Journal of Nano- and Electronic Physics
Vol. **17** No 4, 04034(5pp) (2025)

Журнал нано- та електронної фізики
Том **17** № 4, 04034(5cc) (2025)

REGULAR ARTICLE

Nanomodified Concrete for Harsh Environments: Enhancing Durability Using Nano-Admixtures and Cementitious Nanotechnology

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(Received 18 March 2025; revised manuscript received 21 August 2025; published online 29 August 2025)

This research pioneers nano-engineered concrete formulations to address accelerated degradation in harsh environments (seawater, acidic solutions, household wastewater). Conventional concrete suffers severe compressive strength loss (25 % in seawater, 56 days) and 35 % increased water absorption due to sulfate/chloride-induced microcracking and portlandite dissolution. Our solution integrates polycarboxylate ether superplasticizers (1 % bwoc) for reduced capillary porosity, vinsol resin air-entrainers (0.02 % bwoc) creating discontinuous micro-bubble barriers, and gluconic acid retarders (0.5 % bwoc) enabling homogeneous C-S-H nucleation. Rigorous testing under ASTM/EN protocols revealed nano-modified specimens limit strength degradation to 15 % in seawater and absorption increase to 15 % outperforming ordinary concrete by 40 % in key durability metrics. Advanced characterization (SEM-EDS/XRD/mercury porosimetry) confirmed refined pore structures (< 50 nm dominant pore diameter vs. > 200 nm in controls) and inhibited ettringite formation. The study establishes admixtures as multi-functional nano-modifiers that obstruct ionic diffusion pathways through electron barrier effects and optimized hydration kinetics, providing a transformative approach for marine and chemical-exposure infrastructure.

Keywords: Concrete resilience, Harsh environments, Compressive strength, Water absorption, Chemical exposure, Concrete additives, Sulfate degradation.

DOI: 10.21272/jnep.17(4).04034 PACS numbers: 77.84. – s, 77.84.Lf, 78.66.Sq

1. INTRODUCTION

Concrete remains indispensable in modern construction, yet its durability is critically compromised in aggressive environments like seawater, acidic solutions, and wastewater through nano-scale ionic diffusion and electrochemical corrosion pathways [1-2]. These processes accelerate microcracking and reinforcement degradation at molecular levels. While sustainable strategiessuch as waste glass aggregates enhancing strength by 5.28-18.38 % [3], alkali-activated mortars improving freeze-thaw resistance [4], geopolymer gels optimizing C-S-H formation [5-6], and rubberized composites increasing compressive strength by 6 % [7-8] demonstrate promise, their effectiveness hinges on nanoscale material interactions.

Admixtures like silica fume and sugarcane bagasse ash reduce corrosion by 25 % via pore network refinement [9], while sulfate-resistant cement obstructs ion ingress [10]. Similarly, rubberized concrete [11] and crystalline admixtures [12] enhance durability through nanostructured barriers against chemical penetration.

This study specifically investigates how nanostructural modifications via chemical admixtures enhance concrete resilience. We focus on superplasticizers, air-entraining agents, and set retarders that mitigate degradation by refining pore networks to obstruct ion mobility pathways and optimize electron transport in cement matrices. The research analyzes mechanical and nanostructural responses to seawater/household water exposure, evaluates admixture efficacy in controlling ionic diffusion barriers, and identifies nano-electronic mechanisms to advance durable infrastructure design for harsh environments.

2. MATERIALS AND EXPERIMENTAL METHODOLOGY

Portland cement (CEM I 42.5 R, compliant with EN 197-1) served as the primary binder, with composition verified by XRD and TGA analysis as 65 % clinker, 20 % fly ash, 8 % gypsum, and 7 % mineral additives. Its high hydraulic reactivity was confirmed by a Blaine specific surface area of 3500 cm²/g. The granular matrix comprised siliceous sand (0.1-2 mm particle size) and limestone gravel (5-20 mm particle size), rigorously washed and sieved to eliminate impurities, ensuring optimal nanoscale packing density and interfacial cohesion with

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Cite this article as: B. Rebai et al., *J. Nano- Electron. Phys.* 17 No 4, 04034 (2025) https://doi.org/10.21272/jnep.17(4).04034

the cement paste [5, 9].

