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Performance of Portland cement concretes with 1% nano-Fe_3O_4 addition: Electrochemical stability under chloride and sulfate environments

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HIGHLIGHTS

- Nano-Fe_3O_4 (1%) was used as a partial replacement of cement in concrete.
- Concretes were evaluated through impedance spectroscopy and cyclic voltammetry.
- Nano-Fe_3O_4 concretes presented electrochemical stability, even after ions exposure.

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ABSTRACT

Concretes with 1% nano-Fe_3O_4 addition aged for 300 days in chloride and sulfur dioxide chambers were analyzed by multiple technics and the performance results were evaluated by impedance spectroscopy and cyclic voltammetry. They exhibited a higher electrochemical stability because of the absence of passive film breakdown and an enhanced electrical resistance to charge transfer. The better properties were resulted from a more homogeneous microstructure produced by the byproducts of the reaction between the cement hydrates and the added nano-material. They were supposed be accumulated in pores and voids.

1. Introduction

Recently studies in civil construction [1,2] have been conducted to develop nano-modifications using nanometric ceramic oxides in cement materials to improve the physico-chemical properties of concretes and mortars. Among the most studied materials, nano-silica stands out because of its pozzolanic properties. Ji [3] studied concretes containing 4% nano-SiO_2 by weight of cement and observed a decrease in the water permeability because the material density increase by the high surface area that was promoted by the addition. Jo et al. [4] conducted comparative studies of the characteristics of mortars to which active silica and nano-SiO_2 were added, by analyzing the hydration process of the materials, using correlations for the compressive strength. The nano-scale addition improved the microstructure of the cement paste. This result was obtained both because of an enhanced filler effect and the higher occurrence of pozzolanic reactions, which increased the compressive strength up to 63% over that of the reference mortar and by 45% over that of the 15% addition of active silica (12% nano-SiO_2 was added in both cases). A more recent study indicated that 2–6% additions (by cement weight) improved the resistance of concrete to reaction with sulfate by promoting pozzolanic reactions that produced concretes with a more uniform microstructure (i.e., a lower porosity), which prevented the entrance of aggressive ions [5].

Nanometric titanium dioxide (TiO_2) has been added to cement materials primarily for surface modification, to develop structures that are self-cleaning or that can photocatalyze atmosphere polluting gases [6,7]. Most studies on nano-TiO_2 additions have focused on paving applications. Li et al. [8,9] found that concretes with 1, 3 and 5% additions (mass%/cement mass) exhibited an increase in the abrasion resistance, the axial compressive strength and the flexural fatigue strength. These results were obtained because of

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the promotion of hydration reactions and the corresponding growth of CH crystals and of the C-S-H (hydrated calcium silicates) gel, beyond the filler effect, which resulted in a more homogeneous and less porous concrete. More recently [10], concretes with the same 1% nano-TiO_2 addition by weight of cement were studied to investigate chloride diffusion in structures that were susceptible to erosion. The results showed that the erosion resistance of the material with the addition was 36% higher than that of the reference concrete, and the modified material had a lower vulnerability to penetration by chloride ions (up to 0.135 mm lower), as verified by a colorimetric measurement of the affected area. Both characteristics were related to the improvement of microstructural properties of the material by nanometric addition, as has been previously reported [3–5,8,9].

Li et al. [11] investigated the addition of aluminum (Al) nano-oxides to mortars. The partial replacement of 3, 5 and 7% by cement weight resulted in a material change in the ITZ (the paste/aggregate interface transition zone). This change occurred because the high surface energy of the nano-alumina particles that promoted sand adsorption via *van der Waals* forces. In this case, were seen the enhancement of the interaction of the sand particles with the cement paste during hydrate formation (especially that of C-S-H), thereby reducing the cement porosity and increasing the density of the paste near the ITZ. This modification of the ITZ material properties produced an increase of up to 143% of the mortar's elasticity modulus at 28 days (5% by cement weight). Behfarnia and Salemi [12] performed a comparative study of concretes with nano-Al_2O_3 and nano-SiO_2 additions. The additions improved the properties of all of the mixtures: in particular, the addition of nano-alumina enhanced the freezing resistance of the concrete, which exhibited up to 54% less water adsorption than the reference concrete, even after 300 freezing/thawing cycles.

