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Mechanical Properties and Chloride Penetration Resistance of UHPC Incorporating Tunnel Spoil and Nano-SiO_2

Jinhao Ou[1, *]

[1]College of Operational Support, Rocket Force University of Engineering, Xi'an, China
[*]Corresponding author: 670385212@qq.com

Abstract: Using tunnel spoil in ultra-high-performance concrete (UHPC) is attractive for reducing aggregate consumption, yet its porous nature raises concern when the material is exposed to chloride wet–dry action. In this work, quartz sand was partially replaced by tunnel spoil at 0%, 10%, 20%, and 30%, and nano-SiO_2 was incorporated at 0%, 1%, 2%, and 3%. Compressive strength, electric flux, mass variation, SEM, and XRD were used to examine performance changes at different curing ages and exposure durations. Compressive performance and chloride penetration resistance declined under repeated chloride wetting and drying, whereas longer curing and a moderate combination of tunnel spoil and nano-SiO_2 were associated with lower electric flux, smaller mass variation, and a denser matrix. Within the tested mixtures, 2% nano-SiO_2 + 20% tunnel spoil (N2C2) showed the most favorable overall balance.

Keywords: UHPC; tunnel spoil; nano-SiO_2; chloride wet-dry cycles; chloride penetration resistance; microstructure.

1. Introduction

Chloride-bearing exposure remains a major durability concern for cement-based materials because repeated wetting and drying promotes chloride accumulation near the exposed surface and accelerates internal damage development. UHPC is widely valued for its high strength and compact matrix [1-8], yet its service behavior still needs to be checked when chloride wet–dry action acts for a long period.

Tunnel excavation generates large volumes of spoil, and simple stockpiling creates disposal pressure, land occupation, and avoidable resource loss [9-12]. Replacing part of the aggregate with processed tunnel spoil is therefore attractive, but the material may also bring higher water absorption, internal pores, surface microcracks, and grading-related disturbance to the UHPC matrix [13-18].

These features matter in chloride environments because weak aggregate surfaces and an unstable interfacial transition zone can ease moisture exchange and create preferential ingress paths. Nano-SiO_2 has been used in UHPC to make the binder phase denser and to moderate interfacial weakness through its very fine particle size and high reactivity [8-10], but the benefit depends on dosage and dispersion quality rather than on simple addition alone.

Previous studies have examined UHPC durability, chloride exposure, and the reuse of excavated rock materials [11-18]. Less attention has been paid to UHPC in which tunnel spoil and nano-SiO_2 are introduced together and then subjected to chloride wet–dry cycling. The coupled influence of spoil-related pore features, particle packing, nano-modification, and curing age remains insufficiently discussed.

In this work, quartz sand was partially replaced by tunnel spoil and nano-SiO_2 was varied within the designed dosage range. The discussion focuses on whether the combined use of these two variables can maintain compressive performance and chloride penetration resistance under wet–dry exposure. The results are interpreted together with SEM and XRD observations.

2. Materials and Methods

2.1. Raw materials

P.O 52.5 Portland cement, Class I fly ash, silica fume, quartz sand, tunnel spoil, copper-coated steel fibers, mixing water, polycarboxylate superplasticizer, and nano-SiO_2 were used in this study. Their main physical and chemical properties are listed in Table 1.

Portland cement formed the main binder. Fly ash and silica fume were used as supplementary cementitious materials, and the measured SiO_2 content of silica fume was 96.44%.

Quartz sand served as the reference aggregate, and processed tunnel spoil was used as a partial replacement. Copper-coated steel fibers were added for crack bridging, municipal tap water was used for mixing, and a polycarboxylate-based superplasticizer was used to maintain flowability at a low water-to-binder ratio. Nano-SiO_2 was selected as one of the main variables.

2.2. Mix proportions

A 16-group orthogonal design was used to vary nano-SiO_2 dosage and tunnel spoil replacement ratio. The water-to-binder ratio, total binder content, superplasticizer dosage, steel fiber content, specimen preparation procedure, and curing regime were kept the same for all mixtures.

