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Surface Modification of Fly Ash Concrete Through Nanophase Incorporation for Enhanced Chemical Deterioration Resistance

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Abstract

The global warming gas, CO_2, is liberated when clay and limestone are crumbled for the production of cement. About 8–10% of the universal CO_2 emissions are emitting from the cement factories. With concerns arising over environmental issues associated with cement usage, it is the need of the hour to reduce its consumption. Fly ash, the waste material from thermal power plants, is a widely used supplementary cementitious material that extends the life of the concrete structures. The intervening of nanotechnology into construction industry has provided wider opportunities to better the performance of concrete in rigorous conditions, especially acids and alkali environment. This work endeavours to study the effect of surface-modified fly ash concrete through the addition of nanoparticles against sulphate attack and calcium leaching. Nanophase modification was performed by integrating nano-TiO_2 and $CaCO_3$ for enhanced durability and corrosion resistance. Four types of concrete mix, namely fly ash concrete (FA), FA with 2% TiO_2 nanoparticles (FAT), FA with 2% $CaCO_3$ nanoparticles and FA with 2% TiO_2:$CaCO_3$ (FATC) nanoparticles, were designed and casted as cylindrical concrete blocks. The specimens were immersed in 1% sulphuric acid solution and sea water to study the resistance of concrete against sulphate attack and calcium leaching, respectively. Results showed that nanophase modification of fly ash concrete improved the resistance to sulphuric acid attack and calcium leaching. Among the nanophase-modified specimens, FAT and FATC specimens showed superior performance.

Keywords Concrete · Surface modification · Nanoparticles · Deterioration · Sulphate attack · Calcium leaching

1 Introduction

Concrete, the widely used construction material, is a coalescence of cement, water and aggregates. Cement industries account for about 10% of the global CO_2 emissions with 0.9 tons of CO_2 being emitted per ton of cement production. It has been estimated that every person on the planet utilizes more than 3 tons of concrete on an average per year. Thus, it becomes a major concern which requires eco-cordial solutions [1, 2]. The incorporation of waste materials into concrete paved the way to the development of green concrete, which eventually reduced the cement content and thus CO_2 emission. The need for reduction in CO_2 emissions during the cement-making process encouraged the search for supplementary cementitious material (SCM) compounds such as fly ash, rice husk ash, slag that can be blended into concrete. In recent years, utilization of fly ash as a cement replacement component has gained popularity owing to several economical and environmental reasons [3]. Fly ash is utilized in concrete as a cement replacement to impart the durability and strength by pozzolanic and filler effects [4]. It is also cheap, and one can get the desired properties in concrete by utilizing large volume (> 40%) of fly ash [5, 6]. The spherical-shaped fly ash particles react with calcium hydroxide and produce hydration products that vigorously decrease the concrete porosity, thereby making the concrete structures less permeable to truculent chemicals [7]. The minute pore size of the concrete leads to a minor efficacious permeability for chloride ions or other components [8]. A holistic study

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was conducted by Vishwakarma et al. [9] to evaluate fly ash concrete properties, its durability and biodeterioration characteristics in comparison with normal concrete. In their study, it was proven that fly ash concrete emerged superior with excellent strength and durability. However, they too reported some drawbacks like higher carbonation depth, calcium leaching and slow rate of hydration [9]. Several researchers [10–19] have incorporated nanoparticles of SiO_2, TiO_2, Fe_2O_3, Al_2O_3 and $CaCO_3$ to enhance hydration, overall strength, durability, antibacterial activity, etc. Thus, in this present study, it has been decided to introduce TiO_2 and $CaCO_3$ nanoparticles concurrently to surmount the shortfalls associated with fly ash concrete. Generally, fly ash concrete is reported to have good resistance against sulphate attack [20], and to the contrary, some studies also indicate that fly ash adversely affects the leaching property [21]. Hence, this research is an attempt to fabricate an innovative surface-modified and skin-thickened fly ash concrete through the addition of nanoparticles. This present study specifically looks into the enhancement of resistance to sulphuric acid attack and calcium leaching of newly developed, nanophase-modified fly ash concrete.

2 Materials and Methods

2.1 Casting of Concrete

Ordinary Portland Cement (OPC) 43 grade confirming to IS 8112-1989, siliceous type fly ash confirming to IS 3812 (Part-I)-2003 standards, crushed sand as fine aggregate with a maximum size of 4.75 mm and fineness modulus of 2.52 and black granite as coarse aggregate with maximum size of 20 and 12.5 mm conforming to IS 383 were used for the fabrication of concrete specimens. The mix proportion of cement/water/sand/coarse aggregate was 1:0.44:1.6:2.907. Sulfonated naphthalene formaldehyde (SNF)—Supaplast HP [S] with high water retarding capability, was used as the admixture confirming to ASTM C-494 type G standards.

