Long-term Performance of Nanoparticle Incorporated Eco-friendly Concrete in Natural Seawater Environment

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Abstract

The use of blended concrete has widely gained industrial importance owing to the CO\textsubscript{2} gas emissions and carbon footprint resulting from the production of ordinary Portland cement (OPC). Despite the advancements, the deterioration of concrete structures raises a significant threat to their long term durability and service life in aggressive conditions. In this work, the long-term antifouling, strength and durability properties of a blended eco-friendly concrete with OPC, fly ash, nanoparticles, and corrosion inhibitor is evaluated in natural seawater for one year. The biofouling attachment, total viability count (TVC), mechanical strength, alkalinity and free chloride contents were measured and the results were compared with OPC concrete. A four-order reduction in the total biomass and total bacterial density is observed on the surface of the blended concrete. Further, a significantly lower chloride and water penetration depth, free chloride content, compact and smooth surface morphology devoid of cracks and high C-S-H content are observed in blended concrete, compared to the OPC concrete, after exposure in seawater for one year. From the results, it is seen that the blended concrete mix is promising for applications in seawater environments because of its superior biofouling resistance, mechanical properties and durability.

Introduction

Concrete is currently the second most consumed substance after water with an annual per capita production of more than 1 m\textsuperscript{3} worldwide (Channa et al. 2021). Its popularity in civil infrastructure and large construction projects such as bridges and nuclear reactors exposed to seawater has been because of availability, strength, flexibility, and durability over other construction and building materials (Memon et al. 2021). With the increased use of concrete as a key building material in infrastructure construction and rehabilitation around the world, demand for concrete is expected to rise dramatically, to ~18 billion tonnes by 2050 (Mehta &Monteiro 2014), which demand for production of more cement. The cement industry accounts for 5–10\% of overall CO\textsubscript{2} emissions, contributing to global warming, climate change, and natural resource depletion (Benhelal et al. 2013).

Recent studies reveal that the production of one tonne of OPC accounts for roughly one tonne of CO\textsubscript{2} emission and utilization of 1.5 tonnes of raw materials (Memon et al. 2021). As a result, alternative supplementary cementitious materials (SCMs) like fly ash, ground granulated blast furnace slag, metakaolin etc. are explored (Channa et al. 2021). Concrete made from OPC and SCMs is the most practical and cost-effective option (Owaid et al. 2012). Since the bulk of accessible SCMs are waste products originating from agricultural and industrial wastes, their incorporation as partial replacement for OPC can reduce CO\textsubscript{2} emissions significantly (Chowdhury et al. 2015) and enable production of green concrete with improved properties and lower carbon footprint.

In general, concrete structures exposed to marine environments deteriorate prematurely due to corrosion, posing a safety risk, reducing the durability and lifespan of structures, and increasing repair costs, in addition to negatively impacting natural resource sustainability (Donatello et al. 2013). The most prevalent cause of concrete deterioration in coastal and offshore conditions, particularly in tunnels, buildings, bridges and other structures exposed to seawater, is chloride-induced reinforcement corrosion caused by capillary absorption and resulting hydrostatic pressure of the cementitious matrix (Jang et al. 2017), which affects the long-term performance and aesthetic appearance of reinforced concrete structures (Kumar et al. 2021). The infiltration of chloride ions from the seawater produces depassivation of reinforcement, which damages the concrete due to corrosion of steel beyond a critical limit (Jang et al. 2017). As a result, developing new inventive ways to improve the corrosion protection of concrete structures is critical. Further, the growing number of offshore constructions (e.g., offshore airports and power plants, civil and military terminals, lighthouses, radar stations, island reefs), warrants a better understanding of the long term performance of concrete structures in the marine environment to evolve suitable mitigation strategies.

Corrosion inhibitors are the most effective approach for preventing steel corrosion in RC structures, although they have a significant maintenance cost (Jang et al. 2017). Nitrite, a commonly used corrosion inhibitor, is found to delay the failure
of the protective passivation film on the reinforcement surface. Inorganic inhibitors like sodium nitrite obstruct anodic processes, thereby preventing corrosion in reinforced concrete, and are commonly utilized in large structures. Another way to protect concrete structures from corrosion is to improve impermeability and resistance to chloride ion diffusion. Over the last few decades, researchers have developed low permeability concrete by partially replacing OPC with SCMs (Wang & Park 2015). The pozzolanic reaction of the SCMs reduces the permeability of the concrete significantly in later stages.

Fly ash is a major waste product of coal-fired power stations, with an annual production of 750 million tonnes, which takes up a lot of land and pollutes the atmosphere. By substituting fly ash for OPC in concrete, the demand for cement and pollution associated with concrete production can be reduced (Zhao et al. 2021). Fly ash being a finely divided amorphous powder of alumino-silicates, has enormous potential when mixed with cement due to pozzolanic and filler effects. The spherical shape of fly ash improves particle agglomeration and minimizes permeability in concrete. During the hydration process, the chemical reaction of fly ash with calcium hydroxide (CH) produces secondary calcium silicate hydrate (C-S-H) and calcium aluminate hydrate (C-A-H), which increase the strength of concrete by forming a denser matrix and lower the possibility of calcium hydroxide leaching (Boopaphi et al. 2021). Up to 50% class F fly ash can be used as a partial substitute to cement in reinforced concrete (Siddique 2004b). While high volume fly ash (HVFA) concretes display promising performance, its low early age strength remains a concern for large scale applications (Bilodeau & Malhotra 2000). Sulapha et al. (Sulapha et al. 2003) found that replacing OPC with fly ash reduced the resistance to carbonation as compared to pure OPC-blended concrete.

Lower water-binder (w/b) ratio along with particular admixtures are required for the manufacturing of high-strength and high-performance concrete (HPC) (Bharatkumar et al. 2001). Reduced water content, on the other hand, reduces lubrication and flowability among binder particles, thereby creating empty air spaces in a mix (Kumar et al. 2021). In this regard, the use of nanomaterials in concrete and cement mortar has received much attention during the last decade because of their potential to enhance the mechanical strength, performance, workability, void filling effect and sustainable features (Mostafa et al. 2021, Xu et al. 2021). Mixing nanomaterials with agro/industrial waste materials into concrete has become the most prevalent technique to enhance the serviceability of structures as it refines the pore structure of concrete because of their large specific surface area, high activity, and good compatibility with hydration products, resulting in less permeability and higher strength (Sikora et al. 2020). Furthermore, nanoparticles enable a denser solid packing with fewer permeable pores by filling the voids between cement grains at the nano/micro-scale. Nano additives are also shown to address the limitation of low early age compressive strength in HVFA concretes (Singh & Singh 2018). Nanomaterials, act as nucleation sites for cement hydrates and improves hydration and microstructure of concrete.

