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Effect of carbon nanotubes (CNTs) on chloride penetration resistance and physical-mechanical properties of cementitious materials

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Abstract

According to currently enforced Eurocode 2 for the design of reinforced concrete structures, it is essential to protect the steel reinforcement from corrosion and concrete from degradation under aggressive environmental conditions such as marine, urban, industrial, soils, to which these are normally exposed. In this context, this experimental study investigates the enhancement of the physico-mechanical properties of common cement-based mortars and the electro-chemical properties of reinforcing steel, through the addition of nanomaterials in the mix.

For the experimental set-up, cylindrical and cubic specimens of different dimensions were cast and were partially immersed in sodium chloride solution for eight (8) months. Two (2) groups were considered: cement-based mortar composites with 0.2 wt.% CNTs addition and conventional (reference) specimens without any addition of nanomaterials, for comparison. The influence of adding CNTs on chloride penetration resistance was subsequently evaluated using standardized and non-standardized testing techniques: physico-mechanical tests (flexural strength and porosity), mass loss of steel, electrochemical measurements (corrosion current, HCP) and total chloride content calculation.

The test results showed that using CNTs as addition in mortar production led to protection of steel rebars against pitting corrosion; moreover, a significant improvement in flexural strength and porosity of mortars was also observed compared to the reference specimens without CNTs.

Objective

The main objective of this research is the theoretical and experimental study of the utilization of Multi-Walled Carbon Nanotubes (MWCNTs) for the production of high-performance cementitious mortars with improved flexural strength and chloride penetration resistance.

Raw materials, preparation of specimens and methods

For the measurements of Half-cell potential (HCP), 100 mm reinforced cementitious mortars with a diameter of Ø50 mm were prepared in the lab, on which 100 mm long Tempcore B500C reinforcement steel with a diameter of 10 mm was axially placed. CEM I 42.5N cement was used as a binder, while calcareous fine aggregates (0 – 4 mm) and water from the supplied network were also utilized in the preparation of the mixtures. In all mixture groups a constant ratio of raw materials was used (cement:sand:water = 1: 3: 0.65). The choice of high w:c ratio was intentional to produce relatively weak mortars, which would highlight the effect of CNTs. The steel rebars were cleaned according to ISO / DIS 8407.3 with a hydrochloric acid (HCl) solution containing organic inhibitor in order to remove the oxides and impurities on their surface. The rebars were then immersed in deionized water and acetone to remove grease and oil from their surface. In this study, low content (0.2 wt.%) of Multi-walled carbon nanotubes (MWCNTs) were used as admixtures for the preparation of cement mortars. The nanomaterials were supplied by SAT nano Technology Material Co. Ltd. For the compaction of mortars, mechanical vibration was used, immediately after casting, to reduce the air content of the mixtures. The rebars were 20 mm away from the bottom surface of the molds so as not to be directly exposed to corrosion conditions. The surface of mortars and the protruding part of the reinforcements were then covered with Araldite epoxy resin to prevent galvanic corrosion. The specimens were water-cured for seven (7) days with relative humidity RH ≥ 99% ± 1% and temperature T = 25 ± 1^{o}C to avoid cracking due to hydration heat release.

The test methods which were adopted for the estimation of the mechanical characteristics, the physical properties, the durability and chloride penetration resistance of reinforced mortars were the following:

- The flexural strength (three-point bending test) of nanocomposite and conventional mortars was measured by loading prismatic specimens (40 x 40 x 160 mm^3) with a span length (120 mm) at least three times of the width (40 mm).
- The apparent density and open porosity of lime mortars were estimated using vacuum saturation; for the tests, cubic specimens with dimensions 50 x 50 x 50 mm^3 were used. The test samples were full-dried in an oven at 110±5 ^{o}C, before being subjected to vacuum saturation with water for 24 h.
- The sorptivity was measured on cubic specimens of similar dimensions as previously, using the method proposed by Gummerson et al. During the test, the level of methanol was kept constant, at a level equal to constantly 2 – 3 mm over the bottom side of the specimens, while its temperature was continuously recorded. The sorptivity (S_i) of the specimens was estimated as the slope of the corresponding current intensity (i) vs square root of time (^t) graph.
- Half-cell potential measurements were conducted following ASTM C-867, in order to evaluate the corrosion rate of steel bars embedded in mortars. The Half-cell potential difference was measured using a high-impedance voltammeter and calculated between the working electrode (steel bar) and a reference electrode (Ag/AgCl).
- The corrosion current were measured using the Stern-Geary method. Specifically for the measurements of the corrosion current, the Gecorr 8 device was used. It measures the Corrosion Rate of reinforced concrete, applying the technique of polarization resistance (Rp).