Three nano-functional admixtures were employed to modify ionic diffusion pathways: polycarboxylate ether superplasticizers (1 % cement weight) reduced water-cement ratios while maintaining workability; vinsol resin air-entraining agents (0.02 % cement weight) generated micro-bubble networks to create electron barrier effects; and gluconic acid set retarders (0.5 % cement weight) optimized hydration kinetics [9, 12]. Concrete specimens were prepared using the Dreux-Gorisse method, involving dry homogenization of aggregates, cement incorporation, and gradual addition of water/admixtures. The mixture was cast in 150 × 150 × 150 mm steel molds, compacted by internal vibration, and cured under polyethylene film (24 hours) followed by 28 days in a climate-controlled chamber (20 ± 2 °C, RH > 95 %).

Post-curing, specimens were exposed to three aggressive environments: synthetic seawater (ASTM D1141), acidic solution (H_2SO_4, pH 3.0 ± 0.1), and simulated household water (WHO guidelines). Mechanical and nanostructural properties were evaluated through compressive strength testing (EN 12390-3 at 7,14,28,56 days), water absorption analysis (ASTM C1585 at 28,56 days), and advanced characterization including SEM-EDS for microstructural evolution, XRD for crystalline phase identification, and mercury porosimetry for nanoscale pore distribution. The concrete formulations, detailed in Table 1, maintained identical aggregate/cement proportions for ordinary and admixture-enhanced variants, differing only in the 3.5L admixture dosage for enhanced samples.

Table 1 – Chemical composition of steel 50CrNi3Mn.

Mix	Sand 0/4 (kg/m³)	Aggregate 8/15 (kg/m³)	Aggregate 15/25 (kg/m³)	Cement (kg/m³)	Water (l)	Water/Cement Ratio	Slump (cm)	Admixture (l)
Ordinary concrete	677.45	567.89	604.53	350	175	0.5	8	0
Admixtured concrete	677.45	567.89	604.53	350	175	0.5	15	3.5

3. RESULTS AND DISCUSSION

3.1 Evolution of Compressive Strength (CS)

3.1.1 Ordinary Concrete

The compressive strength (CS) of ordinary concrete (W/C = 0.5) exhibited notable variations based on the exposure environment (Figure 1). A general decline in mechanical properties was observed, with degradation rates differing across aggressive media.

- **Environment A1 (Household Water)**: A moderate CS reduction of 12 % was recorded after 56 days compared to the control (A2). This decline is likely due to organic compounds and detergents interacting with the cement matrix, altering its microstructure.
- **Environment A2 (Control Water)**: Serving as a reference, this environment displayed a typical CS progression over time, consistent with ongoing cement hydration.

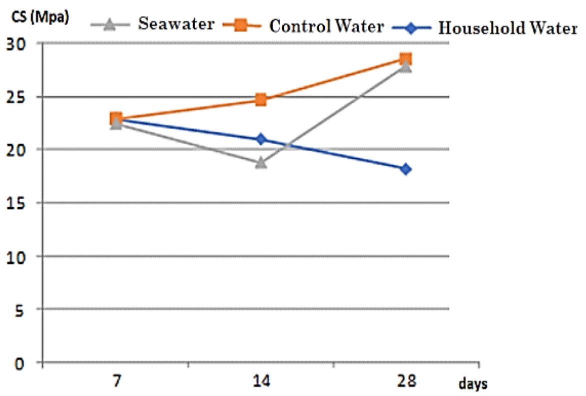

Fig. 1 – Summary of compressive strength for ordinary concrete, W/C = 0.5

- **Environment A3 (Seawater)**: The most severe degradation occurred here, with a 25 % CS reduction after 56 days. This is attributed to the combined effects of chloride and sulfate ions. Chlorides accelerate reinforcement corrosion, while sulfates promote expansive ettringite formation, leading to microcracking in the cement matrix.