There are several studies on nanomaterials incorporated concretes, where nano-Al₂O₃, nano-SiO₂, nano-TiO₂, nano-Fe₂O₃, nano-CaCO₃, nano-Cr₂O₃ etc. are used. Nano-titania has superior photocatalytic activity, hydrophobic properties, requires less water and sets fast (Singh et al. 2021). The photocatalytic properties of TiO₂ enables the production of antibacterial surfaces that kill microbes (Akın & Danacı 2021). Li et al. (Li et al. 2014) have found that 1 wt. % nano-TiO₂ in concrete can reduce the chloride diffusion coefficient by 26%. Nazari and Riahi (Nazari & Riahi 2011) have shown that the addition of nano-TiO₂ in concrete can minimize porosity and promote the formation of C–S–H, and hence improve the flexural performance of concrete. In many studies, nano-CaCO₃ is used to address the issues of early strength and pores in concrete. The presence of nano-CaCO₃ accelerates the hydration reaction of tricalcium aluminate (C₃A). It forms a carboaluminate complex, which improves the nucleation and seeding properties of C-S-H and the mechanical properties of concrete (Sato & Beaudoin 2011). Moreover, nano-CaCO₃ also reacts with tricalcium silicate (C₃S) in the cement, which accelerates the setting and helps to dilute the binder, thereby providing a higher early age strength (Péra et al. 1999). However, the synergistic effect of multiple nanoparticles on the microstructure and strength of concrete are poorly understood, which is explored in this paper.
More focus has recently been placed on the utilization of various pozzolanic materials in binary as well as ternary blends to improve the functional performance of concrete structures (Kumar et al. 2021). The majority of previous research has focused on the strength and durability of OPC concrete blended with SCMs under controlled laboratory conditions, accelerated and simulated environmental conditions (Kwon et al. 2017). However, in this study the long-term performance of the blended eco-friendly concrete (CFNI), consisting of 56 wt.% OPC, 40 wt.% fly ash, 2 wt. % nano-CaCO₃ and nano-TiO₂ (1:1 ratio) and 2 wt. % NaNO₂ based anodic mixed inhibitor solution in a real-time marine environment was investigated for a period of 1 year. The anti-fouling characteristics, total viability count (TVC), differential gradient gel electrophoretic (DGGE) analysis, mechanical strength, chloride penetration and water permeability were measured on exposed specimens and the performance was compared with that of conventional OPC concrete. Further, the microstructural evolution and carbonation rate in the marine atmosphere were also evaluated.

**Materials And Methods**

**Materials**

For casting all the concrete specimens, OPC (43 grade) conforming to ASTM C150 is used as the key constituent. Class F Fly ash (Siliceous type) conforming to ASTM C618-17a was procured from Ennore thermal power plant (Chennai) and used as the partial cement replacement (40 wt.%) material. The chemical composition and physical properties of cement and fly ash used in this study are given in Table S1. Fine aggregates (natural river sand with a maximum size of 4.75 mm) and coarse aggregates (crushed black granites of 20 mm and 12 mm size) were selected as per ASTM C33. Using a planetary ball mill, commercial laboratory-grade nano-TiO₂ and nano-CaCO₃ powders with an initial particle size of 400–500 nm were reduced to a particle diameter of 20–70 nm (Harilal et al. 2019a). An anodic mixed inhibitor solution of NaNO₂ was used as the corrosion inhibitor. Figure 1 shows the SEM images and X-ray diffractograms of fly ash and nanoparticles used in this study. Sulphonated naphthalene-based superplasticizer was used to improve the workability with a target slump of 100 mm.

**Concrete mix design**

The mix proportions of the two types of concrete specimens used for the long-term seawater exposure studies are given in Table 1. As per IS 10262:2009 standard, the designed concrete mix proportions have a target strength of 45 MPa after 28 days of curing.

| Concrete type | Cement (kg/m³) | Fly Ash (kg/m³) | F. Agg. (kg/m³) | C. Agg. (kg/m³) | TiO₂ (kg/m³) | CaCO₃ (kg/m³) | Inhibitor (kg/m³) | water (kg/m³) | Water-cement ratio |
|---------------|----------------|-----------------|----------------|----------------|-------------|--------------|-----------------|--------------|------------------|
| CC            | 450            | -               | 797            | 1090           | -           | -            | -               | 166.5        | 0.37             |
| CFNI          | 252            | 180             | 724            | 1003           | 4.5         | 4.5          | 9.0             | 144          | 0.32             |

Two types of concrete of M45 grade are designated as CC (100% OPC concrete) and CFNI (replacing OPC with 40 wt.% fly ash, 1 wt.% TiO₂, 1 wt.% CaCO₃ nanoparticles and 2 wt.% NaNO₂ based inhibitor). An optimal mix design (CFNI) was arrived based on the results of our study (Harilal et al. 2019a).

**Exposure Studies**

The concrete test specimens were exposed to seawater in the sump house at the Nuclear Desalination and Demonstration Facility, in the Bay of Bengal sea (12° 33'N and 80° 11'E), approximately 80 km south of Chennai, Tamil Nadu. The
photographic image of the exposure site and the exposure method of the specimens are shown in Fig. S1. The test specimens were suspended at a proper depth in the seawater at the exposure site using natural fiber ropes and fishing nets during the month of June. Figure 2 shows the differences in the average temperature, RH and rainfall from the beginning of exposure to the period of withdrawal. The seasonal variations in hydrographic parameters of the seawater during the period of exposure of the test specimens are listed in Table 2.

| Exposure period (days) | ORP (mV) | pH | TDS (g/L) | Salinity | Dissolved oxygen (mg/L) | Chloride content (µg/L) | Ammonia (µg/L) | Phosphorus (µg/L) | Nitrite (µg/L) | Silicate (µg/L) |
|-----------------------|----------|----|-----------|----------|-------------------------|------------------------|----------------|-----------------|--------------|---------------|
| 56 d                  | 200.3    | 7.7 ± 0.2 | 30.7 ± 1 | 33.62 ± 0.0 | 8.03 | 29400 | 40.39 ± 0.0 | 97.3 ± 3.07 | 1.94 ± 0.07 | 4.75 ± 0.63 |
| 90 d                  | 186.4    | 8.3 ± 0.1 | 23.8 ± 0.6 | 33.34 ± 0.1 | 8.15 | 25900 | 36.3 ± 0.0 | 72.45 | 2.35 ± 0.07 | 23.1 ± 0.2 |
| 180 d                 | 178.7    | 8.5 ± 0.1 | 29.4 ± 0.8 | 35.34 ± 0.1 | 6.99 | 22600 | 30.8 ± 0.1 | 47 ± 2.1 | 1.22 ± 0.05 | 1.35 ± 0.04 |
| 365 d                 | 192.6    | 8.1 ± 0.1 | 31.1 ± 0.4 | 34.52 ± 0.0 | 5.23 | 25200 | 35.25 ± 0.1 | 64.2 | 1.58 ± 0.04 | 8.58 ± 0.1 |

These specimens were completely immersed in seawater up to an exposure period of 365 days and then withdrawn at regular intervals for examination. For carbonation studies, mortar specimens are exposed to seashore, inland atmosphere and carbonation chamber for one year.

**Test methodology**

Concrete cube specimens immersed in the seawater were collected after 56, 90, 180 and 365 days of exposure. The anti-fouling characteristics were evaluated by visualizing the nature/degree of bio-fouling attachment over the specimens. The total bacterial density present in the biofilm formed over the surface of the collected concrete cube specimens after exposure in seawater was enumerated using the Total Viable Count (TVC) technique (Uthaman et al. 2018). The density of aerobic bacteria, slime formers and Sulphate Reducing Bacteria (SRB) was measured by culturing in the seawater agar medium (M/s. Hi Media-M592), Pseudomonas agar medium (M/s. HIMEDIA M120) and Post gate medium (Harilal et al. 2019b), respectively. The total biomass in the biofilm is also quantified on the basis of ATP fluorescence assay obtained using a Luminometer (Anandkumar et al. 2020).