Four different types of cylindrical concrete blocks of 100 × 200 mm such as fly ash concrete with 40 wt% replacement of OPC (FA), FA concrete with 2 wt% replacement of OPC by TiO_2 (FAT), 2 wt% replacement of OPC by $CaCO_3$ (FAC) and 2 wt% replacement of OPC by both TiO_2 and $CaCO_3$ (FATC) were cast [22]. After 24 h of casting, all blocks were demolded and cured for 28 days in freshwater in laboratory atmosphere. After curing, the concrete blocks were cut into pieces of 100 × 10 mm size by using concrete cutting machine (Bench Saw concrete cutting machine, Darien Electric Madras). The specimens were polished with 80 grit silicon carbide polishing paper, cleaned and dried for 24 h at room temperature. The parameters like thickness, diameter and weight of the specimens were measured. The specimens were moistened with Millipore water, and pH was measured before exposure.

2.2 Exposure Studies

A duplicate set of each specimen (FA, FAT, FAC and FATC) was exposed in 1000 ml of 1% H_2SO_4 solution (pH range 1–3) in glass jar and withdrawn at regular intervals for post-exposure analysis.

A duplicate set of each specimen (FA, FAT, FAC and FATC) was separately immersed in a glass jar containing sea water from Kalpakkam coast (pH—8.1, chloride—18,981 ppm, salinity—35 ppm and sulphate—2650 ppm) [23] and withdrawn at regular intervals for post-exposure analysis.

2.3 Post-Exposure Studies

2.3.1 Surface pH Measurement Study

pH is an important factor for concrete, as reduction in pH results in its increased deterioration. The surface pH of four different concrete specimens (FA, FAT, FAC and FATC) was determined using flat surface electrode pH meter (SENTIX-3110) before and after exposure in sea water. The pH was measured on five different places of the concrete specimens to get an average value on the total surface. The pH of unexposed concrete specimens was compared with sulphuric acid and sea water-exposed specimens to understand the difference. The reduction of pH is an indicator of the rate of degradation.

2.3.2 Dimensional Measurement Study

The reduction in dimension is one of the vital degradation parameters which quantitatively refer to the degradation of concrete. The dimensional parameters like thickness and diameter were assessed after exposure in sulphuric acid and sea water using Mitutoyo Digimatic Vernier caliper, and the values were recorded.

2.3.3 Weight Loss Study

To investigate the effect of aggressive chemical environment over fly ash and nanophase-modified FA concrete specimens, the weight loss study was performed. Weight of concrete specimens was measured by a digital weighing balance (ATICO-ISO 9001-2008 certified) before and after exposure in both environments. The specimens were taken, washed and dried for 24 h for constant weight gain [24].

By comparing the weight of concrete specimens before and after exposure, weight loss percentage was calculated.

Higher loss in weight refers to enhanced degradation of concrete due to exposure in aggressive environment.

2.3.4 Estimation of Calcium Content by Titration Method

In order to measure the calcium content, concrete specimens was exposed in sea water and withdrawn after 15 and 30 days for analysis. As per IS 3025 (Part 21): 1983 standards, the total hardness of the sea water was measured, using which calcium content was calculated. This EDTA titration method is based on the ability of ethylene diamine tetra acetic acid or its disodium salt to form stable complexes with calcium and magnesium ions. Twenty-five millilitres of sea water was pipette out to a well-cleaned conical flask. One millilitre of buffer solution and a pinch of EBT indicator were added. The end point was identified with the change in colour of the mixture to sky blue.

2.4 Microstructural Characterization Studies

2.4.1 X-ray Diffraction Analysis

X-ray diffraction by powder method was adopted in this present study on the concrete specimens. The diffraction patterns of concrete specimens exposed in sulphuric acid and sea water were examined using Philips PW 1050 X-ray diffractometer with CuKα radiation ($\lambda = 1.5418$ Å) and scattering angle (2θ) between 10° and 100°. The patterns were compared with standard JCPDS database, and the unknown crystalline phases were identified.

2.4.2 Scanning Electron Microscope (FESEM)

The morphology of concrete specimens exposed in sulphuric acid and sea water was characterized using scanning electron microscopy (Nano-eye Desktop Mini-SEM, Korea) at an acceleration voltage of 20 kV. In order to obtain thermal conduction, the concrete specimens were coated with gold particles using Magnetron Coating MCM-100. The elemental mapping of the concrete specimens exposed to sea water was performed using energy-dispersive X-ray spectroscopy (EDX).

3 Results and Discussion

3.1 Sulphuric Acid Attack Resistance Study

The loss in thickness, diameter and weight of FA and nanophase-modified FA (FAT, FAC and FATC) concrete specimens immersed in 1% sulphuric acid is given in Table 1. The minimal reduction in thickness was observed for nanophase-modified FA concrete specimens in comparison with FA concrete specimens. Among all the nanophase-modified FA concrete specimens, FAT (0.31 ± 0.28 mm) followed by FATC (0.43 ± 0.18 mm) showed least reduction in thickness. Loss in diameter was also observed to be very low for FAT (0.64 ± 0.82 mm) followed by FATC (0.71 ± 0.09). The weight loss percentage of unexposed and sulphuric acid-exposed concrete specimens was calculated. The weight loss percentage of FA (0.7 ± 0.21%) concrete was significantly more compared to nanophase-modified FA concrete specimens. The FAT (0.17 ± 0.11%) closely followed by FATC (0.2 ± 0.07) showed minimal weight loss percentage indicating least deterioration.

