# Chapter 11
# Environmental Remediation for Cementitious Systems Using Titania Nanocomposites

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**Abstract** This chapter reports the effect of adding hydrophobic 40 nm diameter nano-sized Titania (NT) particles by functionalizing them to hydrophilic via surface modification or wrapping by new generation pH neutral polymeric admixtures and adding them to cement: sand ratio of 1:3 with a water-cement ratio of 0.4. Mechanical strength results of the cementitious composites were taken at all terms up to 365 days (D). The optimized quantity of NT as found in cement composites is then added to M-40 Grade concrete composites for compressive strength testing at both short and long terms following Indian standard protocols. Simulating seawater behaviors in laboratory conditions, results of sulfate and chloride attacks on standard concrete at medium and long terms were discussed. Results reveal that the application of photocatalytic NT in cementitious systems has an improved effect with respect to non-NT cementitious systems and also the former was more durable and sustainable.

**Keywords** Cement · Composites · Concrete · Environment · Strength · Titania

## 11.1 Introduction

Nature is inherently sensitive with 5 out of 10 risks as identified by World Economic Forum-2020 relating to the environment [1]. Reducing the common energy consumption is the easiest way to help mother Earth. Historically, most of the development comes from exploiting the environment with construction activities being one of the major sources of pollution contributing to air, water, and noise pollution along with dust, waste, and light pollutions with the emissions of hazardous gases that generally go unnoticed. As per the United States Environmental Protection Agency (USEPA), cement manufacturing has been tagged as one of the third largest sources contributing to greenhouse gas emissions followed by steel [2]. As shown in

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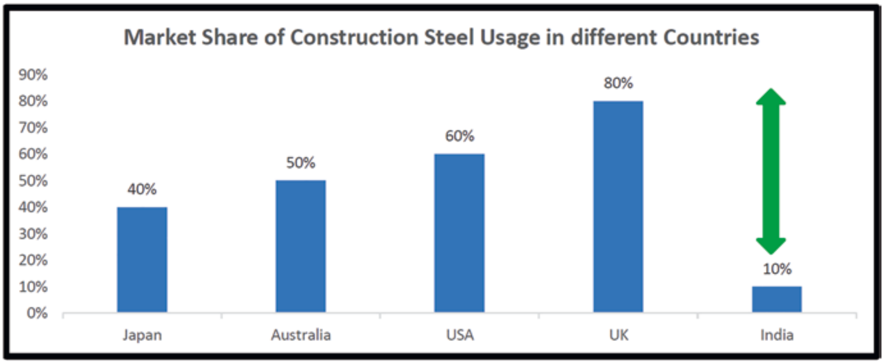

**Fig. 11.1** Market share (in %) of construction steel usage in different countries

Fig. 11.1, some recent report suggests that India's steel usage in construction is a mere 10% compared to Japan (40%), Australia (50%), the USA (60%), and the UK (80%), while our cement concrete construction is highest at around 90% [3]. Human beings have always followed the path of better ways of doing things and in pursuit of that exploring newer materials and technologies. Several technologies have emerged in the domain of concrete which talks of sustainability issues like zero waste, energy-neutral/positive, or pollution-eating. Pozzolanic fly ash is considered a premium waste by-product having a beneficial effect on many concrete properties for many years [4–7]. But now non-pozzolanic, pollution-eating self-healing photocatalytic materials have come up that eat pollutants in the air using sunlight through nanomaterials like Nano Titanium dioxide or Nano Titania (NT).