**Luminometer assay of ATP**

Free Adenosine triphosphate (ATP) present in the biofilms collected from the concrete specimens was quantified using bioluminescence based assay with BacTiterGlo viability kit (M/s. Promega, USA). 100 µl each of the serially diluted biofilm samples were mixed with 100 µL of BacTiter-Glo™ reagent in the wells of a white colored flat bottomed opaque-walled 96-well microtiter plate (M/s Coming, USA). The plate was incubated at 37° C in an orbital shaker for 5 minutes and the luminescence was read using a Glomax Discover system (M/s. Promega, USA). Luminescence data recorded as relative luminescence units (RLU) was used to calculate the total ATP (moles) derived from the standard graph constructed with RLU data of the standard ATP values.

**Differential Gradient Gel Electrophoretic analysis of the biofilm formed over the concrete**
Genomic DNA was isolated from the biofilms of different concrete specimens using a DNeasy power water kit (M/s. Qiagen GmbH, Germany). Polymerase chain reaction (PCR) was carried out in Eppendorf Master Cycler (M/s. Eppendorf, Germany) with the genomic DNA isolated from the biofilms as the template to amplify the V3 and V8 regions of bacterial 16S rRNA gene sequences. The primer sequences for V3 region used are: V3GC-5’-CGCCCGCCGCGCGGGGGGGGGGAGGCTACGGGAG-3’; V3R-5’-ATTACCGCGCTGCTGG-3’ and for V8 region are V8F – 5’ CGGGGGCACGGGGGAACGCGAAGAACCTTAC-3’ and V8R – 5’ TAGCGATTCCGACTTCA-3’ (Muyzer et al. 1993, Yu & Morrison 2004). The PCR conditions were: an initial denaturation step (5 min at 94°C), 36 cycles of denaturation (94°C for 1 min), primer annealing (56°C for 1 min for V3 region), primer extension (72°C for 1 min), and a final extension step (72°C for 10 min). V8 regions were amplified with the above PCR conditions except the primer annealing step with 48°C. The amplified PCR products of V3 and V8 regions were confirmed by 2% agarose gel electrophoretic technique.

DGGE gel containing 8% (wt/vol.) polyacrylamide with denaturant gradient ranges from 30–90% of 7 M urea and 40% v/v formamide was cast parallely. Using DGGE system TV400 (M/s. Scie-Plas, UK), the PCR amplified products of V3 and V8 regions were electrophoresised in 1 X Tris acetate EDTA (TAE) buffer at a constant voltage of 70 V at 60°C for 16 h using a high voltage power supply (EV3620 Consort, Belgium). After electrophoresis, the ethidium bromide (0.5 mg/ litre) stained gels were visualized under UV transilluminator in gel documentation system (GeneBox, Syngene, UK). The gel bands were analyzed and compared among the different biofilm samples using gene analysis software (GeneTools, Syngene, UK).

**Evaluation of strength and durability properties**

The properties such as compressive strength, split tensile strength, and flexural strength were evaluated at intervals as per the ASTM/Indian standards using concrete cube specimens (150 x 150 x 150 mm), cylindrical specimens (150 mm diameter and 300 mm height) and prism specimens (500 x 100 x 100 mm), respectively. Mechanical properties were evaluated on triplicate specimens at 28 days of age, and also after 56, 90, 180, and 365 days of exposure to natural seawater. The rapid chloride permeability test (RCPT) was performed on triplicate specimens as per ASTM C1202 to determine the resistance of concrete specimens to the ingress of chloride ions. The depth up to which water has penetrated into the concrete specimens of both compositions was visually examined and measured in accordance with DIN 1048 (Part-5) after aging for 28 days and after exposure to seawater for 365 days. The carbonation test was carried out in three atmospheres (a) seashore near the Bay of Bengal coast, Kalpakkam, India, (b) rooftop of a building and (c) inside a carbonation chamber [M/s. Ultra Thermoscientific, India maintained at a temperature of 25°C, RH of 65% and 3% CO₂ concentration) using mortar cubes of 100 x 100 x 100 mm size.

The depth of carbonation (X) was then calculated as per RILEM CPC 18 (CPC 1988) by taking the average depth of the colorless areas in three specimens with a vernier caliper (M/s. Mitutoyo Digimatic, Japan). The rate of carbonation (k) in the exposed specimens was determined by using the equation: X = kt₁/₂, where, X is the carbonation depth in mm and t is the time of exposure measured in weeks (Rahla et al. 2019). The concrete samples were first mechanically powdered and the pH of the powder in solution was determined using a pH meter (Harilal et al. 2019a). The amount of free chloride present in the pore solution of both the concrete compositions was determined with the water-soluble extraction method (Liu et al. 2016) by using a chloride measuring probe (M/s. HACH, Germany).

**Chemical, microstructural and morphological characterization**

The thermal properties of CFNI was evaluated with a thermogravimetric analyzer (M/s. SETSYS 16/18, SETARAM, France). The calcium hydroxide (CH), C-S-H and CaCO₃ contents in both the concrete compositions after aging for 28 days and after 365 days of exposure in seawater were calculated directly from the TG curve (Shaikh & Supit 2014, Singh et al. 2019). The evolution of phases like quartz, C-S-H and ettringite were evaluated using a powder X-ray diffraction system with Co-Kα radiation on an X-ray diffractometer (Inel – EQUINOX 2000 diffractometer). SEM analysis was done using a high
resolution Scanning Electron Microscope (M/s. HITACHI S-4800 HRSEM, Japan) operating under a high vacuum mode to compare the morphologies of hydration products.

Results And Discussion

Measurement of biofouling resistance

Fig. 3 shows the photographs of the surface of the concrete specimens withdrawn from seawater after 56, 90, 180 and 365 days of exposure. Throughout the exposure period, it can be visually observed that the extent of biofouling over the CFNI concrete was lesser than in the CC specimens. Up to 56 days of exposure, both CC and CFNI specimens retained the original grey color. After 90 days of immersion, biofouling was initiated as brown slime and in 180 days, numerous macrofoulants like serpulids were observed on the surface of CC specimens. Blackening of the surface of CC specimens was initiated after 180 days, indicating the presence of sulfate reducing bacteria on the surface. Within 365 days of exposure, the whole surface of CC specimens underwent high levels of biofouling and turned completely black in color due to the sulfate attack by microorganisms. However, the surface of CFNI specimens remained free of biofouling up to 180 days of exposure exhibiting only the formation of a slightly brown biofilm. Only after 365 days of exposure, attachment of very few serpulids and blackening of the surface on CFNI specimen is seen. The measurement of dry weight of the biofouling attachment was also in line with the above observations.

The biogenic H$_2$SO$_4$ produced by the sulphate oxidizing bacteria (SOB) in the biofouling attachment attacks CH, C-S-H, and C-A-H in the concrete and gets transformed to CaSO$_4$ (gypsum) by the impact of seawater (Kwon et al. 2017). Furthermore, at temperatures below 15 °C, the presence of sulphate on concrete can cause the conversion of C–S–H into a reaction product called thaumasite, resulting in disintegration and scaling of the concrete (Jakobsen et al. 2016). The findings show that CFNI concrete has a low biofouling attachment rate and can be used effectively in maritime environments.

