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Enhancement of the durability characteristics of concrete nanocomposite pipes with modified graphite nanoplatelets

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HIGHLIGHTS

- Durability performances of dry-cast concrete mix with graphite nanoplatelet were evaluated.
- Graphite nanoplatelets were surface modified to improve their dispersion in mixing water.
- Improvements in durability characteristics of concrete pipes were realized by adding of nanomaterial.

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ABSTRACT

Enhancement of cement-based materials with graphite nanomaterials builds upon and complements the established practice of reinforcing cement-based materials with micro-scale fibers. Among graphite nanomaterials which have reached industrial-scale production, graphite nanoplatelets offer favorable economics for use in concrete. The planar geometry of graphite nanoplatelets is another distinguishing feature of this nanomaterial, which favors its role towards enhancement of the transport and durability characteristics of concrete. An experimental investigation was conducted in order to determine the contributions of graphite nanoplatelets to the durability of dry-cast concrete pipes in aggressive sanitary sewer environment. Laboratory studies were followed with industrial-scale production of concrete pipes incorporating graphite nanoplatelet and/or micro-scale polyvinyl alcohol (PVA) fibers. Special attention was given to dispersion and interfacial interactions of graphite nanoplatelets in concrete. For this purpose, nanoplatelet surfaces were modified by a polyelectrolyte, and the modified nanoplatelets were first dispersed in a fraction of the mixing water prior to addition to concrete. Significant improvements in the transport and durability characteristics of concrete pipes were realized by the addition of modified graphite nanoplatelets. These improvements could be attributed to the close spacing and high specific surface area of graphite nanoplatelets, which effectively hinder sorption of moisture and aggressive chemicals into concrete, and control growth of microcracks under aggressive exposures.

1. Introduction

Concrete pipes, as integral elements of infrastructure systems [1], are utilized in sanitary and storm water sewer systems [2,3]. Maintenance and repair of concrete pipes represent growing economic burdens, especially in the aggressive sanitary sewer environment [1,4].

Concrete pipes are susceptible to chemical and biogenic attacks [5–9]. Microorganisms existing in the sanitary sewer environment produce sulfuric acid, which is responsible for a severe degradation mechanism of concrete pipes which is generally termed "Microbial Induced Concrete Corrosion" [3,6,9,10]. Gypsum ($CaSO_4{\cdot}2H_2O$) forms as a result of the reaction of sulfuric acid and calcium hydroxide (CH); it further reacts with calcium monosulfate hydrate to form the needle-shaped ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$). The resulting gypsum and etrringite products occupy more space than the initial reaction compounds, causing expansion and cracking of concrete. The products of degradation are removed by the pipe internal flow expediting the corrosion process [5,8,11].

The solutions investigated for improving the resistance of concrete pipes against such aggressive conditions include refinement of concrete mix design [12–15], use of sulfate-free aggregates [16], use of pozzolanic materials [17], fiber reinforcement of concrete [3], use of different chemical admixtures [18], surface treatment [19], and proper mixing and thorough curing methods [20]. Progress in nanotechnology has opened new prospects for

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enhancement of the barrier and durability characteristics of concrete [21–25]. The present investigation studies the effects of graphite nanoplatelet (GP) on the barrier and durability characteristics of concrete in sanitary sewer pipes.

Concrete materials provide acceptable levels of engineering properties (compressive strength, moisture resistance and durability) at a relatively low cost [21–24]. Concrete, however, offers limited toughness and impact resistance. Micro-fibers are used for improving the toughness and impact resistance of concrete. The micro-scale diameters and relatively low aspect (length-to-diameter) ratios of these fibers, and their viable volume fractions in concrete, however, yield relatively large fiber-to-fiber spacing and relatively small specific surface area of fibers. These features limit the effectiveness of micro-scale fibers in controlling the flaw (microcrack) size and propagation, and in improving the barrier and durability characteristics of concrete. Micro-scale fibers, on the other hand, are relatively long, and their extended (frictional) pullout can dissipate substantial energy. One can expect a desired synergy between micro-scale fibers and nanomaterials because they function at different scales, and also because nanomaterials could benefit the pullout behavior of micro-scale fibers. Nanomaterials with distinct geometric and engineering properties could be used towards overcoming these drawbacks, and for enhancing the transport and durability characteristics as well as the tensile/flexural strength of concrete. Relatively low-cost graphite nanomaterials offer the promise for rendering unique reinforcement qualities in concrete which bring about balanced gains in mechanical and durability characteristics [25]. Tortuous diffusion paths imposed by the presence of GPs can significantly benefit the moisture barrier and durability characteristics of concrete.

Initial research on enhancement of cementitious materials through introduction of nanomaterials has largely focused on the use of carbon nanotubes [3,8,9,16,19,26] and the use of "nanonets" was proposed [25]. These exploratory investigations have mostly used high-performance cementitious paste and sometimes mortar as the matrix incorporating nanomaterials [27,28].

The study reported herein evaluated the effects of nano- and/or micro-scale reinforcement on the durability characteristics of (dry-cast) concrete pipes. The focus of this investigation was on the moisture sorptivity and acid resistance of concrete pipes [28], which determine their service life in sanitary sewer applications. Eight full-scale concrete pipes were produced at a manufacturing plant using plain concrete and concrete with nano- and/or micro-scale reinforcement. Samples were produced using the concrete prepared at industrial scale; samples were also cored from concrete pipes. Polyvinyl alcohol (PVA) fiber which complements relatively high mechanical properties with desired acid resistance [29,30] was selected as the micro-scale reinforcement. GPs were selected for use in the project because of their distinctly low cost (among nanomaterials), industrial-scale availability, desired geometric attributes (including the planar geometry which favors their contributions to barrier attributes of concrete), and high mechanical qualities.

