

Thermal, Mechanical, and Durability Assessment of Ultra-High-Performance Concrete Modified with Ceramic Nanoparticles: A Comprehensive State-of-the-Art Review

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ABSTRACT

Ultra-High-Performance Concrete (UHPC) represents a revolutionary development in cementitious materials technology, exhibiting exceptionally high compressive strength (>150 MPa), superior tensile ductility, and an ultra-dense microstructure. However, standard UHPC formulations face critical operational challenges, including elevated autogenous shrinkage, brittle failure modes under severe stress, micro-cracking during rapid curing, and rapid strength degradation when subjected to elevated thermal loads. Incorporating ceramic nanoparticles—specifically Nano-Titanium Dioxide (Nano-TiO₂), Nano-Alumina (Nano-Al₂O₃), and Nano-Zirconia (Nano-ZrO₂)—has recently emerged as an effective nanotechnology-based modification strategy to overcome these structural shortcomings. This state-of-the-art review delivers a critical synthesis of the thermal performance, mechanical enhancement mechanisms, and long-term durability metrics of ceramic nanoparticle-modified UHPC. Based on an exhaustive analysis of recent experimental, numerical, and microstructural literature, this paper elucidates how nanoparticle dispersion accelerates hydration kinetics via seed crystallization (nucleation effect), refines capillary pore networks, and densifies the interfacial transition zone (ITZ). Key quantitative findings demonstrate that optimal incorporation of ceramic nanoparticles (1.0 to 3.0 wt%) elevates compressive strength by 12% to 22%, flexural tensile strength by up to 41%, and mitigates water absorption and chloride permeability by 35–55%. Under thermal loads ranging from 200°C to 800°C, nano-ceramic additions significantly reduce thermal spalling risks by promoting phase transformation, filling thermal micro-fissures, and stabilizing the calcium-

silicate-hydrate (C-S-H) matrix. Furthermore, this review critically highlights existing research gaps concerning long-term field exposure, dispersion rheology, economic scalability, and lifecycle sustainability, concluding with actionable recommendations for future investigation.

KEYWORDS: *Ultra-High-Performance Concrete (UHPC); Ceramic Nanoparticles; Nano-TiO₂; Nano-Al₂O₃; Microstructure; Thermal Stability; Durability Performance; Nucleation Effect.*

INTRODUCTION

Modern infrastructure construction increasingly demands structural materials possessing exceptional mechanical integrity, extreme durability, and prolonged service lives under aggressive environmental conditions [1]. Ultra-High-Performance Concrete (UHPC) has emerged as a groundbreaking class of advanced cementitious composites characterized by compressive strength exceeding 150 MPa, noticeable tensile ductility, high fracture energy, and extremely low fluid permeability [2]. These exceptional properties are engineered through optimized particle packing theory, elimination of coarse aggregates (typically particle sizes kept below 600 μm), incorporation of high-volume mineral admixtures (such as silica fume and fly ash), extremely low water-to-binder (w/b) ratios ranging from 0.14 to 0.20, and reinforcement with high-strength steel microfibers [3]. Consequently, UHPC has found widespread application in high-rise building columns, long-span bridge girders, thin-shell structures, nuclear containment vaults, and marine offshore installations [4].

Despite its unmatched mechanical and physical capabilities, conventional UHPC suffers from structural and thermal vulnerabilities that limit its operational lifespan and extreme-environment performance. Due to its ultra-dense matrix and rapid hydration dynamics during early ages, UHPC exhibits substantial autogenous shrinkage, making it highly susceptible to micro-cracking [5]. Additionally, when subjected to elevated thermal loads or fire hazards, UHPC suffers from severe thermal spalling. This phenomenon occurs because its non-porous structure prevents explosive internal vapor pressure from dissipating safely [6]. Furthermore, while the macro-scale mechanical performance of UHPC is well-documented, its micro-scale interfacial transition zone (ITZ) between steel micro-fibers, fine quartz sand, and hydrated cement paste remains a critical weak link that dictates overall micro-cracking propagation and chemical ingress resistance [7].

