shown that the application of nano-Fe_3O_4 in small amounts (up to 0.3 wt%), can lead to an enhancement of mechanical properties and a refinement of pore structure [40]. Our study [44] has shown that, 3 wt% admixture of nano-Fe_3O_4 can be beneficial in refining pore structure and improving the compressive strength of cement mortars. Studies undertaken by Shekari et al. [41] have shown that, the introduction of 1.5 wt% of nano-Fe_3O_4 improves the compressive strength of concretes and reduces both chloride penetration and water absorption. Studies regarding the influence of iron oxide nanoparticles on thermal resistance [42,45] have shown that, even small amounts (1 wt%) of nanomaterial (NM) can be beneficial in improving the fire resistance of cement pastes, by increasing residual compressive strength, decreasing mass loss and compacting microstructure. It has also been reported [45] that, the presence of nano-Fe_2O_3 in cement matrices reduces crack length.

The high density of Fe_3O_4 nanoparticles may be a key to their utilization in the future production of heavyweight concretes [46], allowing to increase their density and enhancing the gamma-ray [47] and electromagnetic interference (EMI) shielding properties [48]. Unfortunately, humid or elevated temperature conditions cause the oxidation of nano-Fe_3O_4 that may result in losing, e.g., EMI shielding capacity [48]. Therefore, various solutions for improving the stability of nano-Fe_3O_4 are extensively studied by researchers. These include the synthesis of nanosized protective layers on the surface of particles [49] that results in molecular hybrids creation. Incorporating the mixture of nanomaterials (e.g. nanosilica and titanium dioxide) to cement-based composites simultaneously improves strength (nanosilica) and provides self-cleaning properties (titanium dioxide) [50,51]. However, the incorporation of molecular hybrids seems more beneficial because it leads to a decrease in the amount of used material. This leaves a lower chance for the workability to be affected, as opposed to nanomaterials that were incorporated separately [52].

Recently, Bolhassani et al. [53] have proposed the incorporation of magnetite-silica core-shell nanostructures to cementitious composites. The magnetite particles acted as a core and were covered by a silica shell, prepared via the Stöber method. This kind of nanocomposite structure did not cause significant reduction of workability, in distinction to the case of nanomaterials incorporated separately. Nanomagnetite (Fe_3O_4) particles (which were used as a core) and commercially available powdered NS, were used as a reference. Strength improvement was highest for powdered NS, although, the use of a magnetite-silica nanocomposite also resulted in a considerable strength increase, as compared with the plain (unmodified) reference samples. In addition, the rate of strength gain was more uniform than in the case of single nanomaterials. These studies also showed that, such nanocomposites can exhibit both pozzolanic activity (due to presence of a silica shell) and the nuclei effect of magnetite particles.

Based on findings described in literature [48,49], it can be presumed that the combination of Fe_3O_4 with NS layer prevents the oxidation of iron oxide nanoparticles in the cement matrix. Moreover, the silica layer on the surface of Fe_3O_4 can increase the specific surface area of molecular hybrid and increase its pozzolanic activity. For that reason it can positively affect the microstructural and mechanical properties of composites. In addition, nanosilica can provide an outstanding effect (in comparison to other nanomaterials) on thermal resistance [33,34]. Therefore, the incorporation of Fe_3O_4/SiO_2 may enhance the mechanical properties not only at room temperature but also at an elevated temperature.

In the current study, the authors argue that, the application of nanocomposites can be beneficial in improving the thermal resistance of cementitious composites. The objective of the investigation is to reveal the thermal resistance of cement mortars modified with magnetite-silica core-shell nanostructures (Fe_3O_4/SiO_2), exposed to temperatures of 200, 300, 450, 600 and 800 °C. For comparison, pristine cement mortar and mortars modified with pristine Fe_3O_4 nanoparticles were also analyzed.

2. Experimental details

2.1. Materials

For cement mortar preparation, CEM I 42.5R (conforming to EN 197-1), 0–2 mm quartz sand aggregate (conforming EN 196-1), tap water and polycarboxylate ether (PCE) superplasticizer and (0.5% by mass of cement) were used. PCE superplasticizer was incorporated in the fixed amount to all mixes, in order to support the dispersion of nanomaterials in the cement matrix. The chemical composition of CEM I 42.5R is presented in Table 1. The water to cement ratio (w/c) was fixed at 0.5 to enable a reasonable cement mortar workability.

Iron oxide nanoparticles were used to prepare core-shell structures with a silica coating. Commercially available nanomagnetite (Fe_3O_4) particles, purchased from Sigma Aldrich (637106), were used as the core nanostructures (for further synthesis processes) and for the preparation of reference cement mortars. The nanomagnetite structures purchased had a size of 50–100 nm, with a purity of 97% (according to information provided by the supplier).