This clearly indicates that nanophase-modified FA concrete specimens exhibit more resistance against sulphuric acid environment. FAT followed by FATC displayed enhanced resistance among all the nanophase-modified FA concrete specimens. Several researchers have demonstrated the beneficial effects of nanoparticles. These may include (1) acting as nanosized fillers and leading to a denser and impermeable microstructure and (2) promoting nucleation sites for the C-S-H formation [25]. The parallel packing of more C-S-H in concrete results in less permeability against vulnerable acids and subsequent improvement in strength, serviceability and aesthetic appearance of the structure [26].

3.1.1 Microstructural Characterization for 1% Sulphuric Acid-Exposed Concrete

Figure 1a shows the XRD pattern of 28-day-cured concrete specimens. The peaks of SiO_2 at 2θ of 21.7°, 26.6° and 50.1° (JCPDS 01-072-1088), calcium silicate hydrate at 2θ of 28.1°, 35.8, 40.5, 60.3° and 68.1° (JCPDS 01-089-7639) and calcium aluminium silicate at 2θ of 24.1° and 54.1° (JCPDS 01-086-0174) were observed in all the four types of 28-day-cured concrete specimens.

Table 1 Deterioration measures of concrete specimens exposed in 1% sulphuric acid solution

Specimen type	Loss in thickness (mm)	Loss in diameter (mm)	Loss in weight (%)
FA	1.39 ± 0.45	0.905 ± 0.32	0.7 ± 0.23
FAT	0.31 ± 0.28	0.64 ± 0.11	0.17 ± 0.11
FAC	0.97 ± 0.16	0.825 ± 0.27	0.5 ± 0.19
FATC	0.43 ± 0.18	0.71 ± 0.09	0.2 ± 0.07