### *11.1.1 Market Share of Construction Steel Usage in Different Countries*

The World Economic Forum (2013) and the Global Agenda Council named self-healing materials as one of the top emerging technologies. Industry 4.0 today is working towards the trend of using smart self-healing materials in cement concrete that respond to the needs of the environment and are also termed intelligent. The durability of concrete is defined as its ability to resist aggressive chemical attacks, weathering actions, abrasion, or any other process of deterioration. There are many factors affecting durability, the main being cement, and water quantity/quality, sulfate, and chloride attacks, permeability, etc. Sulfate attack originates from the presence of sewage in soil or soil foundation containing excessive fertilizers or industrial wastes or automobile exhausts while chloride attacks arise from the salty sea environment within 100 km from the coast. So the durability study of concrete demands the need for the hour. The durability of structures like buildings, water and wastewater treatment plants, transportation structures, tunnels, etc., could be improved in the long run without significant repairs or replacement by using self-healing materials. India has a huge coastline of more than 7500 km with a harsh marine climate while out of the 30 most polluted cities in the world, 21 were in India.

Cement hydration attains more than 90% at 28 days and Indian codes have standardized the 28 days strength results. But cementitious systems continue to hydrate in the long terms, that is, 1 year (365 days), albeit at a very small rate [8, 9]. So in the tests results have been considered both at 28 days and at long terms, that is, 365 days. This chapter discuses that the optimized addition of nano-TiO2 having a mean particle size diameter in the range of 30–40 nm has a distinctive self-healing capacity whereby it increases the mechanical strength of cement composites and also concrete composites w.r.to the controlled samples. Also, the concrete samples cast with these nanomaterials resulted in more workability and whitish appearances. However, this self-healing capacity of nano-TiO2 is more evident when it successfully wards of the aggressive chemical attacks of sulfate/chlorides as shown in Fig. 11.3.

### *11.1.2 Photochemistry Principles of Self-Healing*

The self-healing material in the concrete utilizes ingress water(humidity) and sunlight to start a photochemical reaction which is similar to the photosynthesis of plants resulting in eating up the pollutants from the environment. Light is one of the main reaction components of the self-healing processes. The basic law of photochemistry suggests that

- Only light that is absorbed can produce the photochemical change (Grotthuss, Draper).
- A molecule absorbs a single quantum of light in becoming excited (Stark, Einstein) [10].

NT finds applications in a wide range of industries from food coatings to construction to paints to sunscreen lotions. Its nanodimensions have proved to have more novel unique photo-catalytic properties than its parent bulk material as this chapter reports. The photocatalytic activity begins with the absorption of the sun's light rays with a higher amount of energy than the photocatalyst bandgap, which transfers the valence band (VB) electrons into the conduction band (CB), leading to the production of charge carriers ($e^-/h^+$ pairs). Thus, when sunlight falls on nano-TiO2 doped concrete, electrons are released, which combines with O2 in the atmosphere creating "$O^{2-}$" (Superoxide anion). As a result of this release of electrons, nano-TiO2 takes electrons from the moisture of the air and then returns to its original state. On the other hand, the moisture that lost the electron becomes a hydroxyl radical (•OH) resulting in a loss of moisture from the cement matrix system.

$$TiO_2 + h\gamma\left(\text{Sunlight}\right) \rightarrow TiO_2\left(\text{e}^- + \text{h}^+\right);$$

$$TiO_2\left(e^-\right) + O_2 \rightarrow TiO_2 + O_2^-;$$

$$TiO_2\left(h^+\right) + H_2O \rightarrow TiO_2 + HO + H^+$$

### 11.1.3 Approach Towards Environmental Remediation and Sustainability

Self-healing materials can be effectively used for concrete structures where the structure is more exposed to the environmental atmosphere and where durability is of paramount importance. Also, many important and heritage structures such as Arca Pacis Museum, Rome, Italy; Narita International Airport, Tokyo, Japan; Kaldewei Kompetenz- Center (KKC), Ahlen, Germany; Massacio's (in Capella Brancacci), Beato Angelico's (in San Marco Abbey), and Peiro Delia Francesca's (in Arezzo) wall painting have utilized NT as self-healing photocatalytic materials [11, 12]. The photocatalysis mechanism of the self-healing materials has a disinfection mechanism that includes the decomposition of the cell wall and disinfection of novel viruses such as SARS-CoV and COVID-19 [13]. The disinfection mechanism includes the decomposition of the cell wall and the cytoplasmic membrane is as a result of the generation of highly reactive oxygen species like HO and $O_2^-$ [14] as shown in Fig. 11.2.