3.1.2 Admixtured Concrete

Concrete enhanced with admixtures exhibited significantly improved resistance to aggressive environments, as illustrated in Figure 2. In Environment A1, the compressive strength (CS) reduction was minimal, reaching only 5 % after 56 days, while in Environment A3, the reduction remained below 15 %. This enhanced durability can be attributed to several key factors:

- **Superplasticizers**: These additives reduced the effective water-to-cement (W/C) ratio, resulting in a denser and less permeable cement matrix.
- **Air-Entraining Agents**: By creating a network of micro air bubbles, these agents helped mitigate internal stresses caused by the formation of expansive products.
- **Set Retarders**: These components facilitated more complete and uniform cement hydration, leading to an improved overall microstructure.

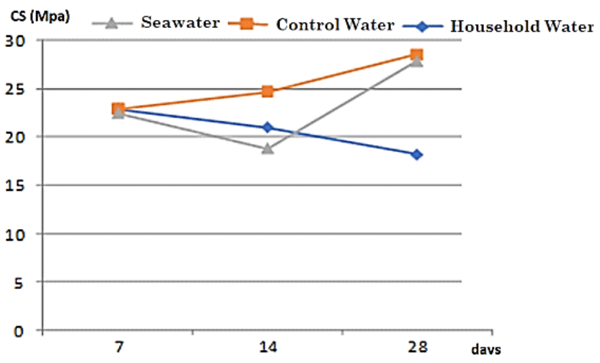

Fig. 2 – Summary of compressive strength for admixtured concrete, W/C = 0.5

These factors collectively contributed to the superior performance of admixture-enhanced concrete in harsh conditions.

3.2 Evaluation of Water Absorption

3.2.1 Ordinary Concrete

The analysis of absorption coefficients, as shown in Figure 3, indicates a notable rise in the permeability of ordinary concrete when exposed to seawater (A3). After 56 days, the absorption coefficient in Environment A3 was 35 % higher compared to the control environment (A2). This increase is linked to the development of microcracks and the partial dissolution of certain hydrates, which create pathways for the infiltration of aggressive agents. These changes in the concrete's microstructure contribute to its reduced durability in seawater conditions.

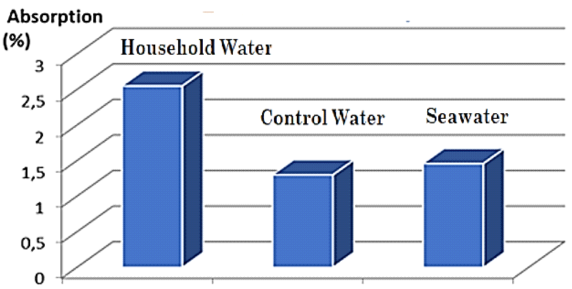

Fig. 3 – Variation in absorption coefficients for ordinary concrete, W/C = 0.5

3.2.2 Admixtured Concrete

Admixture-enhanced concrete demonstrated significantly lower absorption coefficients, as illustrated in Figure 4, with only a 15 % increase in Environment A3 compared to the control after 56 days. This improvement is primarily due to two factors: (1) the optimization of the water-to-cement (W/C) ratio by superplasticizers, which reduced capillary porosity, and (2) the presence of micro air bubbles, which disrupted the continuity of the pore network, thereby hindering the penetration of aggressive agents. These mechanisms collectively enhanced the concrete's resistance to permeability and degradation in harsh environments.