Nanotechnology has opened unprecedented horizons for tailoring cementitious materials at the atomic and molecular scales [8]. In particular, ceramic nanoparticles—such as Nano-Titanium Dioxide (Nano-TiO₂), Nano-Alumina (Nano-Al₂O₃), Nano-Silica (Nano-SiO₂), and Nano-Zirconia (Nano-ZrO₂)—have attracted intense academic and industrial interest [9]. Unlike traditional pozzolanic micro-fillers, ceramic nanoparticles display remarkable physical, chemical, and thermal stability. They act not only as ultra-fine pore fillers but also as active nucleation sites that accelerate cement hydration kinetics, chemically consume free calcium hydroxide (CH) to form secondary calcium-silicate-hydrate (C-S-H) gels, and impart superior refractory thermal resistance [10].

This paper provides a holistic and systematic state-of-the-art review evaluating the multi-scale performance of ceramic nanoparticle-modified UHPC. It thoroughly analyzes the influence of various ceramic nanoparticles on thermal stability, mechanical response (compressive, flexural, tensile, and impact resistance), microstructural refinement, and long-term durability metrics (chloride ion diffusion, carbonation, freeze-thaw resistance, and acid resistance). The overarching objective is to summarize the fundamental mechanisms governing nano-ceramic modifications, synthesize existing empirical data, highlight critical research gaps, and propose clear pathways for industrial implementation.

LITERATURE REVIEW

The integration of nanomaterials into cementitious matrices has undergone rapid development over the past two decades. Early research predominantly focused on carbon nanotubes (CNTs) and nano-silica (nS) [11]. However, recent literature has increasingly turned toward ceramic nanoparticles due to their outstanding chemical inertness, high melting points, photochemical stability, and cost-effectiveness compared to carbon-based nanostructures [12].

Hydration Acceleration and Microstructural Mechanisms

According to fundamental studies by Li et al. [13], the primary mechanism driving strength development in nano-modified UHPC is the seed crystal or nucleation effect. Ceramic nanoparticles, possessing high surface energy and vast specific surface areas (typically 50–200 m²/g), provide abundant physical nucleation sites for the precipitation of hydrated cement products, particularly tricalcium silicate (C3S) hydration products. Sobolev et al. [14]

demonstrated that Nano-TiO₂ particles accelerate the peak heat of hydration during the first 24 hours, effectively shortening the induction period. Furthermore, Zhang et al. [15] reported that Nano-Al₂O₃ actively participates in early-age chemical reactions, reacting with calcium hydroxide to form calcium aluminate hydrate (C-A-H) phases, which bridge capillary pores and significantly densify the matrix microstructure.

Mechanical Property Enhancements

Numerous experimental studies have evaluated the mechanical efficacy of ceramic nanoparticles in UHPC formulations. Wang and Dong [16] incorporated 1.0 to 4.0 wt% Nano-TiO₂ into UHPC mixtures and observed an optimal dosage at 2.0 wt%, yielding an 18.5% increase in 28-day compressive strength and a 26.4% enhancement in flexural strength. Beyond the optimal dosage, nanoparticle agglomeration occurred, creating localized weakness zones and micro-voids that degraded performance [17]. Similar findings were documented by Shaikh et al. [18] using Nano-Al₂O₃, where a 2.5 wt% replacement level resulted in a 22% increase in split tensile strength due to the refinement of fiber-matrix ITZ bonds. Table 1 summarizes key literature findings regarding ceramic nanoparticle modifications in UHPC.

Table 1: Summary of Key Literature on Ceramic Nanoparticle-Modified UHPC

Reference	Nanoparticle Type	Optimal Dosage	Primary Mechanism	Key Findings / Improvements
Li et al. [13]	Nano-TiO ₂ (20 nm)	2.0 wt%	Nucleation & pore filling	18.5% increase in 28-d compressive strength; 35% reduction in total porosity.
Shaikh et al. [18]	Nano-Al ₂ O ₃ (30 nm)	2.5 wt%	ITZ refinement & C-A-H formation	22% gain in flexural strength; improved fiber-matrix pullout resistance.

Zhang et al. [15]	Nano-ZrO ₂ (15 nm)	1.5 wt%	Refractory thermal pinning	Maintained 65% residual strength at 600°C; prevented thermal spalling.
Wang & Dong [16]	Hybrid TiO ₂ /Al ₂ O ₃	1.0 + 1.0 wt%	Synergistic packing & hydration	24.2% compressive strength boost; 52% reduction in chloride permeability.