Experimental Results

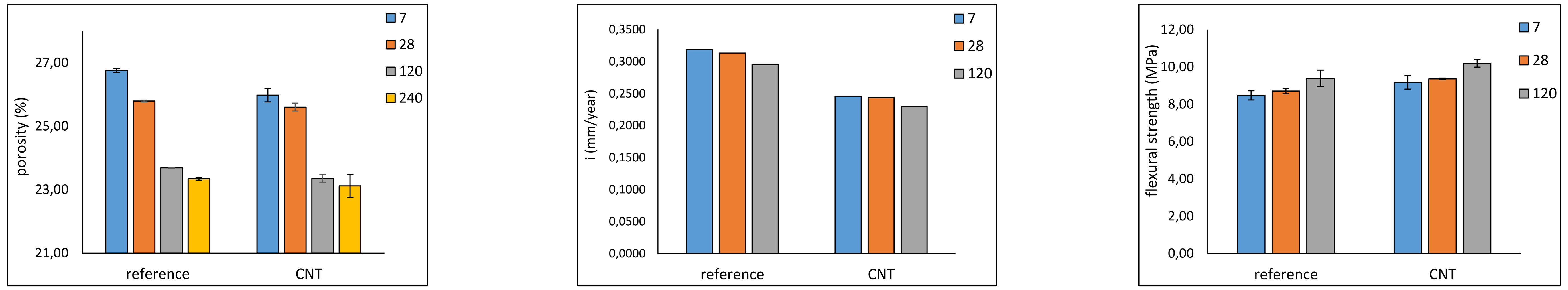

Fig. 1. Porosity (left), capillary absorption (center) and flexural strength (right) of cement mortars after partial immersion in 3.5 wt% NaCl solution.

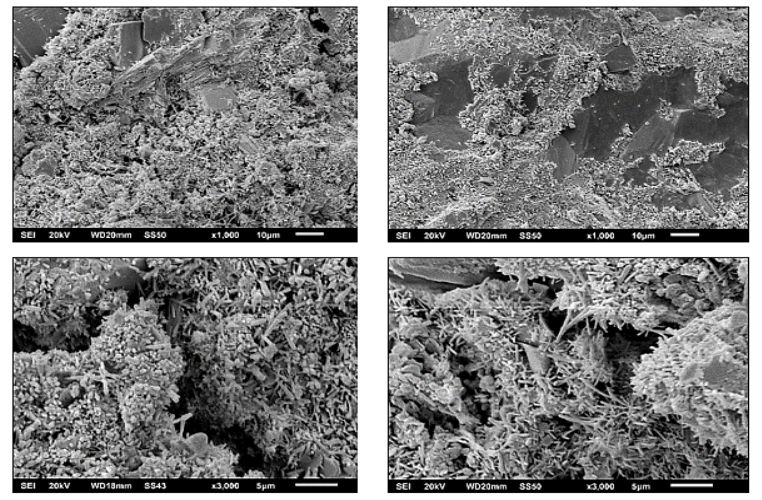

Fig. 2. SEM image of nano-modified composites: Bottom: micro-crack bridging due to CNTs presence, top – left: Dense structure of mortar and top – right: ITZ between cement-aggregates.

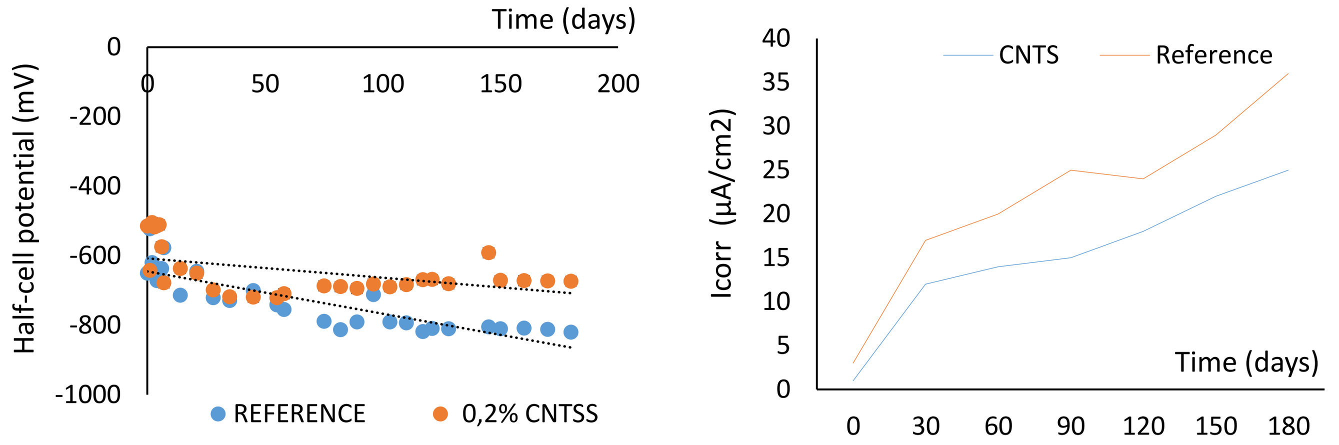

Fig. 3. HCP (left) and corrosion current density (right) of steel rebars embedded in cementitious mortars

Conclusions

The following conclusions can be drawn from the results of the experimental study hereby presented:

- The addition of CNTs induced a positive effect on the chloride penetration resistance of concrete (**Fig. 3**).
- Sorptivity values for nano-modified mortars were lower than those of the reference analogues (**Fig 1 – Center**); this is attributed to the lower porosity of composites at the respective ages (**Fig. 1 – Left**).
- The flexural strength for mortars containing 0.2% CNTs was slightly higher than that of the reference (**Fig. 1 – right**).
- The microscopical analyses were indicated that the nanomaterials demonstrate a network structure that can allow the bridging between narrow cracks in mortar; in addition, it was clearly evident that the ITZ between cement and aggregates fills with CNTs resulting in a dense and solid structure of cement mortar (**Fig. 2**).

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