2. Experimental program

2.1. Materials

The raw materials used for production of concrete pipes were natural coarse aggregate with 19 mm maximum particle size, natural sand (2NS) with maximum particle size of 4.75 mm, Type I Portland cement, Class F fly ash, ground granulated blast furnace slag, water-reducer (Catexol 1000 NP) and set-retarder (Catexol 1000 R). The cement: fly ash: slag: sand: coarse aggregate: water weight ratios in this dry-cast concrete mix were 0.70:0.14:0.16:2.6:2.1:0.36. The water-reducer and set-retarder dosages were 28 and 60 g per 4.5 kg of cementitious materials, respectively. The 28-day compressive strength of plain concrete was 27 MPa. Graphite nanoplatelets which are produced commercially were purchased from XG Sciences. Modified GPs were dispersed in 10% of the concrete mixing water. The graphite nanomaterial considered in this investigation was GP with 6–8 nm thickness and 25 μm average planar dimension. The specific gravity of GP was 2 g/cm^3 (Fig. 1). Polyvinyl alcohol (PVA) fibers were used as micro-scale reinforcement; these PVA fibers had a length of 13 mm, and a diameter of 100 μm. The specific gravity of PVA fibers was 1.3 g/cm^3.

Benefits of modified GPs, used alone or in combination with (micro-scale) PVA fibers, towards enhancing the durability characteristics of concrete pipes were evaluated through industrial-scale production and experimental evaluation of concrete pipes with diameter of 53 cm and length of 2.44 m. A total of eight pipes were manufactured (Fig. 2) according to the procedure described in the following: (i) two with plain concrete; (ii) two with GP at 0.2 vol.% of cementitious materials (0.05 vol.% of concrete); (iii) two with PVA fibers at 3.2 vol.% of cementitious materials (0.8 vol.% of concrete); and (iv) two with GP at 0.2 vol.% and PVA fibers at 3.2 vol.% of cementitious materials. The nanoplatelet volume fraction was selected based on laboratory-scale optimization studies which targeted achievement of balanced gains in the mechanical and sorption characteristics of concrete. The dosage of PVA fibers was selected based on the previous experience with normal-strength concrete.

2.2. Modification of graphite nanoplatelets

Optimal bonding of GPs to the matrix enables mobilization of the exceptionally high tensile strength and the frictional resistance against the tremendous surface area of GPs toward achievement of high strength and toughness levels. The optimal bonding requirements can be met by careful surface modification of graphite nanomaterials. Modified GPs can play multi-faceted roles toward enhancing the mechanical, physical and functional attributes of cementitious materials.

The surface modification method used in this study involved grafting of Polyacrylic Acid (PAA) onto GPs for introducing high concentrations of hydroxyl and carboxyl (OH and COOH) groups on GP surfaces (Fig. 3). A detailed description of this modification technique has been presented by authors elsewhere [31]. The hydroxyl and carboxyl groups introduced on modified GP benefit dispersion of nanoplatelets in water by making their surfaces more hydrophilic and (in the presence of polymers) via electrosteric stabilization. The hydroxyl and carboxyl groups also enable bonding to cement hydrates via coordinate bond formation with Ca^{2+} ions in cement hydrates (Fig. 3), strong cationic and anionic interactions, and other secondary bonding.

Laboratory studies indicated that modification of GP with PAA at 1.0:0.1 GP-to-PAA weight ratio enhances the contributions of GP to the flexural strength of cementitious matrices. The required amount of PAA was added to GP prior to dispersion in water.

2.3. Dispersion of graphite nanoplatelets in water

GPs were dispersed in 10% of the concrete mixing water using the procedure outlined below (the dispersed nanoplatelets was then added to the mixer used for preparation of the concrete):

(1) The required amount of GP was added to water, and the mix was stirred overnight (∼12 h); and
(2) The mix was sonicated for 10 min at 30, 45, 65 and 75% of maximal power (400 W) with 1-min intervals between the intensity increments; and
(3) Repeated step (2).

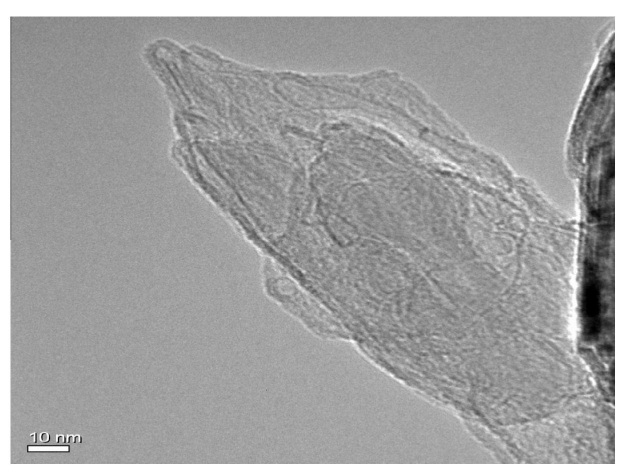

Fig. 1. TEM micrograph of graphite nanoplatelet (GP) with planar geometry.