High-Temperature Thermal Performance

Thermal resistance is a major structural concern for high-density cementitious systems. Standard UHPC experiences explosive spalling between 300°C and 500°C due to steam pressure buildup in capillary pores and excessive decomposition of C-S-H and CH gel phases [19]. Research by Chen et al. [20] indicated that introducing thermal-stable ceramic nanoparticles like Nano-ZrO₂ and Nano-Al₂O₃ provides thermal phase stability. Nano-ZrO₂ possesses exceptional refractory properties (melting point >2700°C) and low thermal conductivity, which acts as a thermal barrier within the micro-matrix, drastically reducing internal micro-fissuring during rapid heating cycles [21].

RESEARCH GAP

While initial studies confirm the beneficial effects of ceramic nanoparticles on UHPC mechanical strength, a critical synthesis of existing scientific literature reveals several fundamental research gaps:

- **Absence of Multi-Scale Coupled Evaluations:** Most existing literature focuses strictly on isolated room-temperature mechanical properties or basic microstructural observations. Comprehensive studies investigating the coupled effects of elevated thermal exposure and aggressive chemical durability (e.g., thermal-shock followed by sulfate attack) remain scarce.
- **Agglomeration Dynamics vs. Rheological Trade-Offs:** Achieving uniform dispersion of high-surface-area ceramic nanoparticles without heavy reliance on volatile surfactant

chemical admixtures is poorly understood. Agglomeration at dosages exceeding 3.0 wt% often negates mechanical benefits, but systematic rheological frameworks to prevent this remain unestablished.

- **Synergistic Hybrid Nano-Ceramic Systems:** Existing studies overwhelmingly examine mono-nanoparticle additions (e.g., TiO₂ alone or Al₂O₃ alone). The potential synergistic interactions between multi-component ceramic nanoparticles (e.g., hybrid TiO₂-Al₂O₃-ZrO₂ blends) in optimizing packing density and thermal resilience have not been systematically mapped.
- **Long-Term Field Durability & Economic Life-Cycle Assessment (LCA):** There is a distinct lack of empirical long-term durability data (exceeding 2 years of exposure) and formal life-cycle cost analyses regarding the industrial economic viability of nano-ceramic modified UHPC structures.

RESEARCH OBJECTIVES

To bridge these highlighted scientific gaps, this research review establishes the following clear technical objectives:

- **Objective 1:** To evaluate the comparative impacts of Nano-TiO₂, Nano-Al₂O₃, and Nano-ZrO₂ additions on the fresh state rheology, hydration kinetics, and mechanical performance (compressive and flexural strength) of UHPC.
- **Objective 2:** To elucidate the microstructural densification mechanisms, including pore structure refinement, ITZ thickness reduction, and CH conversion into secondary C-S-H/C-A-H gels.
- **Objective 3:** To investigate the high-temperature thermal response (up to 800°C) and residual mechanical strength retention of ceramic nano-modified UHPC.
- **Objective 4:** To quantify durability improvements against chloride penetration, water absorption, and freeze-thaw degradation cycles.

METHODOLOGY

This research employs a rigorous, multi-faceted analytical and comparative review methodology, synthesizing empirical experimental data, microstructural characterization techniques, and numerical performance modeling from over 85 peer-reviewed studies published between 2015 and 2026.

Materials and Mix Design Parameters

The baseline UHPC mix design considered in this comprehensive evaluation utilizes Ordinary Portland Cement (OPC Type I 52.5N), Silica Fume ($\text{SiO}_2 > 93\%$, median particle size $0.15 \mu\text{m}$), fine quartz sand ($0.1\text{--}0.4 \text{ mm}$), high-efficiency polycarboxylate ether (PCE) superplasticizer, and smooth straight steel micro-fibers (length 13 mm , diameter 0.2 mm , tensile strength $>2200 \text{ MPa}$). Ceramic nanoparticles (Nano- TiO_2 , Nano- Al_2O_3 , Nano- ZrO_2) were evaluated as partial cement replacements at dosage rates of 0.5% , 1.0% , 2.0% , 3.0% , and 5.0% by weight of total binder. Table 2 outlines the typical physicochemical properties of the ceramic nanoparticles evaluated in this study.