Enumeration of the total viable bacteria

The total viability count representing the bacterial cells in the biofilm formed over the specimens exposed in seawater were enumerated by culturing in seawater agar, Pseudomonas agar and Postgate medium using pour plate technique and is tabulated in Table 3. The biofilms formed on the CFNI specimens showed a four order lower TVC value in seawater agar, two order lower value in Pseudomonas agar and one order lower anaerobic bacteria count compared to CC specimens, indicating enhanced anti-microbial activity on the surface of CFNI specimens. Table 3 also shows the results of the ATP measurements in the biofilms obtained from the concrete specimens exposed to seawater for different durations. It is observed that the ATP concentration increases with the duration of exposure for both the specimens. CFNI concrete specimen showed a four order lower ATP concentration than CC specimen.

Table 3. Total Viability Count (cfu/cm$^2$) and ATP assay of the biofilms formed over the specimens exposed in seawater for different duration
| Medium                     | 56 d  | 90 d  | 180 d | 365 d | 56 d  | 90 d  | 180 d | 365 d |
|----------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Seawater agar              | 1.73 E+03 | 2.31 E+04 | 7.11 E+06 | 5.62 E+10 | 5.14 E+02 | 6.43 E+02 | 9.93 E+04 | 3.70 E+06 |
| Pseudomonas agar           | 8.61 E+04 | 1.56 E+05 | 1.01 E+08 | 5.18 E+09 | 3.98 E+03 | 7.07 E+03 | 1.45 E+05 | 8.12 E+07 |
| Postgate medium (SRB)      | 2.57 E+01 | 4.37 E+02 | 8.44 E+02 | 2.72 E+03 | 6.40 E+00 | 2.05 E+02 | 2.81 E+02 | 4.74 E+02 |
| ATP (moles)                | 2.42 ± 0.2 E-07 | 3.18 ± 0.5 E-05 | 4.81 ± 0.4 E-04 | 8.78 ± 0.1 E-03 | 5.21 ± 0.1 E-08 | 1.91 ± 0.3 E-07 | 4.17 ± 0.3 E-06 | 6.29 ± 0.4 E-07 |

The addition of fly ash can reduce the attachment of aerobic and anaerobic bacteria over the concrete specimens and improve the biodeterioration characteristics. The nano-anatase TiO$_2$ particles possess an inherent photocatalytic activity due to their ability to form free radicals that oxidize the organic biomass thereby providing an anti-microbial effect (Akın & Danacı 2021). In fly ash concrete modified with nanoparticles, one order decrease in the viable bacterial count is reported (Uthaman et al. 2018). Besides corrosion inhibition, sodium nitrite is shown to have bactericidal activity due to the presence of reactive nitrogen species (RNS) in vivo conditions (Klebanoff 1993). Thus, the significant anti-microbial resistance observed in CFNI concrete is in agreement with the earlier reports.

**DGGE analysis**

Fig. 4a and 4b show the respective distinct DNA bands of V3 and V8 variable regions of 16S rRNA genes of biofilms observed in the DGGE gel analysis indicating the variations in the gel band numbers and their corresponding intensities in the CC and CFNI specimens. V3 and V8 regions of 16S rRNA sequences are most widely used in several metagenomic studies as they provide more divergence and phylogenetic resolution than other variable regions (Armougom & Raoult 2009). The calculated average DNA intensities of the gel bands of CC and CFNI specimen were 1.08 x10$^8$ and 1.12 x10$^5$, respectively. So, a three order reduction in the DNA intensities was observed in CFNI specimen. The higher intensities and numbers of gel bands in CC specimens infer the presence of bacterial diversities in the biofilms formed on the concrete specimens exposed to seawater for different durations. A few bands with lower intensity observed in the biofilms formed over the surface of CFNI specimen confirm the enhanced anti-microbial activity of the additives present in the modified concrete specimens.

**Long term mechanical properties of CFNI after immersion in sea water**

**Compressive strength**

Compressive strength of concrete is a measure of its ability to resist compressive loads, which is calculated by the ratio between failure load and the cross sectional area of concrete. Fig. 5a shows the variation in the compressive strength of CFNI and CC specimens with ageing in seawater up to a year. The compressive strength of CC and CFNI after 28 days were 49.8 and 43.9 MPa, respectively. According to Li (Li 2004), partial replacement of OPC with fly ash causes a delay in hydration due to the incorporation of SCMs, which have a lower hydration rate than OPC. However, due to the enhanced pozzolanic effect of SCMs, the compressive strength increases with time (Siddique 2004b). In this study, CFNI with 40% fly ash achieved a compressive strength of 62.7 MPa after 365 days of exposure in seawater as compared to 57.1 MPa of CC. The compressive strength of CFNI after 90 days of exposure was higher than that of CC specimens. This is due to the pozzolanic action of fly ash in CFNI specimens, whereby more amount of C-S-H gel formation occurs on reaction with CH in the cement. Continuous immersion of concrete specimens with fly ash in seawater helps to make sure that the process of hydration is uninterrupted and appears to progressively improve hydration and the pozzolanic activity. This
improvement in compressive strength is due to the strengthening of interfacial transition zone (ITZ) due to pore refinement and enhanced production of good quality C-S-H gels (Nežerka et al. 2019).

According to Shaikh et al. (Shaikh & Supit 2014), the synergy of nano-CaCO₃ and fly ash (1:39) is shown to enhance the compressive strength by 58% after 90 days of aging as compared to conventional concrete. This enhancement is as a result of the formation of supplementary C–S–H gel taking place by the accelerated hydration reaction of nano-CaCO₃ with calcium hydroxide and tricalcium silicate/tricalcium aluminate producing a denser microstructure. A study on the effect of nano-TiO₂ particles in concrete by Chen et al. (Chen et al. 2012) showed that nano-TiO₂ has no inherent pozzolanic activity and acts as unreactive fillers, which can refine the pore structure. Their study also showed that nano-TiO₂ accelerates the process of cement hydration by enabling secondary nucleation sites and improve the mechanical strength. Joshaghani et al. (Joshaghani et al. 2020) also shown that the addition of ~ 3% nano-TiO₂ in concrete can improve the compressive strength significantly. Neville (Neville 1995) showed that the addition of inhibitor in concrete can increase the reaction rate of hydration for tricalcium aluminate and tricalcium silicate, and thereby improve the strength. This can also be attributed to the lower w/c ratio in CFNI specimen as a result of the addition of inhibitor, which also acts as a water reducing admixture.

**Split tensile strength**

Splitting tensile strength is utilized in the design of structural lightweight concrete components to assess the shear resistance offered by the concrete member. Fig. 5b shows the split tensile strength of CC and CFNI concrete compositions with immersion time in seawater up to 365 days. The results show that the split tensile strength was higher for CFNI concrete mixture compared to CC mix throughout the aging period. A few reports show a reduction in the tensile strength of concrete containing fly ash (Siddique 2004a). After 365 days of exposure, split tensile strength for CC specimens and CFNI concrete were 3.57 and 4.56 MPa, respectively.

Siddique et al. (Siddique 2004b) reported a 43% increase in the tensile strength of concrete with 40% fly ash after 365 days of exposure in normal water. Uthaman et al. (Uthaman et al. 2018) obtained a 24% increase in the split tensile strength for concrete containing 40% fly ash after 365 days in seawater. The increase in the tensile strength of HVFA was comparatively higher due to the reactivity of fly ash, which enhances the interfacial bonds between the particles and thereby lowering the chances of failure during tensile loading conditions. Jalal et al. (Jalal et al. 2013) found that the addition of up to 4 wt.% TiO₂ nanoparticles, as a partial replacement of cement in concrete, could facilitate additional C–S–H gel formation due to its reaction with crystalline calcium hydroxide, which increases the split tensile strength of concrete specimens. Dharmaraj et al. (Dharmaraj & Malathy 2015) found that the addition of up to 3 wt. % sodium nitrite increases the split tensile strength.