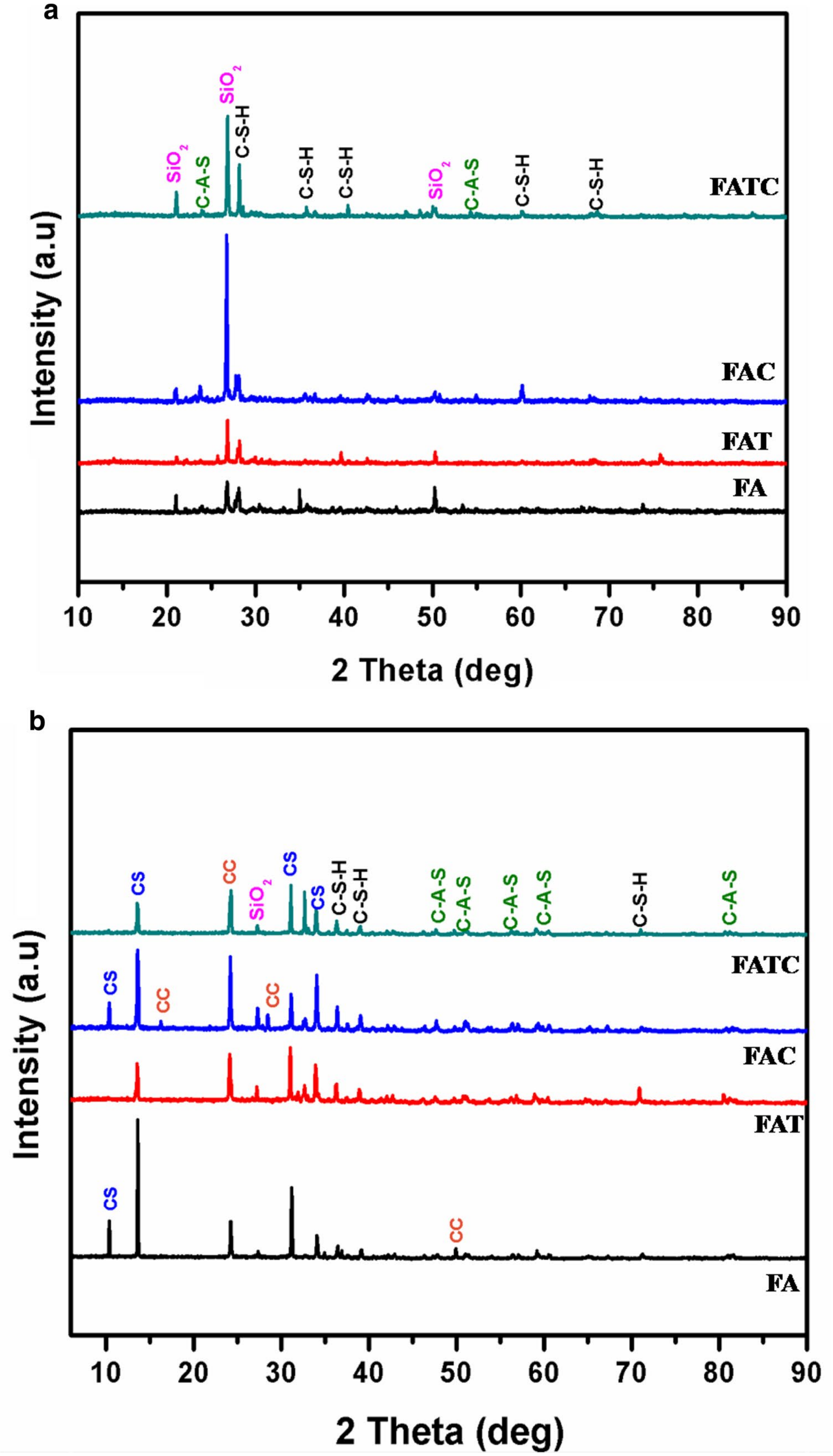

Fig. 1 **a** XRD pattern of 28-day-cured (unexposed) concrete. **b** XRD pattern of concrete specimens exposed in 1% sulphuric acid for 1 month. SiO_2—silicon dioxide, CC—calcium carbonate, C-A-S—calcium aluminium silicate, C-S-H—calcium silicate hydrate, CS—calcium sulphate

Figure 1b shows the XRD pattern of 1-month sulphuric acid-exposed concrete specimens. XRD patterns showed the presence of both calcium sulphate (later formed as ettringite) and calcium carbonate which are known to be corrosion products. More number of calcium carbonate peaks at 2θ of 16.4°, 24.2°, 28.7° and 49.97° (JCPDS 00-037-1496) and high intensity peaks of ettringite were found on FA followed by FAC concrete specimens at 2θ of 10.4°, 13.7°, 31.1° and 34.0° (JCPDS 00-038-0701). Using XRD characterization, Ukrainczyk et al. [27] have identified peaks of ettringite and calcium carbonate to ascertain environmental degradation of concrete structures. However, in the FAT and FATC specimens only minor intensity peaks of ettringite and calcium carbonate were found indicating a delay in ettringite formation. Thus, FAT and FATC specimens showed more resistance against sulphuric acid attack. According to Mori et al. [28], ettringite formation is associated with volume expansion leading to cracking of concrete structures. In addition to physical expansion and cracking, ettringite formation is also reported to reduce concrete strength [29, 30]. During acid attack, sulphate reacts with anhydrous particles of cement paste leading to ettringite and gypsum formation. However, Basista and Weglewski [31] confirm that ettringite formation clearly indicates sulphate attack.

FESEM images of 28-day-cured concrete specimen were compared with 1-month sea water-exposed concrete specimens. Figure 2 shows FESEM images of 28-day-cured concrete specimens. The morphology of nanophase-modified FA concrete specimens showed more hydration products compared to fly ash concrete. Among all the specimens, SEM images of FAC had higher amount of hydration products. Figure 3 shows the FESEM images of concrete specimens exposed to sulphuric acid for 1 month. The images of FA concrete showed high concentration of stacked flat crystals of calcium sulphate (gypsum) [32], which leads to the formation of ettringite that can initiate the cracking of the concrete [33]. The surface morphology of nanophase-modified FA concrete specimens showed lesser concentration of calcium sulphate crystals when compared to FA concrete. However, FATC concrete surface showed complete absence of calcium sulphate crystals formation indicating least degradation.