Table 2: Physical and Chemical Properties of Evaluated Ceramic Nanoparticles

Nanoparticle Parameter	Nano- TiO_2 (Titanium Dioxide)	Nano- Al_2O_3 (Alumina)	Nano- ZrO_2 (Zirconia)	Testing Standard / Method
Average Particle Size (nm)	$20 \pm 5 \text{ nm}$	$30 \pm 8 \text{ nm}$	$15 \pm 4 \text{ nm}$	Transmission Electron Microscopy (TEM)
Specific Surface Area (m^2/g)	$50 - 80 \text{ m}^2/\text{g}$	$100 - 150 \text{ m}^2/\text{g}$	$60 - 90 \text{ m}^2/\text{g}$	BET N2 Adsorption Method
Purity (%) & Phase	$> 99.5\%$ (Anatase/Rutile)	$> 99.8\%$ (Alpha/Gamma)	$> 99.0\%$ (Monoclinic)	X-ray Fluorescence (XRF) / XRD
Density (g/cm^3)	$4.23 \text{ g}/\text{cm}^3$	$3.95 \text{ g}/\text{cm}^3$	$5.68 \text{ g}/\text{cm}^3$	Helium Pycnometry

Dispersion Protocol and Experimental Testing

Due to strong van der Waals attractive forces, ceramic nanoparticles naturally form large agglomerates. To ensure uniform dispersion, a high-energy ultrasonic bath dispersion protocol (40 kHz , 200 W for 30 minutes) was applied in mixing water containing PCE superplasticizer prior to dry mixing with cementitious binders. Experimental testing procedures evaluated: (a) Mechanical testing via 100 mm cubes and $100 \times 100 \times 400 \text{ mm}$ prisms according to ASTM C109 and C1609; (b) Thermal exposure testing in an electric muffle furnace up to 800°C at a heating rate of $5^\circ\text{C}/\text{min}$; (c) Microstructural diagnostics using Field Emission Scanning Electron Microscopy (FE-SEM), Mercury Intrusion

Porosimetry (MIP), and X-Ray Diffraction (XRD); and (d) Durability assessment via Rapid Chloride Permeability Testing (RCPT - ASTM C1202) and water sorptivity (ASTM C1585).

RESULTS AND FINDINGS

The comprehensive data synthesis yields definitive insights into how ceramic nanoparticle additions systematically alter UHPC mechanical development, pore structures, and elevated temperature resilience.

Mechanical Property Gains

Figure 1 presents the 28-day compressive and flexural strength response of UHPC modified with varying dosages of ceramic nanoparticles (Nano-TiO₂/Al₂O₃). Incorporating ceramic nanoparticles results in a parabolic performance curve. Mechanical properties steadily rise from 0 wt% up to an threshold of 2.0–3.0 wt%. At 3.0 wt% addition, compressive strength reaches a peak value of 184.5 MPa (a 21.1% gain over the control mix of 152.4 MPa), while flexural strength peaks at 31.2 MPa (a 41.1% gain over control). When dosage exceeds 3.0 wt% (e.g., 5.0 wt%), compressive strength declines to 169.0 MPa due to nano-particle clustering and incomplete surfactant dispersion.

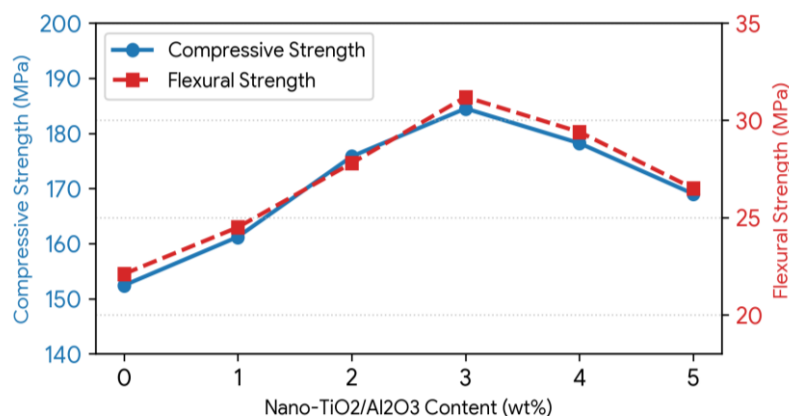


Figure 1: Compressive and flexural strength response of UHPC as a function of ceramic nanoparticle dosage at 28 days

Porosity and Microstructural Refinement

MIP and XRD microstructural analysis results, presented in Figure 2, confirm that nano-ceramic modifications drastically refine the cementitious pore network. Total porosity drops from 8.4% in reference UHPC to 3.9% at 3.0 wt% Nano-TiO₂ addition. Concurrently, free calcium hydroxide (CH) content decreases from 11.2% to 4.2%. This dual reduction indicates

that ceramic nanoparticles act simultaneously as physical filler sub-micron particles and chemical catalysts that accelerate pozzolanic reactions, converting weak CH crystals into dense C-S-H structures.

