



Effect of reduced graphene oxide, alumina and silica nanoparticles on the deterioration characteristics of Portland cement paste exposed to acidic environment

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ABSTRACT

Acid attack on cement concrete results in the development of a degraded layer surrounding the unaffected material, which causes a deterioration of mechanical properties. The effect of reduced graphene oxide, alumina and silica nanoparticles on the deterioration characteristics of 28-day cured cementitious pastes after storage in 0.5 mol/L HNO₃ solution for a period of 56 days is reported in this paper. Samples were collected from the degraded pastes at different time periods and then characterised using various techniques like scanning electron microscopy with energy dispersive spectroscopy, optical microscopy, thermogravimetric analysis, mercury intrusion porosimetry, X-ray computed tomography and nanoindentation. While the porosimetry results showed that the presence of reduced graphene oxide and nano alumina decreased the amount of capillary pores (10 nm–10 μm) by up to 46% and 51% than the control paste after storage in acidic solution for 28 days, the details of the relative zones formed in the paste along with their characteristics were revealed by the microscopy and nanoindentation techniques. Overall, the results suggest that the presence of these nanomaterials refined the pore structure of the cementitious matrix and thereby increased the resistance to leaching of calcium ions from the binder phases exposed to aggressive aqueous media.

1. Introduction

Chemical warehouses, nuclear industry structures, underground tunnels and radioactive waste disposal structures made of cement concrete are commonly exposed to aggressive solutions [1–4]. The binder phase in these structures is highly stable in alkaline conditions (pH > 11.5), which is brought about by the ionic species available in the pore solution (OH⁻, Ca²⁺ and alkali ions such as Na⁺ and K⁻). Diffusion of H⁺ ions from the external solution decreases the alkalinity of the pore solution [5–8]. Under lowered pH conditions, calcium leaching occurs, which is a combined diffusion – dissolution – precipitation process [2,9,10].

According to Berner's diagram [11], the calcium to silica (Ca/Si) ratio is in direct relationship with the amount of Ca²⁺ ions in the pore solution. The decrease in this ratio forces the dissolution of calcium hydroxide (C-H) and subsequently calcium silicate hydrate (C-S-H) gel. Their dissolution is also dependent on the chemical equilibrium of calcium – silicate – water system [4,12]. This decalcification increases the pore connectivity of C-S-H gel and changes the equilibrium Ca/Si ratio which substantially decreases the concrete strength. Along with

these phases, the remaining hydrates like calcium aluminate hydrate (C-A-H), ettringite (AF_t) and monosulphate (AF_m) are also reported to lose the soluble calcium from their well-defined structure. Aluminate and ferrite phases dissolve at much lower pH values than those causing the release of Ca²⁺ ions from the C-H and C-S-H gel. This late dissolution releases Al³⁺ and Fe³⁺ ions into the external solution [13]. The rate of degradation is primarily dependent on the acid type and its concentration and the chemical composition of the binder. In the present study, the effect of three different nanomaterials including reduced graphene oxide (rGO) on the deterioration characteristics of cementitious matrix after storage in nitric acid (HNO₃) solution is investigated. Thus, it is of interest to describe some studies that have addressed this issue. Pavlík [14] had earlier described the HNO₃ attack of hardened cementitious matrix, which is schematically reproduced in Fig. 1.

HNO₃ attack on cementitious matrix produces calcium nitrate (Ca(NO₃)₂) salts which are highly soluble. This attack is characterised by the formation of insoluble precipitates surrounding the unaffected material. The pH in the degraded layer changes from the low values of external solution to the highly alkaline unaffected material. The precipitates are made of Si, Fe and traces of Al, and are highly porous, soft

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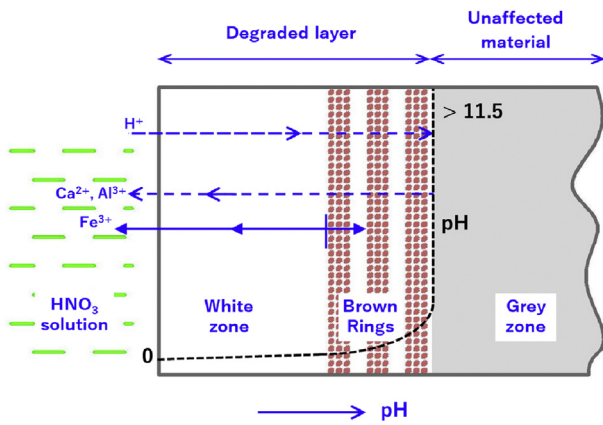


Fig. 1. Schematic illustration of a cut-section of cement paste exposed to HNO_3 environment as described by Pavlik [14].

and have surface cracks in them. These shallow cracks may occur because of decalcification shrinkage. Si and Fe based precipitates are found to be white and brown in colour respectively whereas the unaffected grey material is still occupied with the normal cement hydrates [1,3,5,12,14–18]. The outermost siliceous gel is structurally amorphous and precipitates when the Ca^{2+} concentrations are lesser than 2 mol/L in the pore solution [19]. The intermediate brown discoloration is probably governed by the precipitation of $\text{Fe}(\text{OH})_3$ [3].