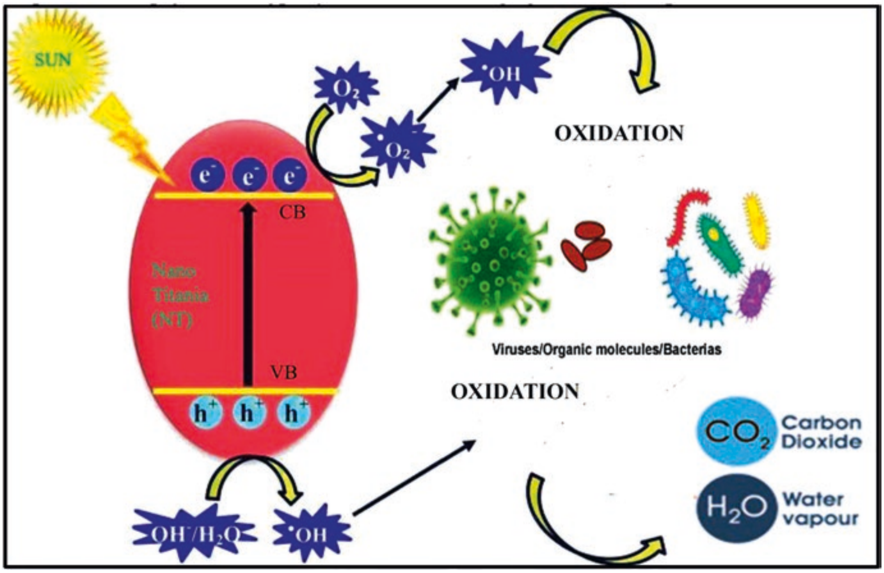

Fig. 11.2 Schematic representation showing the oxidation mechanism of NT

Energy conservation using the latest technology like nanotechnology would help to conceptualize the principle of sustainability in today's climate change landscape, especially after the Covid-19 pandemic. Nanotechnology is said to have the potential to address the sustainability issues confronting the world, and out of 17 Sustainability Development Goals (SDGs), it can directly influence four main themes, namely, Sustainable resources, Safety, Healthcare, and Energy. Nanotechnology's self-healing Nano Titania (NT) is an eco-friendly sustainable material as it can be synthesized from both agricultural by-products [15, 16] and waste paints [17]. Application of this nanomaterial in concrete production needs its dispersion in potable water which means a good amount of drinking water requirement in the process. But India's water demand has been projected to exceed supply by a factor of two by 2030 as projected by National Institution for Transforming India (NITI) Ayog and its water equation has not been met in the Millennium Development Goals (MDGs). The Nanomaterials need to be dispersed in a new 3rd generation polymeric admixture which can effectively minimize cement concrete's water requirement by an amount of 15–30% [18]. Remarkably both polymers and nanomaterials especially carbon-based CNTs can be produced from CO2 [19] leading to more carbon-neutral and sustainable development.

## 11.2 Materials and Methods

As shown in Fig. 11.3, untreated Nano Titanium Dioxide or Nano Titania (NT) in its rutile form was supplied by M/s Kerala Minerals and Metals Ltd. (KMML) costing around Rs. 2000/kg. It may be mentioned that Rutile is the most common natural form of TiO2, has among the highest refractive indices of any known mineral, and also exhibits high dispersion. The other materials used were Portland cement – OPC (43 Grade) conforming to IS:8112-1989, Fine Aggregate (FA) – Natural River sand conforming to Zone II of IS:383-1970, Coarse Aggregate (CA)-Local Pakur variety (20 mm nominal size) also conforming to Zone II of IS:383-1970, Potable water conforming to IS: 3025-1987, Admixture (Superplasticizers) – Polycarboxylate

**Fig. 11.3** KMML's untreated nano titanium dioxide in IIEST Lab

Ether (PCE) conforming to IS: 9103-1999 and Nano Materials viz. Nano Titania (NT) (Tables 11.1 and 11.2).