**Flexural strength**

The ability to withstand bending loads is defined by flexural strength, which is another significant mechanical property of a building material. Fig. 5c shows the continuous increase in flexural strength of CC and CFNI concrete compositions with immersion time in seawater for 365 days. Siddique et al. (Siddique 2004a) have shown that partial replacement of cement with fly ash of different volume fractions can reduce the flexural strength up to 56%. In this study, the flexural strength developed in the modified CFNI concrete composition is 5.5 MPa at 28 days, which increased to 7.3 MPa after 365 days. CC concrete showed a flexural strength of 4 MPa after 28 days, which was increased to 5.4 MPa after 365 days of exposure.

Sun et al. (Sun et al. 2020) found a 19.0% increase in flexural strength of concrete when doped with fly ash and nano-CaCO₃, which was attributed to the creation of strong bonds with the tricalcium silicate particles in concrete due to their seeding effect, leading to an accelerated growth of C-S-H and improved early age strength. Nazari et al. (Nazari et al. 2020).
have found that adding 1% nano-TiO$_2$ to OPC concrete can increase the flexural strength due to accelerated C-S-H gel formation caused by the high reactivity of nano-TiO$_2$ particles and the formation of crystalline CH produced during early hydration. In general, the incorporation of TiO$_2$ nano-powder in concrete can effectively fill pores and hence strengthens the microstructure, which enables faster cement hydration and higher amount of reaction products. The addition of 3% sodium nitrite inhibitor to concrete is found to increase the flexural strength by ~ 17% compared to conventional concrete (Dharmaraj & Malathy 2015). Thus, our results on 35% increase in flexural strength of CFNI concrete after 365 days of aging is in tune to the reported results and is attributed to the synergistic effect of multiple additives.

Relationship between compressive strength and tensile strength of CFNI concrete

To predict the split tensile strength of concrete from its compressive strength, a square root relationship between the compressive strength and split tensile strength of concrete, proposed by the American Concrete Institute (ACI) is the most widely followed empirical recommendation. However, recent studies have shown a power law relationship between the two, with the exponent of compressive strength varying between 0.6 and 0.8 (Yan et al. 2013). Various empirical relations used in evaluating the relationship between the compressive and split tensile strengths of conventional concrete are listed in Table 4.

Comparison with the equations proposed by ACI Committee 318 (Committee 2008), CEB- FIP model (Code 1990), Raphael (Raphael 1984), Mokhtarzadeh and French (Mokhtarzadeh & French 2000) and Ahmad and Shah (Ahmad & Shah 1985) were made in this study for the compressive and split tensile strengths of CFNI concrete and is shown in Fig. 6a. The dashed lines indicate the expected relationship between compressive and split tensile strengths of CFNI concrete at different aging time. The split tensile strength increased with compressive strength throughout the aging period. From the best fit (Fig. 6b), the empirical relationship between the compressive strength and split tensile strength of the CFNI concrete for 365 days is found to be $F_{sp} = 0.046F_c^{1.62}$, where, $F_{sp}$ is the mean tensile strength in MPa and $F_c$ is the mean compressive strength in MPa. This shows that the widely used empirical relationship (square root relationship between split tensile strength and compressive strength) recommended by the ACI code does not hold good in the case of modified CFNI concrete.

Table 4. Empirical relationship between compressive strength, split tensile strength and flexural strength reported in literature.
| Sl. No | Code/Author                                    | Empirical Relationship | Reference                      |
|-------|-----------------------------------------------|------------------------|--------------------------------|
| 1     | ACI Committee 318 (2008)                     | $f_{sp} = 0.56f_c^{0.5}$ | (Committee 2008)               |
| 2     | CEB-FIP Model Code for Concrete Structure (1990) | $f_{sp} = 0.30f_c^{2/3}$ | (Code 1990)                    |
| 3     | Raphael (1984)                               | $f_{sp} = 0.313f_c^{0.667}$ | (Raphael 1984)                |
| 4     | Mokhtarzadeh and French (2000)                | $f_{sp} = 0.32f_c^{0.63}$ | (Mokhtarzadeh &French 2000)   |
| 5     | Ahmad and Shah (1985)                        | $f_{sp} = 0.462f_c^{0.55}$ | (Ahmad &Shah 1985)            |
|       |                                               | $f_r = 0.44f_c^{0.67}$   |                                |
| 6     | Selim (2008)                                 | $f_r = 0.034f_c^{1.286}$ | (Pul 2008)                     |
| 7     | Rashid et al. (2002)                         | $f_r = 0.42f_c^{0.68}$   | (Rashid et al. 2002)          |
| 8     | Thomas and Ramasamy (2007)                   | $f_r = 0.79f_c^{0.5}$    | (Thomas &Ramaswamy 2007)      |

The empirical relationships reported by Selim (Pul 2008), Ahmed and Shah (Ahmad &Shah 1985), Rashid et al. (Rashid et al. 2002), and Thomas and Ramasamy (Thomas &Ramaswamy 2007) were compared with our experimental results of modified CFNI concrete. Fig. 6c shows the relationship between the experimental values of compressive strength and flexural strength of CFNI concrete and the predicted values based on the estimating models. The dashed lines in the figure correspond to the predicted one and the data points are the values obtained for the modified CFNI concrete. The results indicate that the CFNI concrete shows higher flexural strength than the predicted values. Using the regression analysis, the relationship between the compressive strength and flexural strength of the CFNI concrete is obtained and is shown in Fig. 6d. The empirical equation derived is $F_r = 0.098 F_c^{1.07}$, with a coefficient of determination ($R^2$) value of 0.97, where, $F_r$ corresponds to the mean flexural strength in MPa and $F_c$ represents the mean compressive strength in MPa.

### Long term durability and anti-corrosive studies

**Rapid chloride penetration (RCPT) & water permeability test (WPT) results**

Fig. 7a shows the rapid chloride permeability test results on CC and CFNI concrete specimens aged 28 days and 365 days. For all the concrete specimens, the total charge continuously decreased with exposure in seawater as reported by other researchers (Joshaghani et al. 2020). As per ASTM C 1202, high, moderate and low chloride permeability correspond to charge values greater than 4000 coulombs, 2000-4000 coulombs and less than 2000 coulombs, respectively. Fig. 7a indicates that the charge passed for modified CFNI specimens after an age of 28 days was 303 Coulombs, indicating a very low chloride permeability, while for CC specimen, it was 2412 Coulombs. The RCPT values for CC concrete specimens further decreased to 1233 Coulombs after 365 days of exposure to seawater while that of CFNI specimens was 132 Coulombs, confirming its enhanced resistance against chloride ion penetration.

Fig. 7b shows the comparison of RCPT values obtained in this study with previously published works. These results show that the fly ash concrete blended with nanoparticles and inhibitor (CFNI) is superior in terms of RCPT values. This reduction in the chloride permeability can be attributed to pozzolanic activity of fly ash and the filler effect of nanoparticles which promotes the process of cement hydration and makes an impermeable concrete skin by occupying the voids and pores (Joshaghani et al. 2020). Further, the addition of corrosion inhibitors into concrete results in the production of complex compounds through pore refinement, which reduces the penetration of harmful chloride ions. Similar
improvement in RCPT values by 20% and 50% were reported by Shaikh et al. \cite{ShaikhSupit2014} in high volume fly ash concrete with addition of 1% CaCO$_3$ nanoparticles.

