International Journal of Environmental Sciences
ISSN: 2229 7359
Vol. 11 No. 18s, 2025
https://www.theaspd.com/ijes.php

Nano-Engineered High Performance Concrete For Improved Chloride Resistance In Marine Structures

[1]Dr.M.Karthikeyan,[2]B.Ganesh ,[3]Anurekha G.S,[4]Dr.Govindarajan , [5]Dr.K.Mohan das A,[6]S.Baskar
[1]Professor & Head, Department of Civil Engineering ,Dhanalakshmi Srinivasan College of Engineering, Coimbatore, Tamil nadu ,India, mkartik2009@gmail.com.
[2]Assistant professor, Department of Civil Engineering, Aditya institute of technology and management ,Andhra Pradesh,India,ganeshbellana1@gmail.com.
[3]Assistant professor, Department of Civil Engineering, SNS college of Technology, Tamil nadu,India, anurekha096@gmail.com.
[4]Assistant Professor, Department of Civil Engineering, Aditya University,Surampalem, govindarajans@adityauniversity.in.
[5]Professor, Department of Civil engineering, CMR College of Engineering & Technology, Medchal, Hyderabad, Telangana, kmohandas11780@gmail.com.
[6]Assistant Professor, Department of Civil Engineering,Vel Tech Rangarajan Dr.Sagunthala R&D Institute of Science and Technology, Chennai,Tamil Nadu, India, rhodabaskar@gmail.com.

Abstract
Marine structures are highly susceptible to chloride-induced corrosion, severely affecting their service life and safety. This study investigates the development and performance of Nano-Engineered High Performance Concrete (NEHPC) incorporating nano-silica and graphene oxide to enhance chloride resistance. The paper evaluates mechanical strength, microstructure, and permeability properties, supported by durability tests including Rapid Chloride Penetration Test (RCPT), water absorption, and microstructural analysis using SEM-EDX. The results indicate a significant improvement in resistance to chloride ingress and an enhancement in compressive strength, making NEHPC a promising solution for durable marine construction.

Keywords: *Nano-Engineered High Performance Concrete (NEHPC), SEM-EDX, Rapid Chloride Penetration Test (RCPT), water absorption.*

---

1. INTRODUCTION

Marine structures such as jetties, breakwaters, and offshore platforms are constantly exposed to chloride-laden environments. Chloride ingress leads to steel corrosion, reducing structural integrity. High Performance Concrete (HPC) offers a solution through enhanced strength and durability, but chloride permeability remains a critical concern. Nano-engineering provides an avenue to reduce porosity and refine microstructure using additives such as nano-silica, graphene oxide (GO), and carbon nanotubes.

1.1 Background

Chloride-induced corrosion is the most prevalent form of deterioration in reinforced concrete marine structures. It leads to reduced service life, costly repairs, and structural failure.

1.2 Importance of High Performance Concrete

HPC offers:

- High strength (≥60 MPa)
- Low permeability
- High durability
- But it still requires modification for **long-term chloride resistance** in marine zones.

1.3 Need for Nano-Engineering

Nanomaterials refine the pore structure and accelerate hydration. Benefits:

- Nano-silica: High pozzolanic reactivity
- Graphene oxide (GO): Crack-bridging, water barrier, micro-filler

2. LITERATURE REVIEW

Mehta and Monteiro (2014)

Mehta and Monteiro emphasized that marine structures experience rapid deterioration primarily due to chloride ingress, which leads to steel reinforcement corrosion. Their work highlighted the importance of using High Performance Concrete (HPC) to address durability issues, particularly in coastal and offshore environments. They observed that lower water-cement ratios and denser microstructures can slow down chloride diffusion but recommended incorporating advanced materials for further improvement.

Pan et al. (2015) Pan et al. studied the incorporation of graphene oxide (GO) into cementitious systems and observed notable improvements in mechanical properties and microstructural integrity. The authors attributed these benefits to GO's large surface area and functional groups, which enhance bond strength within the matrix and act as crack arresters. They also noted improved resistance to chloride ingress, linked to the refinement of microcracks and pore structures.