Recent studies reported that the addition of well-dispersed graphene oxide (0.01–0.06 wt%), nano silica (0.5–6 wt%) and nano alumina (0.2–5 wt%) improved the strength and durability-related properties of cementitious composites, which could be possibly because of the filler effect provided by such nanomaterials, and their positive influence on cement hydration kinetics [19–30]. In particular, the reduced graphene oxide (rGO) (sheet-like structure) has its basal plane and edges decorated with hydroxyl/epoxide and carboxyl/carbonyl groups, which therefore assist such nanosheets to effectively disperse in water due to electrostatic stabilisation. Besides, its addition reduces the need for the use of surfactants in the cementitious matrix, which are typically added to prevent nanomaterials agglomeration caused by van der Waals' forces of attraction. Wang et al. [31] reported that carboxyl groups of graphene oxide (GO) interact well with the cement hydrates, and create a 3D network structure in the cementitious matrix. Nano silica is popular nowadays, as its minor addition seems to improve acid resistance of cement concrete [30]. Its effective dispersion in cementitious matrix first refines the pore structure and then increases the pozzolanic conversion of portlandite to C-S-H gel [19,30,32,33], where the former dissolves first when exposed to acidic environment. Gaitero et al. [34] reported that the nano silica presence increased the silicate chains length in C-S-H and thereby stabilised the Ca/Si ratio in concrete. The effect of rGO, alumina and silica nanoparticles on the deterioration characteristics of 28-day cured cementitious pastes after storage in 0.5 M (molar concentration) HNO_3 solution for 56 days were evaluated for the first time in this study. Samples were collected from these degraded pastes at different time periods and then characterised using various techniques like scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS), optical microscopy (OM), thermogravimetric analysis (TGA), mercury intrusion porosimetry (MIP), X-ray computed tomography (CT) and nanoindentation (NI).

2. Experimental program

2.1. Materials, specimen preparation and acid immersion test

Prismatic specimens of size $10 \times 10 \times 50 \text{ mm}$ were prepared using acrylic moulds for the acid immersion test. Apart from the control mix, three paste mixes were incorporated with rGO, alumina and silica

nanoparticles at concentrations of 0.02%, 0.2% and 4% by weight of cement respectively. These four mixes were designated as Control, RGO, Al_2O_3 and SiO_2 . Distilled water and 53 grade Portland cement conforming to IS 12269 [35] (62.16 wt% CaO, 20.95 wt% SiO_2 , 5.14 wt% Al_2O_3 , 3.06 wt% Fe_2O_3 , 3.08 wt% SO_3 , 1.33 wt% MgO and 0.009 wt% Cl) were used in the preparation of all mixes having w/c ratio of 0.32.

Reduced Graphene Oxide (rGO) sheets were extracted from natural graphite using modified Hummers' method. The synthesis procedure was earlier reported in Murugan et al. [20]. The remaining nanomaterials were procured from Sigma Aldrich, India. The mean particle size and specific surface area of alumina and silica nanoparticles were specified by the manufacturers as 50 nm and $40 \text{ m}^2/\text{g}$, and 12 nm and $225 \text{ m}^2/\text{g}$ respectively. The highest theoretical specific surface area of pristine graphene is around $2600 \text{ m}^2/\text{g}$ as reported in Singh et al. [36]. Fig. 2 shows the EDS spectra of these three nanomaterials.

To enhance the dispersibility of nanomaterials as well as to increase the workability of fresh cement pastes, polycarboxylic ether (PCE) based superplasticizer at 0.05 wt% was added in all pastes at the time of mixing. Prior to mixing cement, the solution containing nanomaterials, PCE and distilled water was sonicated using Sonics Vibra-Cell ultrasonic liquid processor (probe sonication) for 30 min. Small amounts of sample from these solutions were collected and then analysed using Dynamic Light Scattering (DLS) method (Horiba Nanopartica SZ-100, Japan) (Fig. 2b).

The DLS technique determines the size distribution profile of particles in suspension. The actual particle sizes of alumina and silica nanoparticles as specified earlier, were not observed anywhere in the DLS plot. This suggests that these nanomaterials were agglomerated, possibly due to the use of insufficient amounts of superplasticizer (dosage was fixed based on workability of the paste). The majority of rGO sheets synthesized by modified Hummers' method are reported to have size range in between 5 nm and 1500 nm [37]. In this study, the as-synthesized rGO sheets were determined to have two size ranges—80–102 nm and 450–1000 nm respectively. The thickness of these sheets cannot be determined effectively using the DLS method, and thereby it is difficult to comment whether the sheets are separate or stacked.

The fresh mixes were compacted with the help of a vibration table. The prismatic specimens were demoulded after 24 h from the time of mixing and then cured in saturated limewater solution up to 28 days. In this paper, the limewater cured specimens are designated as t + 0. The t + 0 specimens were immersed in 0.5 mol/L HNO_3 solution for a period of 56 days. A high acid concentration which is not simulating the real-field conditions was adopted to accelerate the deterioration process in cement pastes and therefore to achieve quick results. The deterioration process was further accelerated by periodically renewing the external solution after 3.5, 8, 11.5, 17, 23.75 and 28 days. This helps to consistently maintain a strong and aggressive acidic environment surrounding the cement pastes. This acid renewal was done whenever the pH of external solution, which increases because of cement leaching, reached a level of around 4 (as suggested in Ref. [38]). To avoid carbonation, the immersion test was performed inside a glove box, which was purged with inert gas (N_2). The specimens were taken out after 28 and 56 days of storage, and were designated as t + 28 and t + 56 respectively. Small samples (about 1 mm cube) removed from the specimens were then continuously stored in isopropyl alcohol (IPA) to stop the microstructural changes prior to characterisation studies.

2.2. Characterisation techniques

The method of sample collection from the prismatic specimens is schematically illustrated in Fig. 2c. Prisms from each of the four mixtures before and after acid exposure were sectioned into five pieces (of 10 mm) using diamond-tipped saw. The middle sections from all acid exposed prisms were noticed to have a soft and weak degraded layer

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