Where C = CaO (calcium oxide); S = $SiO_2$ (silicon dioxide); A = $Al_2O_3$ (aluminum oxide); F = $Fe_2O_3$ (iron oxide); $\underline{S}$ = $SO_3$ (sulfate); H = $H_2O$ (water).

### 11.2.1 Dissipation of Nano Titania (NT)

As Nano Titania (NT) is insoluble in water, these nanomaterials cannot be added directly to the cementitious mix as done with the other member materials of cement composites. When mixed with water, these NTs tend to form agglomerates due to attractive Van der Waals forces. Ultrasonication energy was used to dissipate the NT clusters and to detach individual NTs from bundles for making them functional.

**Table 11.1** Typical % mineralogical compositions (mass fraction) of Portland cement as supplied by manufacturers

| Mineral type | % Compositions |
|---|---|
| Alite ($C_3S$) | 62.2% |
| Belite ($C_2S$) | 14.1% |
| Celite ($C_3A$) | 9.9% |
| Felite ($C_4AF$) | 5.4% |
| Gypsum ($C\underline{S}H_2$) | 1.4% |
| Bassanite | 1.6% |
| Anhydrite | 0.8% |
| Periclase | 1.3% |
| Arcanite | 0.45% |
| Aphthitalite | 0.1% |
| Calcite | 2.8% |
| Total | 100.0 |

**Table 11.2** Specific properties of Nano Titania (NT) used as supplied by M/s Kerala Minerals and Metals Ltd

| Item type | Description |
|---|---|
| Nano titanium oxide purity (%) | 97% |
| Rutile content (%) | 98% |
| pH | 7 (Neutral) |
| Physical appearance | Whitish powder |
| Average particle size diameter (TEM) | 30–40 nm |
| Moisture (%) | 1.75–2% |
| Bulk density | 0.31 gm/cc |
| Water solubility | In soluble |

NTs were added to a superplasticizer called Polycarboxylate Ether (PCE) and ultrasonicated in 250 W Piezo-U-Sonic Ultrasonic Cleaner for about 30 min in the IIESTS laboratory. Existing works of the literature suggest that better the functionalization/ultrasonication more uniform is the mix obtained resulting in the accuracy of the desired strength [20, 21].

### 11.2.2 Sample Preparation for Optimized Cement Composites

One part of Portland cement by weight was mixed with three parts of sand by weight and potable water was added as per IS:4031 standards but keeping the water/cement(w/c) ratio fixed at 0.4. Lastly, Nano Titania (NT) in dosages of 1% and 2.5% by weight of cement as per existing literature surveys [22, 23] after dispersion in 1% Polycarboxylate Ether (PCE) admixture solution was added to the cementitious mix. The casting of 7 cm (approx.) dimension cubes was done and cured in IIESTS curing chamber containing normal drinking water. Three (03) sets of cubes were tested in a compression testing machine at standardized 28 days and at a longer term of 365 days, respectively, after making them surface saturated dry (SSD) and not before arriving at their bulk density figures. The load shall be applied without shock and increased continuously at a rate of approximately 140 kg/cm$^2$/min.

### 11.2.3 Sample Preparation for $MgCl_2$/$MgSO_4$ Aqueous Solution

The $MgCl_2$ and $MgSO_4$ solutions were prepared by adding 1 mole of $MgCl_2$ (95.21 gm) and 1 mole of $MgSO_4$ (120.37 gm) in 1 liter of potable water to get a 1M aqueous solution of the desired solutions. As seawater contains both $Cl_2$ and $SO_4$ ions, the solutions resembled that of marine environments. Simulation of an environment relating to or that found in the sea was necessary to study the behavior of concrete systems in the same.