Li and collaborators [13] developed smart materials for civil construction applications in which 3, 5 and 10% nano-Fe_2O_3 by cement weight were added to mortar. The authors investigated the resulting mechanical properties and the "self-monitoring" capability of mechanical stress and structural damage of the modified materials. The modified materials exhibited an approximately 20% increase in both the compressive and flexural strengths over that of traditional mortar because the nanoparticles acted as binding nuclei for the cement hydrates, thereby improving the mechanical properties of the mortar (in addition to limiting crystal growth and enhancing the filler effect in the matrix). The authors analyzed the "self-monitoring" properties of the modified material by developing mathematical models to correlate the mechanical properties of the mortar with its electrical resistance, such that the material could be used as a sensor for these properties.

Preliminary studies were performed to determine the effect of adding nano-Fe_3O_4 on the properties of hardened cement pastes (contents of 0.05, 0.1 and 0.3% by cement weight were used as partial replacements of the binder in an aqueous magnetic fluid mixture). The following properties were investigated: the hydration characteristics, the axial compressive strength and the tensile strength by diametral compression and the penetration of chloride ions in high-performance concretes (with 0 and 1.5% additions) [14–16]. As for other nano-additions, the use of nano-magnetite improved the mechanical properties of the concretes in terms of the hydration time and reduced chloride ion penetration over that of the reference material. Amin et al. [14] showed that these property changes resulted from the formation of the ilavite compound (as verified by X-ray diffraction, XRD, of the paste), a product by the reaction between $Ca(OH)_2$ and Fe_3O_4, which had void-filling properties that were similar to ettringite. The resulting cement matrix had a dense and homogeneous microstructure.

Despite the promising characteristics of the cement paste and high-performance concrete with nano-Fe_3O_4 addition, as demonstrated in studies by Amin et al. [14], and Shekari and Razzaghi [15], the aforementioned results were preliminary, being based only on analysis after hydration. Thus, in the present study, the mechanical, physico-chemical and the relative durability properties of concretes with nano-Fe_3O_4 additions of 1% (by cement weight) were characterized by conducting electrochemical tests on samples that were exposed to chloride and sulfate ions for approximately 300 days. The results were compared to the reference concrete (without addition) to determine the mechanisms by which the addition enhanced the performance of the cement paste.

2. Experimental methodology

2.1. Materials and dosage procedure

The following materials were used to prepare the concretes: commercial cement CP IV 32 (pozzolanic Portland cement); natural basaltic rocks that were crushed to fine and coarse aggregates; and commercial nano-powder iron oxide Fe_3O_4, which was 97% pure with particle sizes below 100 nm.

The cement and the aggregates were characterized according to international technical standards [17,18]. The chemical characterization was performed using X-ray fluorescence (XRF), where the polycrystalline samples were analyzed in a PANalytical Axios Max Spectrophotometer [19].

The nano-Fe_3O_4 was characterized by XRD using polycrystalline powder samples in a PANalytical EMPYREAN diffraction instrument with Cu-Kα radiation, a wavelength λ of 1.54051 Å, a 2θ scanning range between 0° and 70°, a 40 kV voltage, a 40 mA current, a 0.001 s pass and a 0.002 p/s pass speed. The chemical phases in the compound were identified by comparison with the International Centre for Diffraction Data (ICDD) database.

The reference (RC) and nano-Fe_3O_4 (NFC) concretes were prepared from the characterized materials according to the trace obtained in the laboratory for material proportions of 1:1.46:3.55:0.56 (cement:fine aggregate:coarse aggregate:water/cement ratio, respectively). The cement consumption was 383 kg m^{-3}. 1% of nano-magnetite was added as a partial replacement by cement weight, using similar methodologies to those used by Amin et al. [14] and Shekari and Razzaghi [15]. The nano-addition was homogenized before dosing by manual mixing with the cement.

The samples were molded in (100 × 200) mm and (150 × 300) mm cylindrical molds to perform characterization tests of the mechanical and physical properties of the concretes. Other prismatic specimens (40 × 100 × 90) mm containing carbon steel (CA 50) and graphite electrodes were prepared as developed by Kanning et al. [20]. The rebar exposed area was 0.643 m^2.

The concretes were cured in air for 24 h and then released from the molds. Afterwards the specimens were maintained in a wet chamber for an average age of 28 days (or the time corresponding to the threshold of the specific test, as detailed in the following sections).

2.2. Mechanical and physical properties of 1% nano-Fe_3O_4 concretes

The mechanical and physical properties of the concretes were comparatively evaluated for both mixtures using the primary tests from technical standards [21], as: i) axial compressive strength test performed after wet curing for 7, 28 and 91 days, according to NBR 5739 [22]; ii) tensile strength by diametral compression performed after 28 days of wet curing, according to the Brazilian Standard NBR 7222 [23]; iii) static compressive elasticity modulus performed according to NBR 8522 [24], after 28 and 91 days of wet