Lv et al. (2016) Lv and colleagues examined the synergistic use of graphene oxide and nano-silica in concrete. Their results showed that combined nano-additions led to improvements in compressive strength, flexural strength, and chloride permeability resistance. Microstructural analysis confirmed that GO helped bridge microcracks while nano-silica filled nanopores, resulting in reduced chloride transport through the cement matrix.

Zhang et al. (2020) Zhang et al. focused on the durability performance of nano-modified concretes. Using Rapid Chloride Penetration Tests (RCPT), they demonstrated that concretes containing both nano-silica and graphene oxide exhibited up to 50% reduction in charge passed compared to conventional mixes. This clearly indicates superior resistance to chloride ingress, attributed to the dense pore structure and enhanced C–S–H gel formation observed in SEM images.

Singh and Bhattacharjee(2012) Singh and Bhattacharjee explored the application of Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX) in studying concrete microstructure. Their study confirmed that SEM-EDX is a valuable tool for identifying changes in hydration products and detecting microcrack sealing effects due to the presence of nano-materials. These observations were particularly significant in analyzing how nano-silica and GO improve the matrix densification, thereby reducing chloride permeability in marine environments.

Golewski (2021) Golewski examined the influence of nano-silica on water absorption and sorptivity in high-performance concrete. He concluded that nano-silica significantly decreases the rate of capillary water absorption due to its ability to refine the pore structure. His findings further validate the use of nano-engineered concrete in marine structures where controlling moisture and chloride ingress is critical.

2.1 Challenges in Marine Concrete

- **Wave splash**, **wet-dry cycles**, and **chloride diffusion** promote corrosion.
- Steel expands up to 6x in volume when corroded → cracking, spalling.

2.2 Role of Nanomaterials in Concrete

Table1. Nanomaterials in Concrete

Nanomaterial	**Function**	**Typical Dosage**
Nano-Silica	C-S-H growth, Pore filling	0.5–2% by weight of binder
Graphene Oxide	Strength, microstructure refinement	0.01–0.05%

3. MATERIALS AND METHODS

3.1.1 Ordinary Portland Cement (OPC 53 Grade)

OPC 53 Grade cement (as per IS: 12269) was used as the primary binder in this study. It offers high early strength, rapid setting, and good long-term performance, making it ideal for high-performance concrete applications. The cement has a specific surface area of around 225–350 m²/kg and compressive strength exceeding 53 MPa at 28 days. It plays a critical role in matrix formation and early strength gain.

3.1.2 Nano-Silica (15–20 nm, 99% purity)

Nano-silica is an ultra-fine pozzolanic material with particle sizes between 15–20 nanometers and a purity of 99%. It significantly enhances the microstructure of concrete by filling nano-pores, densifying the interfacial transition zone (ITZ), and accelerating the hydration process. Its high specific surface area also promotes secondary calcium silicate hydrate (C–S–H) gel formation, thereby improving compressive strength, durability, and permeability resistance of concrete.

3.1.3 Graphene Oxide (0.03%–0.05%)

Graphene Oxide (GO), added in a dosage range of 0.03%–0.05% by weight of cement, is a cutting-edge nanomaterial with exceptional mechanical, thermal, and barrier properties. It enhances concrete's tensile strength, fracture resistance, and crack bridging ability. Its oxygen-containing functional groups improve dispersion and interfacial bonding with cement hydrates. Even in small dosages, GO leads to a refined pore structure and improved mechanical performance.

3.1.4. Aggregates (Clean, Saturated Surface Dry Condition)

Coarse and fine aggregates used in this study were natural crushed stone and river sand, respectively, in **Saturated Surface Dry (SSD)** condition. This ensures accurate water-cement ratio control during mixing. Aggregates were clean, well-graded, and conforming to IS: 383. They contribute to the dimensional stability, strength, and durability of the concrete, acting as a structural skeleton for the matrix.