### 11.2.4 Sample Preparation for Cement Concrete Composites

Standard concrete of M-40 grade was prepared by mixing sand (FA) and stone (CA) after a proper sieve analyzing it in the IIESTS laboratory. Cubes of 100 mm dimensions were cast with cement, FA, CA, and water in proportions as per the mix design followed by IS: 10262-2009 for M-40 Grade concrete for 100 mm slump keeping the w/c = 0.4. The mix proportions were cement = 400 kg/m$^3$, CA=1293 kg/m$^3$ [CA1(90%) = 163 kg/m$^3$; CA2(10%) = 129 kg/m$^3$], FA = 688 kg/m$^3$, water = 157 kg/m$^3$ [22]. The % fractions of CA1 (12.5 mm passing) and CA2 (20 mm passing) were obtained from sieving the coarse aggregates and reviewed as per IS:383. Nano Titania (NT) were added in optimized proportions as obtained. The cubes were then ordinary cured underwater in IIESTS curing tank and tested for compressive strength at 28 days and then immersed under $MgCl_2$ and $MgSO_4$ solutions as shown in Fig. 11.4 for testing at 90 days and 180 days, respectively, as per IS:516 (Fig. 11.5).

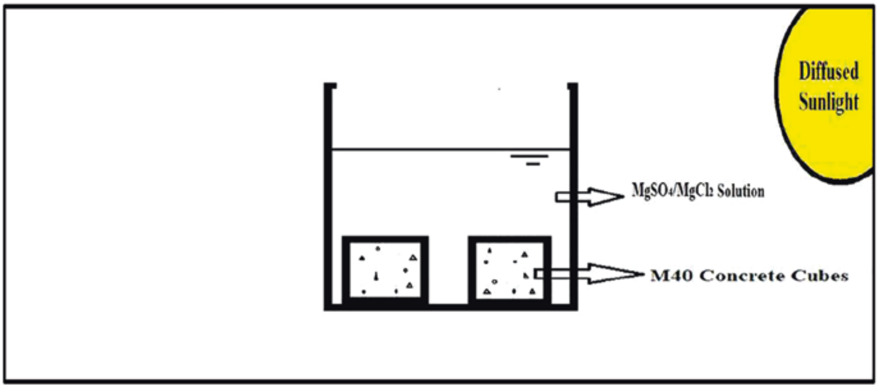

Fig. 11.4 Schematic representation of $MgCl_2$ and $MgSO_4$ exposure conditions for Concrete

**Fig. 11.5** Casted Nano Titania (NT) Cementitious Composites (left) and Reference Specimen (right)

## 11.3 Test Results

Table 11.3 shows the results obtained for the various properties like bulk density and the compressive strength of the cement composites at all dosages of NT.

Table 11.4 shows the results obtained for the compressive strength of the cement concrete composites at optimized dosages of NT at all exposure conditions (Figs. 11.6, 11.7, and 11.8).

## 11.4 Discussion of Results

The test results are described as follows.

(i) To find out the optimum dosage of NT to be added to the cement composites, a literature survey was undertaken and 1% and 2.5% NT by weight of cement were tried. As per Table 11.2, at 28 days it was found that 1% NT by weight of cement gave the maximum cube strength of 36.71 N/mm$^2$ which sustained at 365 days (1 year) also at 41.16 N/mm$^2$ having 37% strength gain w.r.to the reference specimen (see Fig. 11.7). As discussed previously, the high strength