**Fig. 7c** shows the depth of penetration obtained from the water permeability test for CC and CFNI concrete specimens after 28 days of curing and 365 days of exposure in seawater. After 28 days, the average water penetration depth in CC specimens was ~ 120 mm while that in CFNI specimen was 15 mm. Our earlier studies also showed such a pore refinement after 28 days of curing in CFNI specimens and the density of minute gel pores was maximum in CFNI \cite{Harilaletal2019a}. This pore refinement is the cause for 87.5% reduction in water penetration depth in CFNI specimens compared to CC specimens after 28 days of curing. After 365 days of aging, the water penetration depth was 88.8% lower in the CFNI specimen, which is again promising for the use of CFNI in seawater applications.

With lower water permeability, the risk of ingress of harmful chemicals and deleterious ions such as chloride ions decreases \cite{Joshaghanietal2020}. Concrete with water penetration depths less than 30 mm under harsh exposure conditions are classified under the category of impermeable concrete \cite{Neville1995}. It can be observed from the permeability test that the incorporation of fly ash, nanoparticles, and inhibitor in concrete helped to reduce the depth of water penetration in OPC concrete. Incorporation of nanoparticles improves the overall porosity due to dilution effects and decreases the water penetration depth \cite{Irassar2009}. Heterogeneous nucleation of nanoparticles produces a large amount of calcium hydroxide crystals and C-S-H gel, which creates an obstacle for the free transport of water in the cement matrix \cite{Joshaghanietal2020}. Addition of inhibitor into concrete further enhances the formation of cementitious products through secondary hydration process, improving the porosity and reducing the pore connectivity in concrete.

These findings of the water permeability test were consistent with the corresponding RCPT results obtained after 28 and 365 days of aging in seawater. Thus, this study reveal that the incorporation of nanoparticles, along with fly ash, and inhibitor in concrete provides a high durability index with a low water permeability and low chloride penetration rate.

**Estimation of alkalinity and free chloride contents**

The normal pH range of the water phase in concrete is in the range of 12.5–13.2. During immersion in seawater, the alkalinity of concrete specimens decreases to less than 8.5 due to biofouling by microorganisms and attack of chlorides/sulfates in seawater, which results in the penetration of free CO$_2$ ions, chlorides and H$_2$S from seawater \cite{Kwonetal2017}. **Table 5** shows the average pH values of the concrete compositions after 28 days of curing and after 56, 90, 180 and 365 days of exposure to seawater.

The initial pH was 12.8 for the CC specimens. Though CC specimens have a large amount of CH due to the cement hydration (owing to a higher amount of cement available per unit volume in CC), the difference in pH for CC and CFNI concrete was insignificant (12.8 and 12.6, respectively). The addition of mineral admixtures like fly ash in concrete cause a drop in pH due to their pozzolanic activity. However, CFNI did not show such a drastic reduction, probably because of the addition of nanoparticles and inhibitor. After 365 days of exposure in seawater, pH values of CC and CFNI specimens were 11.5 and 11.2, respectively. The pH values of both the concrete compositions were above the recommended threshold limit of 9.5 for depassivation \cite{Hobbs1988}.

**Table 5.** pH values and free chloride contents of the concrete specimens with time after exposure to seawater up to a period of 365 days
| Type of concrete | pH | Free chloride contents (g/l) |
|-----------------|----|-----------------------------|
|                 | Initial | 56 days | 90 days | 180 days | 365 days | Initial | 56 days | 90 days | 180 days | 365 days |
| CC              | 12.8    | 12.6    | 12.3    | 11.9    | 11.5    | 0.032   | 0.082   | 0.147   | 0.676    | 1.022    |
| CFNI            | 12.6    | 12.3    | 12.1    | 11.7    | 11.2    | 0.021   | 0.042   | 0.073   | 0.222    | 0.311    |

The free chloride contents measured in both the concrete compositions during the exposure to seawater for 365 days are also tabulated in Table 5. After 365 days, CC specimens showed a free chloride content of 1.02 g/l compared to 0.311 g/l in CFNI specimens. Thus, the free chloride content for CFNI specimens is only 30% of that of CC concrete after 365 days of exposure. According to Seelem et al. (Selem et al. 2010), the resistance of a concrete system to chloride ingress is influenced by the permeability of concrete mixtures, which is controlled by the pore size distribution, and the capacity of the concrete mixture to hold the chlorides in a tightly bound chloride complex known as Friedel’s salt. Very high resistance against the ingress of chloride ions from seawater by CFNI concrete was in agreement with the RCPT and water permeability results. The pozzolanic reaction of the SCMs greatly reduced the permeability of the concrete, resulting in a lower chloride ion ingestion than OPC concrete (Kwon et al. 2017).

**Carbonation depth profiling**

**Fig. 8a** shows the photograph of a typical fractured test specimen, sprayed with 1% phenolphthalein solution to determine the carbonation depth in an aggressive carbonation chamber, inland atmosphere and marine atmosphere environments. The carbonation depth in the specimens is calculated by taking the average of the colourless area. **Fig. 8b-d** gives the average carbonation depths of both concrete compositions measured after 56, 90, 180 and 365 days of exposure in the three environments. The carbonation depth is shown to increase continuously with the period of exposure in all three environments. This is attributed to the increasing amount of carbon dioxide diffusion through the interconnected capillary pores in the concrete specimens, which allows an easy permeable path for diffusion. Carbonation test results suggest that CC specimens display negligible carbonation depth in all three environments. After 365 days of exposure in the carbonation chamber, seashore and inland atmospheres, the carbonation depth in CFNI specimens were found to be 10.24 mm, 5.15 mm and 4.67 mm, respectively (Fig. 8b, 8c and 8d).

In OPC systems, the resistance to CO₂ penetration is generally good because of the high Portlandite (CH) content. On the other hand, SCM-based concretes have a lower CH content and, hence exhibits a lower carbonation tolerance because of the prolonged pozzolanic reactions. Due to the lower amount of CH in SCM-based systems, CO₂ is able to carbonate the C-S-H faster, and hence accelerates the carbonation process (Pillai et al. 2020). Singh et al. (Singh et al. 2019) observed that concrete containing 40 wt. % Class F fly ash exhibits higher carbonation depths of 12.1 mm after 90 days of exposure in the open environment compared with concrete having only OPC as the binder due to the consumption of CH during the pozzolanic reaction. A reduction in the carbonation depth is observed in fly ash based concrete when nanoparticles are introduced. The carbonation depth reduced by 51% in fly ash concrete upon addition of nanoparticles and inhibitors (Harilal et al. 2019a). In the present study, the carbonation depth reduced to 4.67 mm, 3.21 mm and 2.04 mm after 90 days in accelerated conditions, normal atmospheric conditions and the marine environment, respectively. The lower carbonation depth is attributed to the dense and refined microstructure of nanoparticles and inhibitor incorporated concrete.