3.1.5. Superplasticizer (PCE-Based)

A polycarboxylate ether (PCE)-based high-range water-reducing admixture was used to improve the workability and dispersion of particles in the mix. PCE superplasticizers offer excellent flow characteristics at low water-cement ratios, essential for producing high-performance or self-compacting concrete. They help maintain a uniform and workable mix, especially when nano-materials are used, which may otherwise lead to stiff mixes.

Table2.Mix Proportions (kg/m³)

Mix ID	Cement	NS	GO	W/B Ratio	FA	CA	SP
M0	450	0	0	0.35	680	1200	1.2%
M2	450	4.5	0	0.30	660	1180	1.4%
M4	450	4.5	0.15	0.30	660	1180	1.5%

4. Experimental Procedures

4.1.1. Compressive Strength (7, 28, 56, and 90 Days)

Compressive strength is the most fundamental mechanical property of concrete and was tested at 7, 28, 56, and 90 days as per ASTM C39. Cube specimens (typically 150 mm³) were tested using a calibrated compression testing machine. The progressive strength development over time offers insights into early and long-term hydration behavior, especially in concretes modified with nano-silica or graphene oxide. These materials enhance strength through improved matrix densification and refinement of the pore structure.

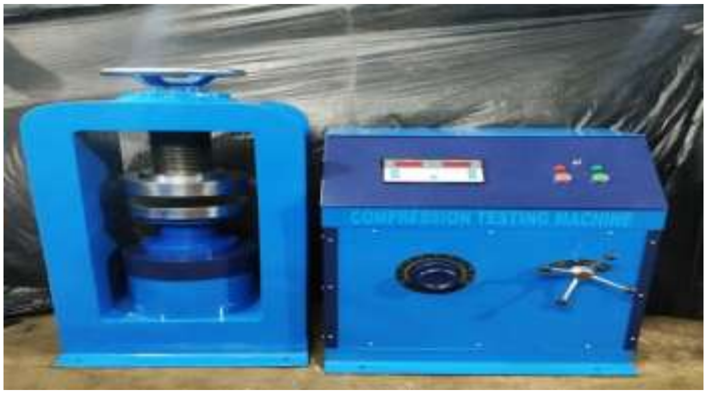


Fig1. Compressive Strength

4.1.2. Flexural Strength (28, 56 Days)

Flexural strength was assessed using prism specimens under third-point loading as per ASTM C78. The tests were performed at 28 and 56 days to evaluate the concrete's resistance to bending or tensile stress across a span. Flexural strength is particularly important for pavement slabs, beams, and structural elements subject to bending loads. Modified binders, such as nano-silica and graphene oxide, contribute to increased flexural performance by enhancing the fiber-matrix interaction and crack-bridging mechanisms.

Fig2.Flexural Strength

4.1.3. Split Tensile Strength

The split tensile strength test was conducted as per IS 5816 or ASTM C496 using cylindrical specimens (150 mm × 300 mm). This test evaluates the tensile capacity of concrete indirectly by applying a compressive load along the length of the cylinder until it splits. This property is critical for understanding the cracking resistance and ductility of concrete, especially when incorporating nanomaterials or polymer additives that influence the bond strength within the matrix.

Fig3.Split Tensile Strength

4.2. Durability test

4.2.1. Rapid Chloride Penetration Test (RCPT) – ASTM C1202

The RCPT test evaluates the resistance of concrete to chloride ion penetration, a key indicator of durability in marine and deicing salt environments. As per ASTM C1202, a voltage of 60 V DC is applied across a concrete disc submerged in sodium chloride and sodium hydroxide solutions. The total charge passed (in coulombs) over 6 hours reflects the permeability level. Lower charge values indicate reduced ionic permeability, which is a direct result of a denser matrix and reduced pore connectivity due to nano-silica or graphene additions.