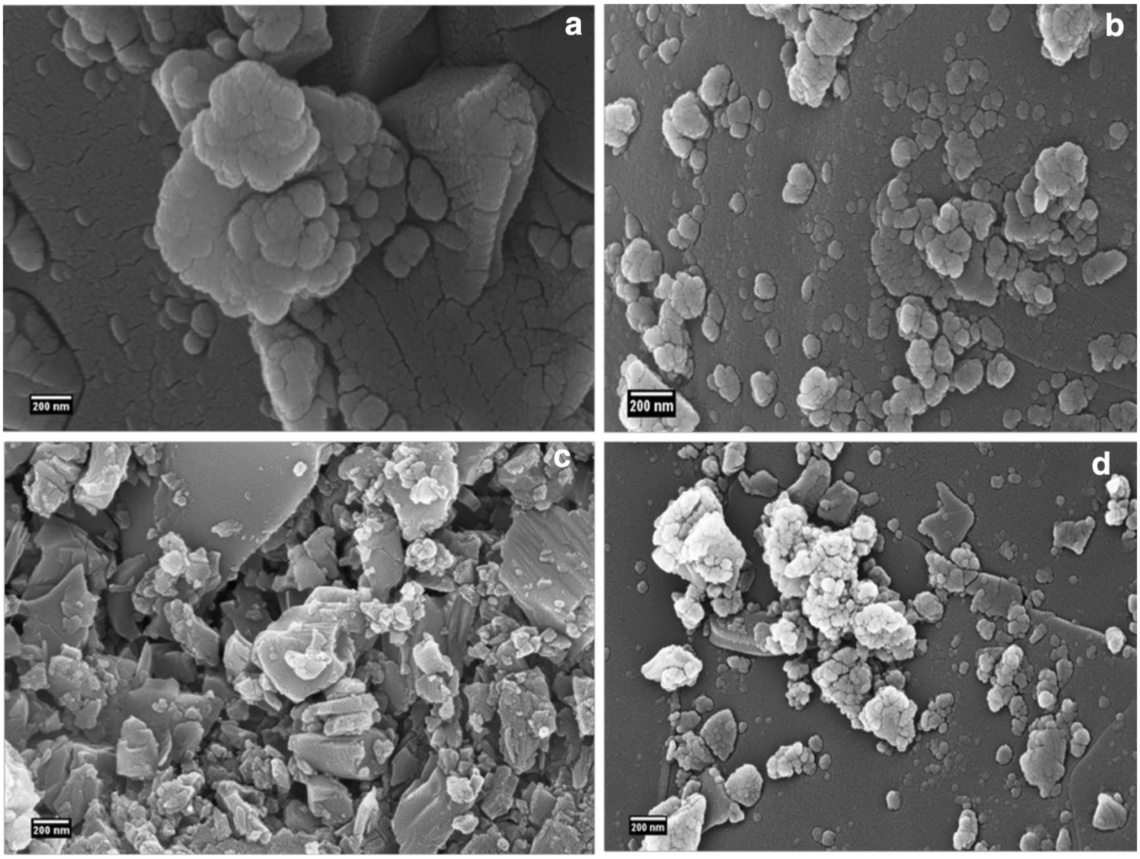

Fig. 2 FESEM images of 28-day-cured (unexposed) concrete specimens. **a** FA, **b** FAT, **c** FAC, **d** FATC

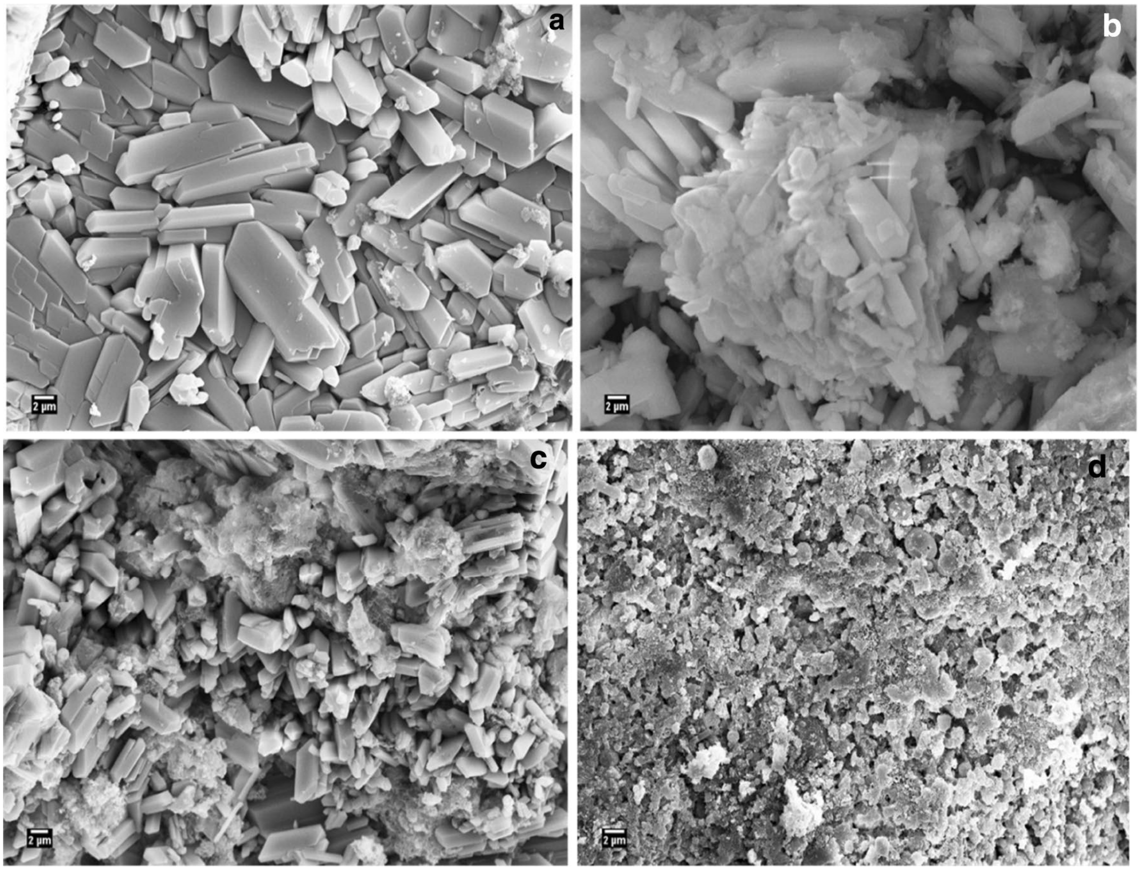

Fig. 3 FESEM images of concrete specimens exposed in 1% sulphuric acid for 1 month. **a** FA, **b** FAT, **c** FAC, **d** FATC