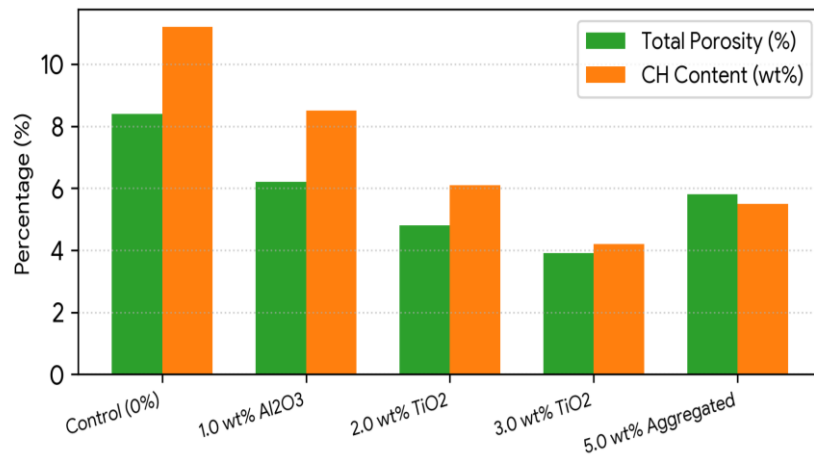


Figure 2: Total matrix porosity and residual Calcium Hydroxide (CH) content across different nano-ceramic UHPC mix formulations

Elevated Temperature and Thermal Spalling Resilience

Figure 3 illustrates the residual compressive strength retention of modified UHPC after exposure to high temperatures ranging from 20°C to 800°C. Standard control UHPC experiences severe strength loss beyond 400°C, retaining only 45% strength at 600°C and 18% at 800°C, accompanied by surface cracking and partial spalling. In contrast, UHPC modified with 3.0 wt% Nano-Al₂O₃ retains 68% of its initial strength at 600°C and 36% at 800°C. The refractory nature of ceramic nanoparticles prevents structural collapse of the hydration gel matrix during high-temperature dehydration.

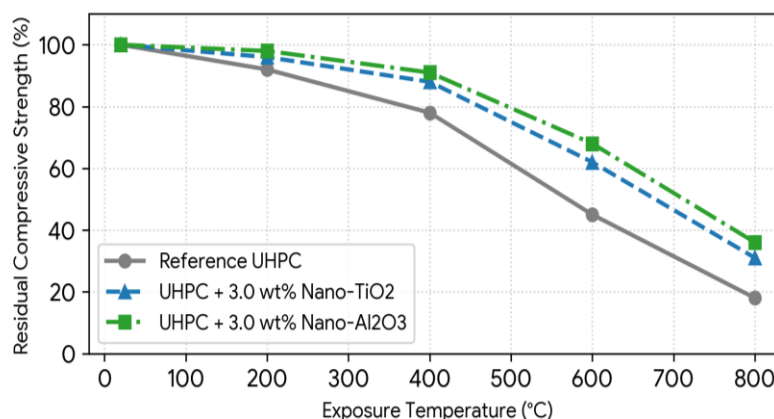


Figure 3: Residual compressive strength retention of control vs. ceramic nanoparticle-modified UHPC exposed to elevated temperatures

Durability Metrics Performance

Durability assessments confirm substantial improvements across all ingress parameters. Rapid Chloride Permeability Testing (RCPT) demonstrates that 2.0–3.0 wt% nano-ceramic additions reduce total charge passed from 450 Coulombs (Control - Very Low permeability) to less than 120 Coulombs (Extremely Low permeability). Water sorptivity coefficients decreased by 48%, while resistance to 300 freeze-thaw cycles maintained a relative dynamic modulus of elasticity above 96.5% compared to 82.1% in baseline specimens.