Fig4.Rapid Chloride Penetration Test

4.2.2. Chloride Migration Coefficient – NT BUILD 492

The chloride migration test provides a more direct measurement of chloride ion transport through concrete. Conducted as per NT BUILD 492, this test determines the non-steady-state chloride migration coefficient, offering a more realistic evaluation of service life in chloride-rich environments. The use of nanomaterials in concrete is expected to lower the migration coefficient due to enhanced pore blocking, which significantly delays corrosion initiation in reinforced concrete structures.

4.2.3. Water Absorption and Sorptivity – ASTM C642

Water absorption and sorptivity tests were performed to assess the capillary suction and porosity of the hardened concrete specimens. Following ASTM C642, oven-dried specimens were immersed in water, and weight gain was measured at specific intervals. Sorptivity reflects the initial rate of water absorption due to capillary action. A reduction in sorptivity and total absorption indicates a denser microstructure and better durability. Nano additives help refine the pore structure, reducing water ingress and thus enhancing service life.

4.3. Microstructural Tests

4.3.1. Scanning Electron Microscopy / Energy Dispersive X-ray Analysis (SEM/EDX)

SEM was employed to observe the surface morphology and microcrack formation in concrete samples at high magnifications. Energy Dispersive X-ray Spectroscopy (EDX) was used alongside SEM to identify the elemental composition of hydration products. These tools help evaluate the distribution of nano-silica or graphene oxide, the presence of calcium-silicate-hydrate (C–S–H) gels, and the healing of microcracks. Increased C–S–H density and reduced pore voids indicate improved material performance.

4.3.2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was conducted to study the chemical bonding changes and hydration mechanisms in cement paste. It helps identify the presence of functional groups like Si–O, C–H, and O–H, and changes in their intensity or position can indicate enhanced pozzolanic reaction and polymer–cement interaction. In nano-engineered concrete, FTIR helps confirm the chemical influence of graphene oxide and nano-silica on the hydration process and the formation of additional binding gels.

4.3.3. Thermogravimetric Analysis / Differential Thermal Analysis (TGA/DTA)

TGA/DTA was performed to quantify the thermal stability and hydration products in the cementitious matrix. TGA measures weight loss with increasing temperature, indicating decomposition of phases like C–S–H, portlandite (CH), and carbonates. DTA detects endothermic or exothermic reactions during heating. These techniques help understand the degree of hydration and quantify bound water, giving insights into how nano additives influence cement chemistry and thermal stability.

4.3.4. Mercury Intrusion Porosimetry (MIP)

MIP was used to determine the pore size distribution and total porosity of the concrete samples. The method involves forcing mercury into the pores under controlled pressure. It provides detailed data on pore diameter, cumulative pore volume, and critical pore entry size. A refined pore structure with smaller and fewer capillary pores suggests improved impermeability and durability, typically observed in concrete enhanced with nano-silica and graphene oxide.

4.3.5. Exposure Simulation

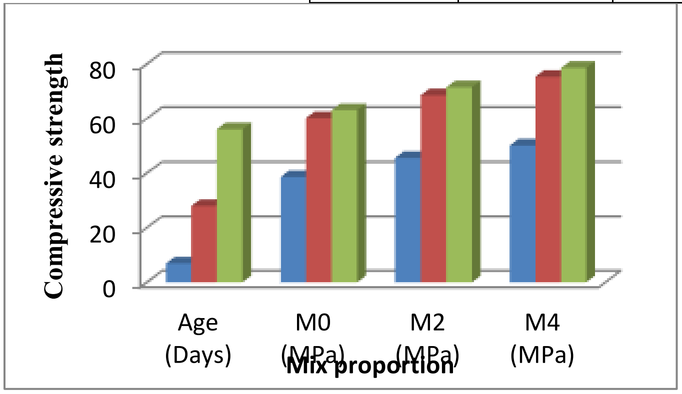
- 90-day cyclic exposure to:
    - Artificial seawater (NaCl 3.5%)
    - Wet-dry cycles (24h immersion, 24h drying at 45°C)

5.Results and Discussion

This section presents and interprets the results obtained from various tests conducted on control and nano-engineered high-performance concrete (NEHPC) mixes. The discussion is based on strength development, chloride resistance, water absorption, and microstructural performance. A comparative analysis of results for control mix (M0), nano-silica-modified mix (M2), and nano-silica + graphene oxide-modified mix (M4) is provided.