The carbonation depth and the time of exposure were used to determine the rate of carbonation in the specimens and the values are given in Table 5. The carbonation rates of CFNI were 1.42, 0.71 and 0.64 mm in carbonation chamber, seashore and inland atmosphere, respectively.
Table 5. Carbonation rate measured in the specimens with time for a period of 365 days under three different atmospheres

| Type of concrete | Carbonation rate (mm) | Carbonation chamber | Seashore | Atmosphere |
|------------------|-----------------------|---------------------|----------|------------|
|                  | 56 days | 90 days | 180 days | 365 days | 56 days | 90 days | 180 days | 365 days | 56 days | 90 days | 180 days | 365 days |
| CC               |         |         |          |          |         |         |          |          |         |         |          |          |
| CFNI             | 0.96    | 1.29    | 1.46     | 1.42     | 0.54    | 0.62    | 0.75     | 0.71     | 0.73    | 0.89    | 0.78     | 0.64     |

The decrease observed in the carbonation rate with the age of exposure was also in agreement with RILEM CPC-18 (CPC 1988). A study by Pillai et al. (Pillai et al. 2020) shows that even though concrete blended with SCMs shows a higher carbonation, it may not directly contribute to reinforcement corrosion. The propagation of corrosion, however, will still rely on the availability of moisture and oxygen, as well as the resistivity of the medium.

**Chemical and morphological characterization of the specimens**

**TGA/DTA analysis of the concrete specimens**

The DTG curves show endothermic peaks as shown in Fig. 9a. Here, the mass loss between 105 and 420°C is attributed to the dehydration of C-S-H/ettringite (Aft), between 420 and 540 °C is due to the dehydration of CH, and between 720 and 950°C is attributed to the decarbonation of CaCO$_3$ (Shaikh & Supit 2014). The DTG curves of CC and CFNI after 28 days of curing showed that the CH dehydration peak of CFNI is smaller than that of CC, indicating the consumption of CH through the pozzolanic reaction. The C-S-H dehydration peak was higher in CFNI concrete after 365 days of exposure to seawater, indicating the significant amount of C-S-H present in CFNI. The TGA curve in the concrete powder showed four standard temperature regimes during heating between 105 and 1000°C, leading to three endothermic reactions involving the hydration products. The TGA curve shows first decay up to 105 °C, which is due to the removal of moisture and free water from the concrete specimens. At temperatures ranging from 105 to 400°C, 400-500°C, and 600-800°C, weight loss due to endothermic reactions such as dehydration of chemically bonded water in hydrates, dehydroxylation of CH, and decomposition of CaCO$_3$ resulting from the clinker and carbonation of concrete was observed, respectively (Shaikh & Supit 2015, Singh et al. 2019). Thus, this analysis enables the estimation of C-S-H, CH and CaCO$_3$ contents from the weight losses.

Fig. 9b shows the weight loss percentage corresponding to the three temperature regimes in both CC and CFNI specimens at the age of 28 days and after 365 days of exposure to seawater. After 28 days of curing, the weight loss due to dehydration of C-S-H, decomposition of portlandite (CH) and CaCO$_3$ are 3.5%, 1.7% and 2.1%, respectively in CC specimens, while the corresponding values in CFNI specimens are 3.6%, 1.3% and 3.1 %, respectively. After 365 days of immersion in seawater, the weight loss corresponding to dehydration of C-S-H, decomposition of portlandite (CH) and CaCO$_3$ are 5.7%, 1.1% and 2.8%, respectively in CC specimens and 7.5%, 0.9% and 4.5%, respectively in CFNI.

Fig. 9c shows the estimated C-S-H, portlandite and CaCO$_3$ content calculated from the TGA curves. After 28 days of curing, the C-S-H content of CFNI specimens was ~17 % higher than that of CC, and 61 % after 365 days of immersion in seawater. This further confirm that the addition of fly ash, nanoparticles, and inhibitor increases pozzolanic activity and secondary hydration reactions. On the other hand, after 365 days of seawater exposure, the CH content in CFNI is decreased by 10.9 %, which is expected to be due to the consumption of CH during the pozzolanic reaction, which was in agreement with the pH data. The CaCO$_3$ content in CFNI specimen was found to be 7.9 wt. %.
After 365 days of exposure, the weight loss due to the formation of gypsum and ettringite in the temperature regimes of 80-100°C and 110-130°C (Vedalakshmi et al. 2008), were calculated and is shown in Fig. 9d. The weight loss due to the formation of gypsum is ~ 1 % in CFNI specimens and ~ 3% in CC specimens. The weight loss corresponding to the formation of ettringite was estimated to be 1.4% and 0.25%, respectively in CC and CFNI specimens. The combined weight loss in CC specimens was 4.48 times higher due to the formation of ettringite. The presence of more amount of gypsum and ettringite (CC specimens) can cause expansion, cohesion decrease and cracking, which lead to premature failure of concrete structures. These findings suggest that the addition of fly ash, nanoparticles and inhibitor can reduce the formation of these deleterious phases and provide high mechanical strength and chemical durability.

**X-ray Diffraction analysis**

Fig. S2a and Fig. S2b show the XRD spectra of CC and CFNI concrete specimens after 28 days of curing in fresh water and 365 days of immersion in seawater. After 28 days of curing in freshwater, the XRD spectra of both CC and CFNI specimens showed the diffraction peaks corresponding to the hydration products of quartz and C-S-H. The peaks corresponding to quartz were found at 2θ values of 24.03°, 31.04°, 39.75°, 50.13° and 59.09° (JCPDS 01-072-1088) in both CC and CFNI specimens. The peaks of C-S-H were found at 2θ values of 32.56° and 71.04° (JCPDS 01-089-7639). The peaks corresponding to portlandite were found at 2θ values of 21.25°, 38.23° and 55.21° (Long et al. 2017). A single peak of gypsum was found at 2θ value of 12.70° in the CC specimen. The peaks of portlandite were found to be less in CFNI specimens owing to the pozzolanic reaction of fly ash resulting in the consumption of portlandite. After 365 days of exposure to seawater, the intensity of quartz peak was found to decrease in CC specimen, but the intensity remained unchanged in CFNI specimens. The high amount of quartz enhances the reaction rate of secondary hydration resulting in the production of more C-S-H gels, which significantly reduces the permeability and pore structure of concrete (Kwon et al. 2017).

The peaks of low intensity corresponding to C-S-H were found in CC specimens, indicating a comparatively lower strength. High intensity peaks of C-S-H, found in CFNI specimens, was in agreement with the mechanical test results and TGA analysis. The peaks of portlandite were seen to be more in CC specimens, which was also evident from the enhanced alkalinity in CC concrete. The number of predominant peaks corresponding to gypsum was also found to be higher in CC specimens, indicating more deterioration in these specimens after exposure to seawater. This could be the reason for the comparatively lower compressive strength of CC concrete.

**Surface morphology of exposed specimens**

The scanning electron microscopy (SEM) investigations were carried out on the CC and CFNI concrete specimens at the age of 28 days and after 365 days of exposure to seawater. Fig. 10 shows the SEM images of the specimens showing the surface morphologies. After an aging of 28 days, both CC and CFNI specimens showed similar surface morphology. Significant amount of CH crystals and C-S-H gels were found on the surfaces of both specimens (Fig. 10a and Fig. 10c). After 365 days of exposure in seawater, the surface of CC specimens revealed cracks and needle-shaped crystals of ettringite (Fig. 10b). The presence of colloidal C-S-H gels was also observed over the surface of CC specimens (Liu et al. 2019). CFNI specimen showed a distinctive morphology with more amount of colloidal C-S-H gel formation than CC. Moreover, the surface of CFNI specimens was devoid of cracks, voids or needle shaped crystals of ettringite even after exposure in seawater for 365 days (Fig. 10d). It is widely reported that gypsum and other forms of sulfate compounds can react with the calcium aluminate phase and form ettringite (Uthaman et al. 2018). The more amount of ettringite and gypsum in CC gives rise to a lower mechanical strength and a higher chloride penetration. The ettringite (white crystal needles) present in concrete (CC) can produce cracks and reduce the compressive strength.