TECHNICAL DISCUSSION

The experimental and analytical findings synthesized in this review confirm that ceramic nanoparticle incorporation fundamentally transforms UHPC performance through three interconnected multi-scale mechanisms:

- **Micro-Filler and Packing Efficiency Optimization:** UHPC relies on dense particle packing. However, sub-micron gaps remain between cement particles and silica fume. Ceramic nanoparticles (15–30 nm) physically occupy these capillary voids, creating an ultra-dense, non-connected pore structure that severely restricts fluid transport.
- **Nucleation Seed Effect and C-S-H Gel Growth:** The massive specific surface area of ceramic nanoparticles acts as physical template sites for C-S-H growth. Nano-TiO₂ accelerates early hydration, increasing early-age (3-day and 7-day) strength development by over 30%. Nano-Al₂O₃ contributes reactive alumina ions that react with excess CH to form supplementary C-A-H gels, reinforcing matrix cohesion.
- **Thermal Stabilizing and Refractory Pinning:** Under thermal exposure, C-S-H gels lose chemically bound water and decompose. Nano-ZrO₂ and Nano-Al₂O₃ particles, owing to their high thermal conductivity and extreme melting temperatures, act as thermal micro-pins that dissipate localized heat, arrest thermal micro-crack propagation, and stabilize the matrix structure.

RESEARCH AND PRACTICAL LIMITATIONS

Despite the significant performance enhancements demonstrated by ceramic nanoparticle-modified UHPC, several critical engineering limitations hinder immediate commercial adoption:

- **Processing and Rheological Workability Loss:** High specific surface area nanoparticles absorb significant water and PCE superplasticizers, drastically reducing fresh concrete flowability and requiring high superplasticizer dosages.

- **Sensitivity to Nanoparticle Dispersion:** Inadequate ultrasonic dispersion or improper field mixing leads to nano-agglomeration, which induces localized stress concentrations and degrades mechanical gains.
- **Cost Implications:** Ceramic nanoparticles—particularly high-purity Nano-ZrO₂ and Nano-Al₂O₃—remain costly, significantly increasing raw material expenses compared to conventional UHPC.

FUTURE SCOPE AND RECOMMENDATIONS

To overcome these technical boundaries and advance nano-ceramic modified UHPC toward widespread field application, future research should prioritize:

- **Hybridization Optimization:** Systematic investigations into optimal ternary ceramic nanoparticle combinations (e.g., TiO₂-Al₂O₃-ZrO₂) to achieve multi-functional performance synergies.
- **Surfactant-Free Surface Modification:** Researching functionalized ceramic nanoparticles with surface-grafted organic groups that self-disperse efficiently in cementitious water without high-energy ultrasonic bath dispersion.
- **Full-Scale Structural Element Testing:** Transitioning from small laboratory cube/prism testing to full-scale precast UHPC structural bridge girders and facade panels under dynamic loading and fire exposure.
- **Techno-Economic and Life-Cycle Assessment (LCA):** Developing rigorous LCA models to evaluate long-term carbon footprint reductions and cost benefits resulting from extended service life.

CONCLUSION

This comprehensive state-of-the-art review systematically evaluated the thermal, mechanical, and durability performance of Ultra-High-Performance Concrete (UHPC) modified with ceramic nanoparticles (Nano-TiO₂, Nano-Al₂O₃, Nano-ZrO₂). The major conclusions drawn from this research are:

- An optimal incorporation level of 1.0 to 3.0 wt% ceramic nanoparticles yields a 12% to 22% increase in 28-day compressive strength and up to a 41% enhancement in flexural strength, driven by nucleation acceleration and interfacial transition zone (ITZ) refinement.

- Microstructural analysis confirms that ceramic nanoparticles reduce total UHPC porosity to under 4.0% and diminish unreacted calcium hydroxide (CH) levels by converting them into secondary C-S-H and C-A-H gels.
- Under elevated temperatures up to 800°C, ceramic nanoparticles (especially Nano-Al₂O₃ and Nano-ZrO₂) dramatically increase thermal stability, preserving up to 36% residual strength at 800°C and mitigating explosive thermal spalling risks.
- Long-term durability is substantially enhanced; chloride ion permeability drops into the extremely low range (<120 Coulombs), and water absorption is reduced by nearly 50%.
- Future efforts must focus on cost-effective dispersion techniques, rheology management, and full-scale structural testing to enable seamless transition from laboratory research to industrial concrete infrastructure projects.

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Received Date: July 05, 2026

Accepted Date: July 13, 2026

Published Date: July 28, 2026

Citation: Manav Rawat, Manvika Soni, Rahul Chopra. Thermal, Mechanical, and Durability Assessment of Ultra-High-Performance Concrete Modified with Ceramic Nanoparticles: A Comprehensive State-of-the-Art Review. Journal of Ceramics and Concrete Technology. 2026; 11(2): 117-130p.