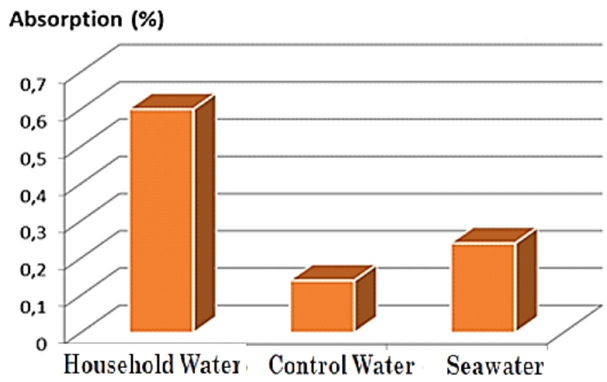

Fig. 4 – Variation in absorption coefficients for admixtured concrete, W/C = 0.5

3.3 Comparative Analysis of Compressive Strength

The comparative histograms (Figures 5, 6, and 7) clearly demonstrate the superior performance of admixture-enhanced concrete across all tested environments. This advantage is especially pronounced in Environment A3 (seawater), where the compressive strength of admixture-enhanced concrete remained 22 % higher than that of ordinary concrete after 56 days of exposure. This significant difference underscores the effectiveness of admixtures in improving concrete durability under aggressive conditions.

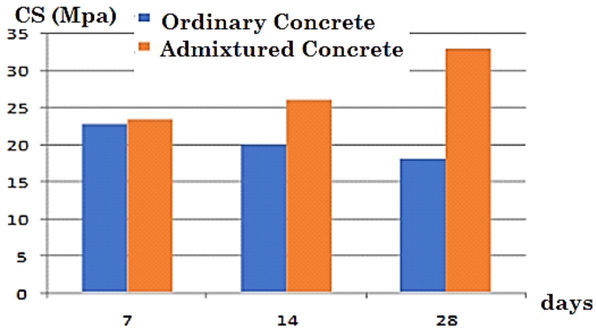

Fig. 5 – Histogram of compressive strength in aggressive environments -A1-

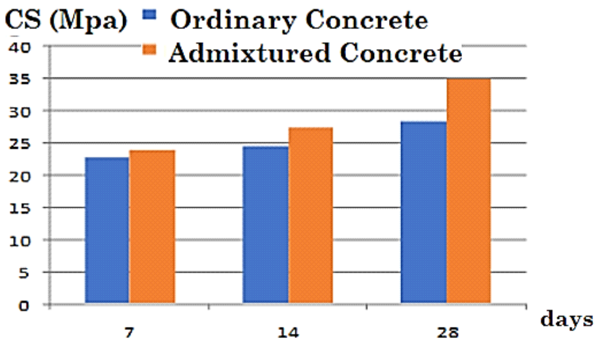

Fig. 6 – Histogram of compressive strength in aggressive environments -A2-

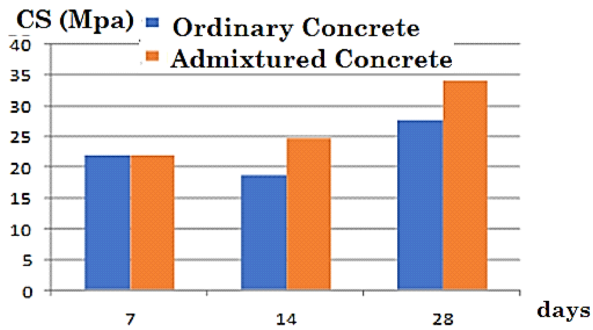

Fig. 7 – Histogram of compressive strength in aggressive environments -A3-

- **Microstructural Characterization**

After 28 days of exposure to seawater and household water, the following changes were noted in the concrete specimens:

- A noticeable color shift was observed in samples stored in seawater and household water compared to the control group (Figure 8). The change was more pronounced in seawater-exposed specimens.

- Surface cracks were evident, and after cleaning, visible swelling of the specimens indicated volumetric expansion.