**Table 11.3** Properties of cement composites with and without various dosage Nano Titania (NT) addition

| % Nano Titania (NT) additions in cement (OPC) | Property parameters | 28 days | 365 days |
|---|---|---|---|
| 0% NT (reference specimen) | Bulk density (kg/m$^3$) | 2300.08 kg/m$^3$ | 2303.91 kg/m$^3$ |
| 1% NT (optimized specimen) | Bulk density (kg/m$^3$) | 2320.39 kg/m$^3$ (0.88%) | 2329.16 kg/m$^3$ (1.09%) |
| 2.5% NT | Bulk density (kg/m$^3$) | 2301.13 kg/m$^3$ (0.05%) | 2291.17 kg/m$^3$ (−0.55%) |
| 0% NT (reference specimen) | Compressive strength (N/mm$^2$) | 31.89 N/mm$^2$ | 30.01 N/mm$^2$ |
| 1% NT (optimized specimen) | Compressive strength (N/mm$^2$) | 36.71 N/mm$^2$ (12.59%) | 41.16 N/mm$^2$ (37.15%) |
| 2.5% NT | Compressive strength (N/mm$^2$) | 34.97 N/mm$^2$ (9.58%) | 28.16 N/mm$^2$ (−6.16%) |

**Table 11.4** Strength of cement concrete composites with and without optimized Nano Titania (NT) addition at different exposures

| % Nano Titania (NT) additions in cement (OPC) | Exposure conditions | Slump | Compressive strength after 90 days | Compressive strength after 180 days |
|---|---|---|---|---|
| 0% NT (reference specimen) | Air | 100 mm | 49.71 N/mm$^2$ | 48.34 N/mm$^2$ |
| 1% NT | $MgCl_2$ | 110 mm | 36.89 N/mm$^2$ (−14.88%) | 62.48 N/mm$^2$ (49.36%) |
| 1% NT | $MgSO_4$ | 110 mm | 35.68 N/mm$^2$ (−17.67%) | 68.67 N/mm$^2$ (64.16%) |