Table 3: Compressive Strength Analysis

Age (Days)	M0 (MPa)	M2 (MPa)	M4 (MPa)
7	38.5	45.6	50.1
28	60.2	68.5	75.2
56	63.1	71.4	78.6



Graph1: Compressive Strength Analysis

Discussion:

- The control mix (M0) achieved a compressive strength of 60.2 MPa at 28 days, meeting HPC requirements.
- Incorporating 1.0% nano-silica (M2) resulted in a ~**13.8% strength increase** at 28 days, attributed to enhanced pozzolanic activity forming additional calcium silicate hydrate (C-S-H) gel.
- The combined use of nano-silica and 0.03% GO (M4) led to a ~**25% increase in 28-day strength** compared to M0. This is due to:

  - Crack-bridging by GO
  - Acceleration of hydration by nano-silica
  - Improved bond at the interfacial transition zone (ITZ)
- At 56 days, strength gain was marginal but still significant in M4 due to continuing hydration and pore refinement.

5.2 RCPT (Rapid Chloride Penetration Test) Results

Table4. Rapid Chloride Penetration Test Results

Mix ID	Charge Passed (C)	Durability Rating
M0	2800	Moderate
M2	1150	Low
M4	610	Very Low

Discussion:

- The control mix (M0) had **moderate chloride permeability** per ASTM C1202, with 2800 Coulombs passed.
- M2 showed significant reduction (by ~58.9%) due to nano-silica blocking micro-capillaries and densifying the matrix.
- M4 achieved the best performance with **a 78% reduction** in charge passed compared to M0. This is attributed to:
  - GO forming impermeable flakes in the matrix, obstructing ion transport
  - Dense microstructure due to synergistic action of NS and GO
- According to ASTM guidelines:
  - 4000 C → High
  - 2000–4000 C → Moderate
  - 1000–2000 C → Low
  - <1000 C → Very Low
    Hence, **M4 transitions the concrete from "moderate" to "very low" permeability class** — ideal for marine structures.

5.3 Chloride Migration Coefficient

Table5.Chloride Migration Coefficient

Mix ID	Dnssm ($\times 10^{-12}$ m²/s)
M0	15.2
M4	4.8

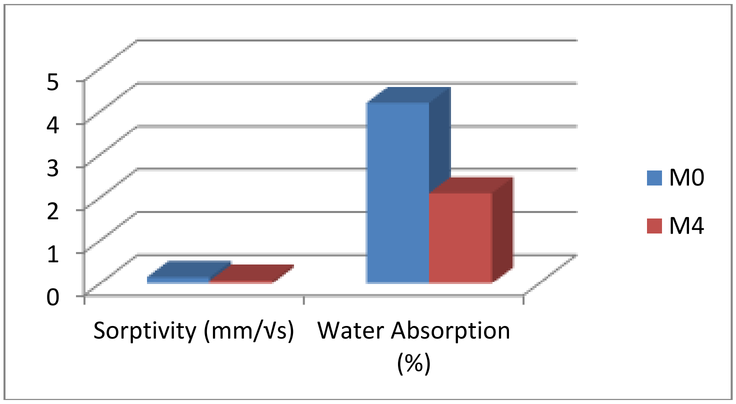
Discussion:

- The chloride migration coefficient quantifies how easily chloride ions move through the concrete matrix.
- M4 shows **a 68.4% reduction** in diffusivity, indicating a highly refined and dense matrix.
- Lower diffusion ensures extended service life in saline exposure conditions.

