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Enhancement of strength and durability of fly ash concrete in seawater environments: Synergistic effect of nanoparticles

Sudha Uthaman [a], Vinita Vishwakarma [a,*,1], R.P. George [b,1], D. Ramachandran [a], Kalpana Kumari [c], R. Preetha [c,1], M. Premila [d], R. Rajaraman [d], U. Kamachi Mudali [e]

[a] Centre for Nanoscience and Nanotechnology, Sathyabama Institute of Science and Technology, Chennai 600 119, India
[b] Corrosion Science and Technology Division, IGCAR, Kalpakkam 603 102, India
[c] Civil Engineering Group, IGCAR, Kalpakkam 603 102, India
[d] Materials Science Group, IGCAR, Kalpakkam 603 102, India
[e] Heavy Water Board, Mumbai 400 094, India

HIGHLIGHTS

- Fly ash concrete specimens were fabricated using TiO_2 and $CaCO_3$ nanoparticles.
- Year-long studies in seawater showed synergistic effect nanoparticles.
- Nano-TiO_2 showed faster hydration with more filler effects and antibacterial.
- Nano-$CaCO_3$ contributed to high pH and compressive strength.
- 1:1 ratio of nano TiO_2 and $CaCO_3$ emerged with superior concrete properties.

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ABSTRACT

Fly ash is used in concrete industry to reduce the amount of cement and to enhance the durability of concrete. Nuclear industry recently adopted fly ash concrete as a government initiative to reduce carbon footprint and also to provide an impermeable skin for the several structures in the cooling water system exposed to marine environment for enhanced durability. Earlier detailed studies on fly ash concrete has shown that despite its superiority over conventional concrete with respect to strength and durability, some concerns such as delayed setting and hydration, low early-age strength, and higher carbonation may pose a problem for its wider application. The present work is an attempt to overcome these deficiencies by nanophase modification of concrete with the incorporation of nano-titania and nano-calcium carbonate at 2% by weight of cement. Four different types of concrete mix were arrived and specimens of different sizes were cast in order to explore the various properties of concrete. After 28 days of curing in potable water, the samples were exposed to seawater at Nuclear Desalination Demonstration Plant (NDDP) sump at Kalpakkam and were withdrawn for testing at different ages like 56, 90, 180 and 365 days. Nanophase modification increased the pozzolanic activity resulting in faster hydration, early-age strength and long-term compressive and split tensile strength, permissible electrical resistivity for corrosion, lower chloride ion penetration, carbonation depth biofilm formation and higher internal pH. Among the different mixes, the synergy of 1% NC and 1% NT emerged superior with excellent concrete properties related to mechanical properties, pore structure, durability and optimum antibacterial activity.

1. Introduction

Fly ash, a waste material from combustion of coal is used in concrete as a partial cement replacement to upgrade the strength and durability by pozzolanic action and filler effects [1]. The desired properties can be achieved using high volume (>40%) of fly ash in concrete [2]. Nuclear industry has a new mandate to plan future nuclear power plants with a design life of 100 years to make nuclear power more economical [3]. Hence, the durability of concrete structures especially under marine exposure assumes great relevance. The sulphates and chlorides from the aggressive

* Corresponding author.
E-mail address: vinitavishwakarma@sathyabama.ac.in (V. Vishwakarma).

[1] Equal contribution to this paper.

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seawater environment can penetrate and deteriorate the concrete leading to its failure [4]. Many workers have reported that interaction of seawater with cement paste leads to carbonation, sulphate attack and chloride ion attack. It is reported that addition of mineral admixtures assures low permeability to aggressive anions and offer excellent durability for concrete structures in seawater [5]. Sandberg have studied the chloride binding of concrete exposed in a marine environment and reported that the transport of chloride ions in the concrete structure depends on the amount of alkali hydroxide [6]. Permeability is the most important property that determines the durability of concrete structures in seawater [7]. When a structure is located in a marine environment, chloride ions can penetrate the porous structure of concrete and reach the steel leading to deterioration [8]. The holistic study conducted by Lindvall [9] revealed that the concrete structures exposed to marine environment showed attachment of foulants on its surface and the extent of marine growth facilitate the ingress of chloride ion penetration. Nuclear Power Corporation of India Limited (NPCIL) has also recently adopted fly ash concrete as a government initiative to reduce carbon footprint and also to provide an impervious skin for the concrete structures [10]. Ramachandran et al have observed that flyash concrete exhibits superior strength and durability properties as compared to normal and modified concrete by superplasticizer in sea water environments [11]. However, their studies also brought into focus some drawbacks of fly ash concrete like slower hydration, low early age strength and higher carbonation depth [11,12]. The use of fly ash as a partial replacement of cement is reported to reduce the tensile strength of concrete [13]. Utilization of fly ash in concrete exposed to water involves the potential leaching of some elements into water. This creates a problem of secondary environmental pollution [14].