Table 2 Surface pH of concrete specimens exposed in sea water

Specimen type	Unexposed (28-day-cured)	1 month
Fly ash (FA)	8.6	7.55
FA with TiO_2 (FAT)	8.67	7.88
FA with $CaCO_3$ (FAC)	8.83	7.61
FA with TiO_2 and $CaCO_3$ (FATC)	8.62	7.54

Table 4 Calcium content of sea water used for the exposure of concrete specimens

Calcium content (mg/l)	
Marking	After 30 days
Sea water	763.4
FA	920.8
FAT	888.99
FAC	1085.38
FATC	805.6

3.2 Calcium Leaching Resistance Study

The surface pH measurement, reduction in dimensions and weight loss studies were carried out before and after exposure in sea water, and the values are tabulated. Degradation in pH values is an indicator of the resistance offered by the concrete specimens against calcium leaching. It can be clearly understood from Table 2 that surface pH decreased with time for all the specimens. FAT exhibited

Table 3 Deterioration measures of concrete specimens exposed in sea water

Specimen type	Loss in thickness (in mm)	Loss in diameter (in mm)	Loss in weight (%)
FA	2.10 ± 0.05	2.93 ± 0.51	2.5 ± 0.5
FAT	0.085 ± 0.065	0.24 ± 0.48	0.75 ± 0.25
FAC	0.63 ± 0.025	0.190 ± 0.295	2.25 ± 0.75
FATC	0.015 ± 0.005	0.39 ± 0.26	0.5 ± 0.2

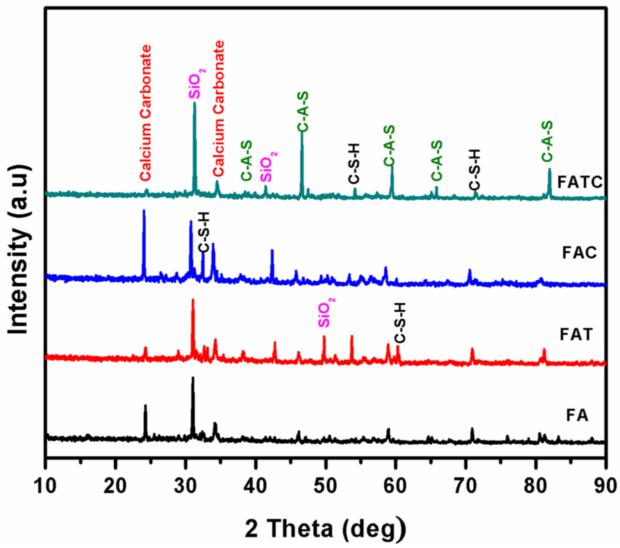

Fig. 4 XRD image of concrete specimens exposed in sea water for 1 month. SiO_2—silicon dioxide, C-A-S—calcium aluminium silicate, C-S-H—calcium silicate hydrate

a comparatively small degradation in pH value even after 1 month of exposure in sea water. However, there was no significant noticeable difference in the pH on all the specimens.

Table 3 shows the reduction in thickness and diameter of sea water-exposed concrete specimens. It is evident from the table that there is an appreciable decrease in the diameter and thickness after 1-month exposure for FA specimens. However, there is a minimal reduction in diameter and thickness for nanophase-modified specimens even after 1 month of exposure. FAT and FATC showed least decrement in dimensions among nanophase-modified FA concrete specimens. FA and FAC specimens showed higher weight loss compared to FAT and FATC specimens.

Table 4 shows the calcium content present in the sea water after the 30-day exposure of concrete specimens. The calcium content of sea water was about 763.4 mg/l. After exposure, the calcium content was found more on FAC and FA concrete specimens than on FAT and FATC concrete specimens. Among all the specimens, FATC was found to have least calcium content which is leached out from the specimen indicating more resistance against calcium leaching.