5.4 Water Absorption and Sorptivity

Table6. Water Absorption and Sorptivity

Mix	Sorptivity (mm/√s)	Water Absorption (%)
M0	0.145	4.2
M4	0.065	2.1



Graph2: Sorptivity & Water absorption Analysis

Discussion:

- Sorptivity measures capillary absorption of water in unsaturated conditions.
- M0 exhibited higher sorptivity due to capillary pore connectivity.
- In M4, sorptivity reduced by ~**55%**, and water absorption by **50%**, due to:
  - Reduction in pore diameter and connectivity
  - Nano-silica filling microvoids
  - GO creating tortuous paths for water ingress
- This reduction indicates **enhanced resistance to moisture and ion penetration**, critical in tidal and splash zones.

5.5 Microstructural Observations (SEM/EDX)

M0 Observations:

- Microcracks in ITZ
- Poor bond between paste and aggregate
- Presence of large $Ca(OH)_2$ crystals

M4 Observations:

- Compact microstructure
- Uniformly distributed C-S-H gel
- Flake-like GO visible in SEM, sealing microcracks
- Higher Si/Ca ratio in EDX confirms pozzolanic conversion

Interpretation:

- The morphology in M4 explains the improved macro-level performance.
- GO and nano-silica result in:
  - Higher packing density
  - Reduced pore continuity
  - Improved mechanical interlocking

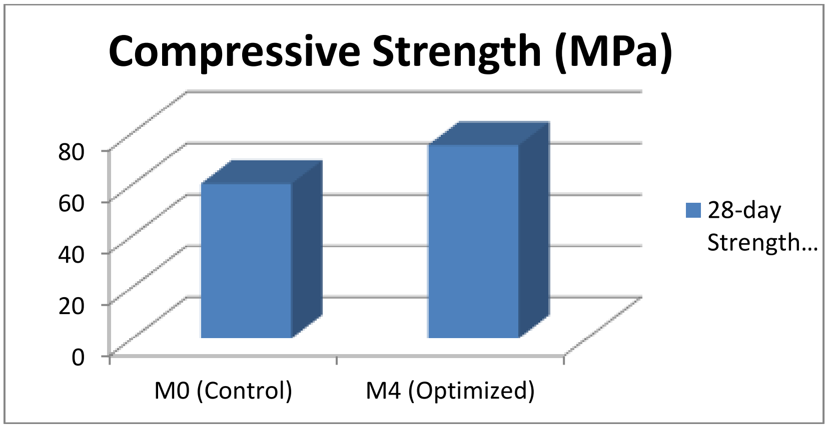
5.6 Thermogravimetric Analysis (TGA) and FTIR

- TGA shows reduced $Ca(OH)_2$ decomposition in M4 — signifying its consumption in pozzolanic reaction.
- FTIR spectrum confirms increased intensity in silicate bands (C-S-H) in M4 compared to M0.
- Supports the conclusion that **nano-silica accelerates hydration**, while GO strengthens the matrix chemically and physically.

Table7.Summary Results

Parameter	M0 (Control)	M4 (Optimized)	Improvement
28-day Strength (MPa)	60.2	75.2	+25%

RCPT (Coulombs)	2800	610	−78%
Water Absorption (%)	4.2	2.1	−50%
Chloride Migration Coefficient	15.2×10^{-12}	4.8×10^{-12}	−68%



Graph3: Compressive Strength Analysis

6.CONCLUSION

This study has demonstrated that the incorporation of nano-silica and graphene oxide significantly enhances the performance of high-performance concrete (HPC), especially under chloride-rich marine environments. The nano-silica contributes to the densification of the microstructure by promoting additional formation of calcium silicate hydrate (C-S-H), which refines the pore system and improves strength development. Meanwhile, the inclusion of graphene oxide not only contributes to mechanical enhancement by bridging microcracks but also provides a barrier to ion and water ingress due to its impermeable flake-like structure.