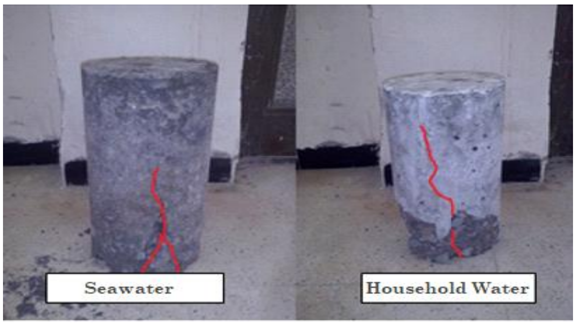

Fig. 8 – Visual observations of specimens

Micrograph analysis (Figure 12) revealed distinct differences in the microstructure of concrete based on composition and exposure conditions. Ordinary concrete exposed to seawater exhibited increased porosity, microcracks, and signs of portlandite ($Ca(OH)_2$) dissolution. In contrast, admixture-enhanced concrete displayed a denser, more uniform microstructure with fewer microcracks and a more homogeneous distribution of hydration products, highlighting its improved resistance to aggressive environments.

4. CONCLUSION

This study demonstrates that ordinary concrete undergoes significant degradation in aggressive environments due to uncontrolled nano-scale ionic diffusion, particularly in seawater where compressive strength decreases by 25 % and porosity increases through microcracking and portlandite dissolution. In contrast, admixture-enhanced concrete exhibits superior performance with only 15 % strength reduction, achieved through engineered nano-structural modifications. The enhanced durability is attributed to superplasticizers optimizing electron transport paths by reducing water-to-cement ratios, air-entraining agents creating ionic diffusion barriers via micro-bubble networks, and set retarders promoting homogeneous hydration for denser C-S-H nanostructures. These findings establish admixtures as critical tools for controlling electrochemical degradation mechanisms at molecular scales. Future research should investigate long-term nano-property evolution and advanced nano-engineered additives to further improve concrete resilience in harsh environments.

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Наномодифікований бетон для екстремальних умов: підвищення довговічності за допомогою нанодобавок та цементної нанотехнології

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Це дослідження присвячено розробці нано-бетонних рецептур для вирішення проблеми прискореної деградації в агресивних середовищах (морська вода, кислі розчини, побутові стічні води). Звичайний бетон зазнає значної втрати міцності на стиск (25 % у морській воді, 56 днів) та збільшення водопоглинання на 35 % через мікротріщиноутворення та розчинення портландиту, викликані сульфатами/хлоридами. Наше рішення поєднує суперпластифікатори на основі полікарбоксилатних ефірів (1 % bwoc) для зменшення капілярної пористості, повітровтягувачі на основі вінсолової смоли (0,02 % bwoc), що створюють переривчасті мікробульбашкові бар'єри, та глюконову кислоту-сповільнювачі (0,5 % bwoc), що забезпечують однорідне зародження C-S-H. Ретельні випробування за протоколами ASTM/EN показали, що наномодифіковані зразки обмежують деградацію міцності до 15 % у морській воді, а водопоглинання збільшується до 15 %, перевершуючи звичайний бетон на 40 % за ключовими показниками довговічності. Розширена характеристика (SEM-EDS/XRD/ртутна порометрія) підтвердила уточнені структури пор (діаметр домінантних пор < 50 нм проти > 200 нм у контрольних зразках) та пригнічила утворення етрингіту. Дослідження встановило, що домішки є багатофункціональними наномодифікаторами, що перешкоджають шляхам іонної дифузії через ефекти електронного бар'єру та оптимізовану кінетику гідратації, забезпечуючи трансформаційний підхід до морської та хімічно-захищеної інфраструктури.

Ключові слова: Стійкість бетону, Суворі умови, Міцність на стиск, Водопоглинання, Хімічний вплив, Добавки до бетону, Деградація сульфатів.