Earlier studies had shown that 40 wt% fly ash additions affect the total leaching depth despite having a beneficial influence on the porosity and compressive strength [33]. In this study, FA concrete showed slightly higher pH reduction and loss in thickness, diameter and weight compared

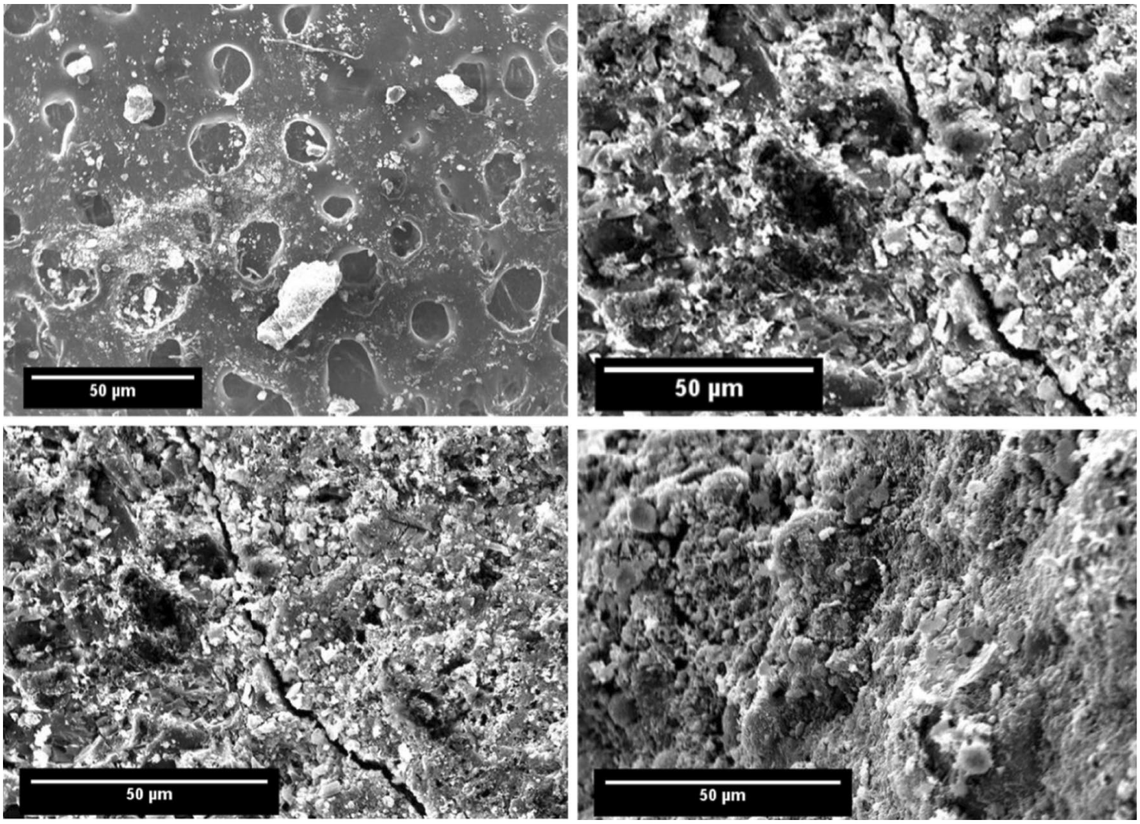

Fig. 5 SEM images of concrete specimens exposed in sea water for 1 month. **a** FA, **b** FAT, **c** FAC, **d** FATC