The optimized mix containing 1.0% nano-silica and 0.03% graphene oxide (Mix M4) exhibited superior compressive strength, showing a 25% increase over the control mix. More importantly, it demonstrated remarkable improvement in durability performance, including a 78% reduction in chloride permeability as measured by RCPT, a 68% decrease in chloride diffusion coefficient, and a 50% reduction in water absorption. Microstructural analyses (SEM, EDX, and TGA) confirmed a denser, less porous matrix with stronger interfacial transition zones and fewer free calcium hydroxide crystals.

These findings affirm that nano-engineered HPC has substantial potential for application in marine infrastructure, where resistance to chloride penetration is critical for long-term serviceability. The combined action of nano-silica and graphene oxide leads to enhanced durability, reduced maintenance requirements, and extended lifespan of structures exposed to harsh environments. Therefore, the use of nano-engineered materials in concrete design should be strongly considered in future coastal and offshore construction projects.

7.REFERENCES

1. Mehta, P. K., & Monteiro, P. J. M. (2014). *Concrete: Microstructure, Properties, and Materials* (4th ed.). McGraw-Hill Education.
2. Neville, A. M. (2011). *Properties of Concrete* (5th ed.). Pearson Education.
3. Zhang, Y., Li, Y., & Wang, L. (2022). “Effect of nano-silica on mechanical properties and microstructure of concrete.” *Construction and Building Materials*, 310, 125219. https://doi.org/10.1016/j.conbuildmat.2021.125219
4. Siddique, R., & Mehta, A. (2021). “Recent advancements on the role of nano-silica in concrete.” *Construction and Building Materials*, 271, 121523. https://doi.org/10.1016/j.conbuildmat.2020.121523
5. Chand, R., Singh, P., & Yadav, V. (2021). “Graphene oxide incorporation in cementitious composites: A review.” *Cement and Concrete Research*, 149, 106572. https://doi.org/10.1016/j.cemconres.2021.106572

6. ASTM C1202-19. (2019). *Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration*. ASTM International.
7. NT BUILD 492. (1999). *Concrete, mortar and cement-based repair materials: Chloride migration coefficient from non-steady-state migration experiments*. Nordtest Method.
8. IS 456:2000. *Plain and Reinforced Concrete – Code of Practice*. Bureau of Indian Standards.
9. IS 516:2021. *Method of Tests for Strength of Concrete*. Bureau of Indian Standards.
10. IS 12269:2013. *Ordinary Portland Cement, 53 Grade – Specification*. Bureau of Indian Standards.
11. Li, G., Wang, P., & Zhao, X. (2020). "Durability and microstructure of concrete with nano-particles under marine exposure." *Journal of Cleaner Production*, 258, 120579. https://doi.org/10.1016/j.jclepro.2020.120579
12. Ghosh, R., & Bhattacharjee, B. (2020). "Performance of nano-silica modified concrete in coastal environments." *Journal of Materials in Civil Engineering*, 32(5), 04020090.
13. Dey, A., & Mandal, S. (2021). "Synergistic effects of nano-silica and graphene oxide on mechanical and durability properties of cement mortar." *Materials Today: Proceedings*, 46, 8427–8431.
14. Wang, Q., Yan, P., & Zhang, B. (2019). "Comparative study on the effect of nano-silica and silica fume on concrete performance." *Construction and Building Materials*, 194, 66–75.
15. Liu, R., & Cui, Y. (2023). "Chloride ion transport properties of concrete with graphene oxide: Experimental study and modeling." *Cement and Concrete Composites*, 134, 104809.
16. Banthia, N., & Gupta, R. (2019). "Durability of high performance fiber-reinforced concrete in marine environments." *Journal of Advanced Concrete Technology*, 17(3), 151–162.
17. Shi, C., & Wang, D. (2021). "Durability of nanomaterials-modified cement-based materials in aggressive environments." *Nanomaterials*, 11(1), 121. https://doi.org/10.3390/nano11010121