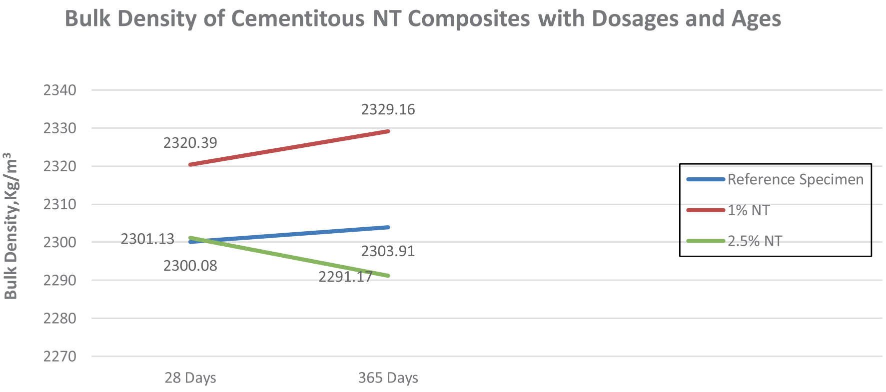

**Fig. 11.6** Bulk density of cementitious NT composites with various dosages and ages

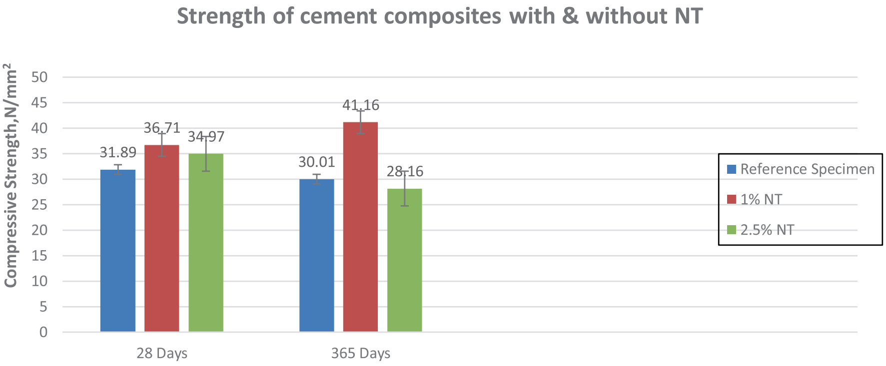

**Fig. 11.7** Compressive strength of cementitious composites with and without NT

of the nanocomposites was due to the nucleation effect of NT. At higher dosages, the strength deviation was observed due to the agglomeration of NT nanoparticles as it exceeded the optimized dosage of 1%. Agglomeration of nanoparticles can be observed for the higher concentration of nanoparticles without proper dispersion technique which might lead to decrease in compressive strength [23, 24]. The bulk density for 1% NT by weight of cement was recorded as the densest mix at both 28 days (Bulk Density = 2320.39 kg/m) and 365 days (Bulk Density = 2329.16 kg/m$^3$) than the reference specimens and the 2.5%NT specimens as shown in Table 11.2 and Fig. 11.6. The control or reference specimen (without any $TiO_2$) achieved less strength at 365 days due to the fact that Portland cement manufacturers have a tendency to increase the % of C3S at the cost of C2S for quick strength gain (see Table 11.1).

(ii) As per Table 11.3, 1% NT concrete composites fared much better than reference specimen both in fresh and hardened properties having 10% more workability(higher slump of 110 mm compared to 100 mm) and showing 49%

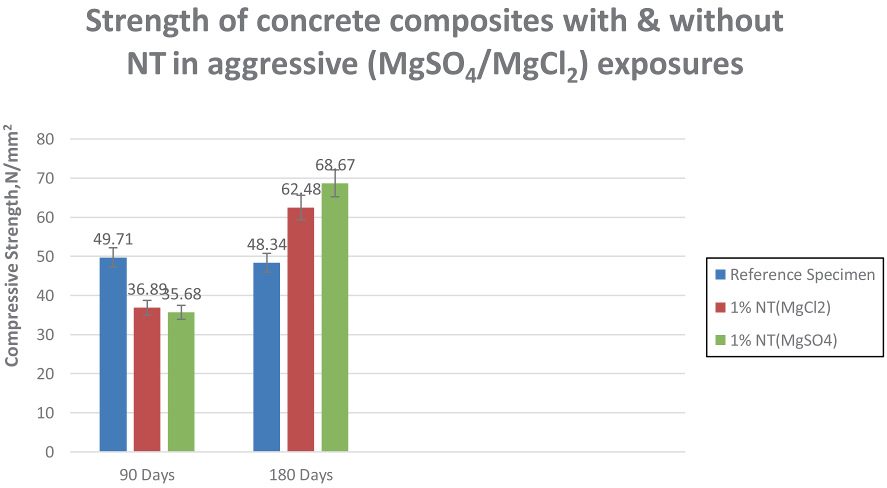

**Fig. 11.8** Compressive strength of concrete composites with and without NT in aggressive (MgSO4/MgCl2) exposures

and 64% strength gain at 180 days at chloride (MgCB) and sulfate ($MgSO_4$) exposure conditions as per Fig. 11.8. This is due to the fact that in presence of moisture when sunlight falls on nano-$TiO_2$ doped concrete, electrons are released, which combines with $O_2$ in the atmosphere creating "$O^{2-}$" (Superoxide anion). As a result of these release of electrons, nano-$TiO_2$ takes electrons from moisture of the air and then return to its original state. On the other hand, the moisture that lost the electron becomes a hydroxyl radical (•OH) resulting in a loss of moisture from the cement matrix system (see Fig. 11.2). As a result, chemical attacks of sulfate and chlorides could not be continued, when the involvement of NT comes into picture. Hence, hydrated products are not being attacked and the cement matrix continues to grow in strength.

(iii) As shown in Fig. 11.5, NT composites have a much fairer appearance (whitish in color) than the greyish cementitious color of ordinary cementitious composites and much energy could be saved in painting the structure of its primer color directly white instead one can straight away go for the finished architectural flavors.