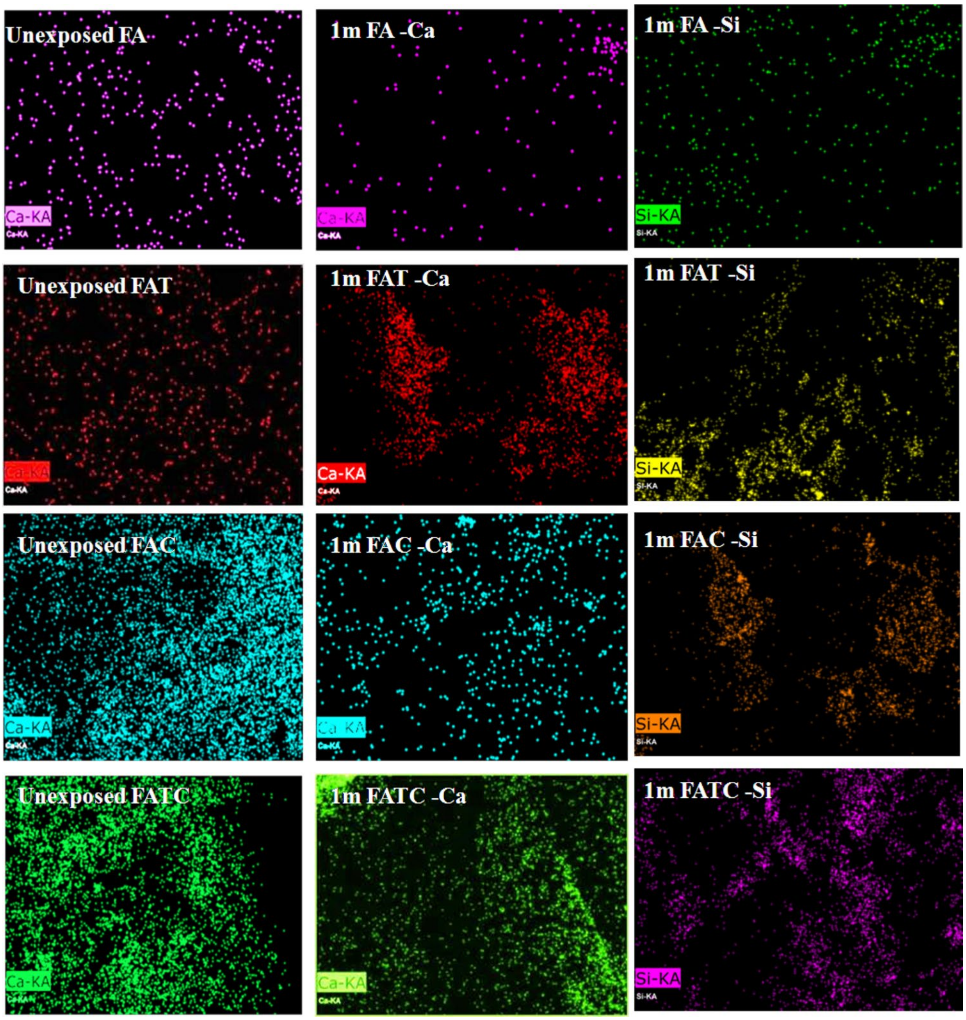

Fig. 6 Elemental mapping images of unexposed and sea water-exposed concrete

to nanophase-modified FA concrete specimens. Among the nanophase-modified specimens, FATC specimen showed higher resistance to calcium leaching.

3.2.1 Microstructural Characterization for Sea Water-Exposed Concrete

Figure 4 illustrates the XRD spectra of 1-month sea water-exposed concrete specimens. The peaks at 2 theta angle of 31.1°, 41.4° and 49.8° showed the presence of SiO_2 (JCPDS 01-072-1088). The peaks at 23.96° and 34.3° (JCPDS 01-083-0578) confirm the presence of calcium carbonate (calcite) [32]. The peaks at 2 theta angle of 32.2°, 54.3°, 71.3° and 60.5° (JCPDS 01-089-7639) confirm the presence of calcium silicate hydrate. Calcium aluminium silicate peaks were at 38.6°, 46.7°, 59.4°, 65.8° and 81.9°. The XRD patterns of nanophase-modified FA concrete showed more peaks of cementitious products like SiO_2, calcite and calcium aluminium silicate. However, these peaks have disappeared on FA concrete after 1 month of exposure in sea water indicating degradation.

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The SEM images of 1-month sea water-exposed concrete specimens are shown in Fig. 5. The surface of the FA concrete with pit-like morphology showed degradation. The surfaces of FAT and FATC specimens showed crack initiations. FATC surface showed least degradation and complete absence of crack initiation.

3.2.2 Elemental Mapping

Figure 6 shows the comparison of calcium elemental mapping on the surfaces of unexposed and sea water-exposed concrete specimens. The silicon elemental mapping on the exposed concrete specimen surfaces was also given to compare with calcium on the exposed surfaces. The images showed that after exposure the highest calcium content was on FATC surface with corresponding lowest silicon content. Thus, calcium silicon ratio is lowest for FATC specimens after 1-month exposure. Gaitero et al. [34] have reported that the lowest calcium silicon ratio is an indication of least calcium leaching. According to them, the fly ash concrete without the addition of nanoparticles showed more amount of unreacted fly ash particles due to the lower polymerization rate leading to more calcium leaching [34]. Hence, in this study also it was clearly identified that the addition of nanoparticles markedly enhanced the pore structure of the concrete resulting in less calcium leaching.

4 Conclusion

The main aim of this study was to fabricate surface-modified and skin-thickened concrete specimen with enhanced deterioration resistance in aggressive environments. This work specifically looked into reducing the cement content by reusing the waste material, fly ash, and enhancing the resistance of fly ash concrete against sulphuric acid attack and calcium leaching by incorporating nano-TiO_2 and nano-$CaCO_3$. All the surface-modified and skin-thickened nanophase-modified FA concrete (FAT, FAC and FATC) specimens showed better resistance to sulphate attack and calcium leaching compared to FA concrete. The minimal reduction in pH, thickness, diameter and weight loss percentage was found on FAT and FATC concrete specimens exposed to 1% sulphuric acid and sea water environments. FATC was found to have minimum leaching of calcium from the surface. XRD analysis showed delay in ettringite formation on FATC surface indicating resistance to sulphate attack. FESEM micrographs of concrete surface showed complete absence of calcium sulphate crystals formation confirming least degradation. XRD patterns of FATC concrete surface exposed to sea water retained all the peaks of hydration products even after 1 month indicating the absence of calcium leaching. Elemental mapping on FATC concrete surface showed lowest calcium silicon ratio which confirms the least calcium leaching. Thus, fly ash concrete modified with nano-TiO_2 and $CaCO_3$ (FATC concrete) that is eco-friendly green concrete emerged superior with excellent resistance to sulphate attack and calcium leaching.

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