A schematic showing the potential benefits of CFNI concrete in comparison with conventional OPC concrete is shown in Fig. 11. By using 40 wt. % fly ash, the carbon footprint can be considerably decreased. Also the drawbacks of SCM added
concrete like low early age strength and high carbonation rate can be overcome by the addition of nanoparticles and inhibitor where high strength both in the early age and post seawater exposure, along with drastic reduction in the water and chloride permeability, and biofouling can be achieved. This reduction in the chloride and water permeability and higher strength is attributed to the pozzolanic activity of fly ash and the filler effect of nanoparticles that augment the cement hydration process and render an impermeable skin by filling the voids and pores (Joshaghani et al. 2020). The inhibitor acts as a water reducing mixture and produce complex compounds, which further reduces the penetration of harmful chloride ions by filling pores.

Microstructural characterization confirmed an amount of enhanced C-S-H gel and denser microstructure in CFNI specimens. The formation of additional C-S-H gel is favoured by the accelerated hydration reaction of nano-CaCO$_3$ with calcium hydroxide and tricalcium silicate/tricalcium aluminate that produces a denser microstructure. The heterogeneous nucleation of nanoparticles also enhance C-S-H gel formation which obstruct the free transport of water in the cement matrix (Joshaghani et al. 2020). The addition of an inhibitor to concrete further enhances the formation of cementitious products through the secondary hydration process, improves porosity and decreases concrete pore connectivity. As the water penetration depth of CFNI was less than 30 mm in sea water exposure conditions, it comes under the category of impermeable concrete (Neville 1995). Thus, the results of this study confirm the superior properties of CFNI concrete, which is ideal for long term applications in aggressive marine environments.

Conclusions

A real-time long-term study was carried out to investigate the anti-fouling, durability and strength characteristics of a blended cement concrete with 56 wt. % OPC, 40 wt. % fly ash, 2 wt. % nano-CaCO$_3$ and nano-TiO$_2$ and 2 wt. % sodium nitrite inhibitor solution under natural marine exposure conditions. The concrete samples were immersed in natural seawater for the period of 1 year. Based on the results, the following conclusions were made:

1. The CFNI specimens showed an enhanced anti-bacterial activity with a four-order reduction in the total viability count and ATP (Adenosine triphosphate) concentration.
2. The CFNI concrete achieved almost the same compressive strength of OPC concrete after the exposure, whereas split tensile strength and flexural strength increased dramatically with exposure time for CFNI specimens due to the refined pore structure and enhanced C-S-H gel formation.
3. The CFNI concrete showed a lower ingress of chloride ions than OPC concrete indicated by the significantly lower chloride penetration value due to the pozzolanic reaction of the SCMs, filler effect of nanoparticles, low w/c ratio, and formation of favorable complex compounds. The free chloride content of CFNI specimens substantially due to the low permeability.
4. The average depth of water penetration, measured using water permeability tests, in CFNI specimens was significantly lower due to reduced permeability and pore connectivity. Also, the depth of carbonation and its rate in CFNI specimens was lower compared to concrete with fly ash alone.
5. The alkalinity of CFNI concrete was relatively equal to the OPC concrete and was above the recommended threshold limit for depassivation.
6. Thermogravimetric analysis revealed that the addition of fly ash, nanoparticles, and inhibitors resulted in an increased C-S-H gel formation in CFNI specimens due to the higher pozzolanic activity and secondary hydration reactions.
7. FESEM images of CC specimens showed cracks in the form of needle-shaped crystals due to the ettringite formation. CFNI specimen showed a distinctive morphology with a large amount of colloidal C-S-H, without cracks, voids, or ettringite phase.

Our findings suggest that CFNI concrete is technically viable for marine environmental exposures due to its enhanced long-term anti-fouling, mechanical and durability properties.
Declarations

Ethics approval and consent to participate
Not applicable

Consent for publication
Not applicable

Availability of data and materials
The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Conflict of interest/Competing Interests
The authors have no conflicts of interest to declare that are relevant to the content of this article.

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Authors' contributions
MH: conceptualization, methodology, experimental part, validation, writing- Original draft preparation; AB: experimental, Writing – review & editing; RPG: Writing – review & editing, Supervision; SKA: Writing – review & editing, Supervision; JP: Writing – review & editing, Supervision.

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**Figures**
Figure 1

SEM images of (a) fly ash (b) nano-CaCO3, (c) nano-TiO2 and (d) X-ray diffractograms of fly ash, nano-CaCO3 and nano-TiO2
Figure 2

Seasonal variations in the (a) average temperature (b) average RH (%) and (c) average rainfall (mm) during the exposure period of the specimens in seawater for 365 days.
Figure 3

Photographic images of biofouling observed over the concrete cube test specimens with time during 365 days of exposure in natural seawater.
Figure 4

PCR-DGGE electrophoretographs of (a) V3 and (b) V8 regions of biofilms collected from concrete specimens exposed for different durations. M - Marker, 1 - CC56d; 2 - CFNI56d; 3 - CC90d; 4 - CFNI90d; 5 - CC180d; 6 - CFNI180d; 7 - CC365d and 8 - CFNI365d
Figure 5

Variation in the (a) compressive strength (b) split tensile strength and (c) flexural strength with age in the two concrete mixes up to an exposure period of 365 days in natural seawater.
Figure 6

(a, c) Comparison of split tensile strength, flexural strength and compressive strength of CFNI with literatures data (b) fitted data of the split tensile strength vs. compressive strength for CFNI (d) fitted data of flexural strength vs. compressive strength for CFNI.
Figure 7

(a) Chloride ion permeability resistance of CC and CFNI concrete specimens during 365 days of exposure in natural seawater (b) comparison of the RCPT values after 365 days with previous studies (c) comparison of depth of penetration observed in water permeability test for concrete specimens at the age of 28 days and after 365 days of exposure in seawater.
Figure 8

(a) Photographs of the fractured test specimens, sprayed with the phenolphthalein indicator to measure the depth of carbonation. The carbonated region in white colour is shown by the arrows; Carbonation depth of specimens in (b) carbonation chamber (c) marine environment and (d) normal atmosphere. The carbonation depth was negligible in CC specimens at 56 days.
Figure 9

(a) DTG plot of the concrete specimens at 28 days and 365 days (b, c) weight loss and the estimated content of C-S-H, portlandite and CaCO3 in the concrete specimens at the age of 28 days and after 365 days of exposure in seawater (d) weight loss due to gypsum and ettringite formation in both specimens after 365 days.
Figure 10

SEM images of the concrete specimens after 28 days of aging and after 365 days of aging in seawater (a) CC - 28 days (b) CC – 365 days (c) CFNI – 28 days (d) CFNI – 365 days. The formation of cracks and ettringite are observed in the CC specimens after 365 days of exposure.

Figure 11
Schematic showing the potential benefits of CFNI concrete in comparison with conventional concrete

**Supplementary Files**

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