Recently, many researchers have started addition of different nanoparticles to improve physical and chemical properties of concrete structures [15–26]. It has been reported that nanoparticles can act just like fillers and densify the microstructure of concrete or they can also form heterogeneous nuclei for accelerating cement hydration; all contributing to reduction in porosity [24]. Several nanoparticles were incorporated by different researchers, SiO_2 [15–18], Al_2O_3 [19,20], TiO_2 [21], Fe_2O_3 [22] and $CaCO_3$ [23,24] in the range of 0.5–5% of cement replacement which enhanced the strength and other properties of the modified concrete compared to conventional concrete without nanoparticles. It is found that SiO_2 nanoparticles up to 4% by wt. of cement acted as fillers and also improved pore structure by decreasing harmful pores [16]. Ali Nazari et al., has also conducted an extensive study on the effect of nano-Al_2O_3 and found that the 2% nano-Al_2O_3 particles blended concrete, emerged with significantly higher compressive strength [20]. The inclusion of 1% nano-Fe_2O_3 into the concrete matrix at the early ages increased the percentage of water absorption and later the mechanical strength [22]. The increased rate of water absorption increases the number of capillary pores in concrete which in turn reduces the desired performance of concrete [27]. Jayapalan et al. [25], investigated the effect of chemically non-reactive anatase TiO_2 nanoparticles on early-age hydration of cement and found that addition of 5% TiO_2 accelerated the rate of cement hydration by the heterogeneous nucleation effect. The addition of TiO_2 to cement is increased the heat of hydration, accelerated the rate of reaction at early stages of hydration and enhanced the antimicrobial activity by the destructing the microbes [26]. The $CaCO_3$ nanoparticles was first considered as only filler in cement to replace OPC, but later showed positive effects in terms of strength and acceleration of hydration rate [28]. All these studies refer to the nanoparticle modification conventional concrete (100% OPC).

The main objective of this work was to overcome the drawbacks of fly ash concrete by nanophase modification. In the fly ash concrete containing 40 wt% fly ash and 60 wt% OPC, 2 wt% of OPC is replaced using nano-titania and nano-calcium carbonate individually and in combination. Based on our earlier screening studies reported elsewhere [29] where a nanophase replacement of OPC was studied in the range of 0.5–3 wt%, it was found that 2 wt% replacement of OPC is the optimum level of nanoparticle substitution. Optimum workability and strength, very low RCPT values and lowest reduction of pH was achieved with 2 wt% nanoparticle replacement. Nazari et al. [30] and Xu et al. [31] have also reported that enhancement of concrete properties by 2 wt% of $CaCO_3$ TiO_2 nanoparticle modification respectively. Hence it was decided to select 2 wt% substitutions for the long-term exposure studies in seawater environment. The various concrete properties related to strength, durability and antibacterial characteristics were evaluated by casting specimens of different shape and sizes for all the four types of concrete mixes. The specimens were cured in potable water at laboratory conditions for 28 days and thereafter exposed to seawater for a year. Advanced characterization tools like SEM, XRD and IR spectroscopy were used to get an insight into the role of nanoparticles in improving the integrity of concrete.

2. Experimental methods and materials

2.1. Materials and mix proportion

Ordinary Portland Cement (43 Grade) conforming to IS 8112 – 1989 [32] was used in this study. Black granite (Hard Blue Granite Rock Aggregate - Machine Crushed) was used as coarse aggregate, with maximum size of 20 mm and 12.5 mm meeting the requirements of IS 383 [33]. High range water reducer type superplasticizer containing sulphonated naphthalene formaldehyde as base was used as chemical admixture. Crushed sand and river sand with a maximum size of 4.75 mm and meeting zone II requirements were used as fine aggregate. The partial replacement of cement was 40% by siliceous type fly ash conforming to IS 3812 [34]. The commercial grade anatase phase titanium dioxide (TiO_2) and calcium carbonate ($CaCO_3$) with size ranging from 100 to 600 nm was purchased. To attain nanosized particles, TiO_2 and $CaCO_3$ powders were ground using ball mill (SPEX 8000M-230 dual mixer mill, 230 V/50 Hz) to achieve the size of the particles within the range of 50–80 nm.

The total powder content which includes cement, fly ash and nanoparticles for all the mixes was 375 kg/m^3 and OPC was replaced with fly ash (40% by wt. of cement). The nanoparticles were replaced at 2 wt% by cement. Concrete cube specimens of 150 mm size were used for compressive strength test and cylindrical specimen of 100 mm diameter and 200 mm height were used for RCPT and split tensile strength test. Resistivity analysis was done on prism specimens of 350 mm length and 100 mm depth with a thermo mechanically treated (TMT) rebar of 10 mm diameter embedded in it. Mortar specimens of 35 mm diameter and 10 mm thick were prepared to visualize the biofilms under epifluorescence microscope and 100 mm cube mortar specimens were cast to perform carbonation studies. The mix proportion and casting details of the specimens are given in Table 1.

Table 1
Mix proportion of concrete (kg/m^3).

Sample designation	Cement	Fly ash	Fine aggregates		Coarse aggregates	Superplasticizer	Nano-TiO_2	Nano-$CaCO_3$
			River sand	Crushed sand				
FA	225.0	150	549	235	1130	4.5	–	–
FAT	220.5					4.8	4.5	–
FAC	220.5					4.8	–	4.5
FATC	220.5					4.8	2.25	2.25