Thus, NT concrete has the inherent characteristics to absorb ultraviolet sun rays, and Titanium being a transition element with variable oxidation states, it can directly quantum leap from the valence band to the conduction band directly by eating pollutants in the process thus resulting in greater sustainability. The use of NT can enhance the growth of C-S-H gel [25, 26]; several researchers reported that the incorporation of nanomaterials such as carbon nanotube, graphene, and NT works as a nucleating agent for the higher growth of C-S-H gel that might help to improve the mechanical performance of the cementitious composite [22, 23, 27–29]. So, nano-$TiO_2$ could help in manufacturing high-strength concrete which in turn helps

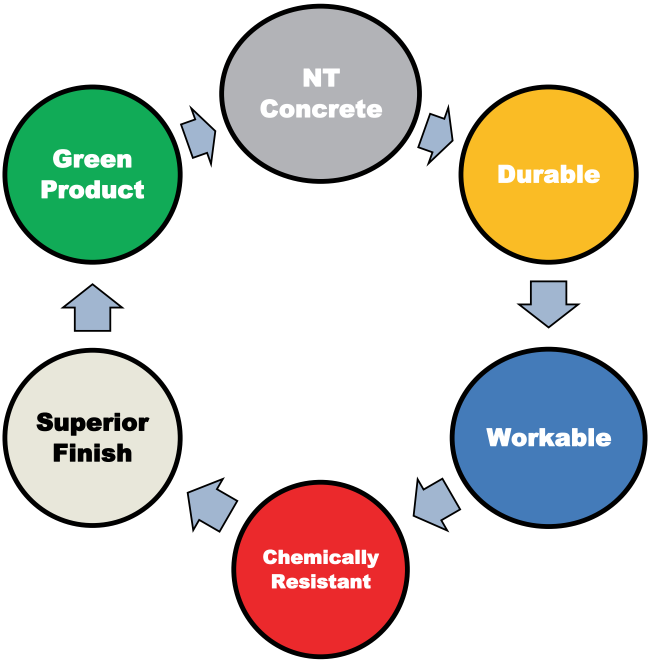

**Fig. 11.9** Various aspects of Nano Titania (NT) used in concrete

to make the concrete more durable, causing it to be more workable or flowable which is the main reason for its increased resistance to chemical attacks like $SO_4^{-2}$/$Cl^{-1}$. Hence, with smoother exterior finish resulting in more deleterious substances, decomposition makes the end product greener as shown in Fig. 11.9.

## 11.5 Conclusions

Steel reduction, which is the general practice of Indian construction industry, needs to shift focus to high performance testing protocols on cement concrete in industry 4.0 regimes. The suitability of advanced nanomaterials in these conventional cementitious systems should be further reviewed through performance-based testing models for its long-term applicability characteristics. Though much research needs to be carried out in the nano-application areas, the NT optimization in cement composites has been found out to be 1% by weight of cement which was confirmed by literature studies. Despite having novel properties, application of NT in real estate or research projects in India has settled in the flipper side of the coin when compared to other developed countries like the USA, Japan, Europe, or even China. The main obstacle in NT implementation in cement concrete seems to be its cost and proper standardization. The scalability factors would certainly reduce its costing in near future but standardization of nano materials still remains a dream. The compressive strength results of NT concrete under aggressive environments ($MgSO_4$/$MgCl_2$) exposures revels its durability characteristics under severe exposures which confirms its long-term sustainability. Thus, considering the cost-benefit implications and if the policy parameters are not paralyzed by the concerned powers, then NT applications in built environment should benefit not only end users but also relieve detrimental environmental issues.

However, it may be inferred that those issues related to the environment need initiatives not only at policy level but significant action requires to be implemented at the microbuilt environmental level also. Every individual or institution or organization needs to take up this social responsibility by curbing wastage of all forms of energies and protecting the built environment through nano applications. Then only conservation and sustainable usage of natural resources and lowering of pollution levels can take the world out of any immediate and imminent grave situation.

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