The total content of the cementitious system was fixed at 950 kg/m^3, consisting of 760 kg/m^3 Portland cement, 142.5 kg/m^3 silica fume, and 47.5 kg/m^3 fly ash. The dosage of polycarboxylate high-performance superplasticizer was uniformly set at 2% of the total binder content, corresponding to approximately 19 kg/m^3. The dosage of SH-13 mm copper-coated steel fibers was fixed at 78 kg/m^3. The mixing water satisfied the requirements specified in the relevant standards, and the reference amount of quartz sand in the control mixture was 980.50 kg/m^3.

Nano-SiO_2 dosages of 0%, 1%, 2%, and 3% were denoted as N0, N1, N2, and N3. Tunnel spoil replacement ratios of 0%, 10%, 20%, and 30% were denoted as C0, C1, C2, and C3. Their full-factorial combination produced 16 groups from N0C0 to N3C3, allowing both individual and coupled effects to be compared within one test matrix.

The same preparation and curing procedures were used for all mixtures to maintain comparability among groups.

Table 1. Mix proportions of UHPC mixtures

Mixture ID	Nano-SiO_2 dosage	Tunnel spoil replacement ratio
N0C0–N0C3	0%	0%, 10%, 20%, 30%
N1C0–N1C3	1%	0%, 10%, 20%, 30%
N2C0–N2C3	2%	0%, 10%, 20%, 30%
N3C0–N3C3	3%	0%, 10%, 20%, 30%

2.3. Specimen preparation and curing

The materials were weighed according to the design proportions. Aggregates and cementitious materials were dry-mixed first, after which nano-SiO_2 and copper-coated steel fibers were added. Mixing water premixed with the polycarboxylate superplasticizer was then introduced gradually until a uniform fresh mixture was obtained.

Specimens with a size of 100 mm × 100 mm × 100 mm were cast in steel molds. The mixture was placed in layers, compacted on a vibrating table, and surface-finished after vibration.

After casting, the specimens were covered, demolded after about 24 h, and cured at 20 ± 2 °C and RH above 95%. Two curing ages, 28 d and 56 d, were used for the subsequent tests.

2.4. Chloride wet-dry cycle test

An accelerated chloride wet–dry salt-spray test was used to simulate chloride-rich exposure. The salt-spray procedure followed GB/T 10125-2021, and the durability evaluation followed GB/T 50082-2009. Specimens cured for 28 d and 56 d were tested. Five faces of each cube were sealed with epoxy resin, leaving one exposed face for chloride ingress. A 5 wt.% NaCl solution was used in a YFZ-160 salt-spray chamber, and each cycle was 24 h: 12 h salt-spray exposure + 12 h air drying.

The exposure durations were 18 d, 36 d, 54 d, 72 d, and 90 d. After each period, the specimens were removed and kept in a ventilated environment until the surface moisture condition became stable before testing.

Surface condition, mass variation, and residual compressive strength were recorded after exposure so that visible deterioration, moisture- and salt-related mass response, and load-bearing capacity could be compared among mixtures.

2.5. Test methods

Compressive strength, electric flux, and mass variation were used as the main performance indices, and SEM/XRD observations were used for interpretation.

Compressive strength was measured on 100 mm × 100 mm × 100 mm cubes with a YAW-2000 hydraulic testing machine at a stress rate of 1 MPa/s. The maximum failure load was recorded, and residual compressive strength after chloride exposure was used to assess mechanical retention.

Electric flux testing was carried out on slices cut from specimens at the specified curing age. The slices were prepared to the required thickness, ground flat, vacuum-saturated, and sealed on the lateral surface so that ion transport mainly occurred through the test section. The accumulated charge during the prescribed electrical test period was taken as the electric flux for comparison among mixtures.

After each salt-spray exposure period, specimen mass was measured once the surface condition became stable, and the corresponding mass variation rate was calculated. The exposed surfaces were also inspected for roughening, salt deposition, local peeling, and spalling.

For SEM observation, small samples of about 10 mm × 10 mm × 5 mm were taken from the interior of selected specimens. The samples were dried, gold-coated, and examined for matrix compactness, pore and microcrack distribution, hydration-product morphology, and the aggregate-paste interfacial transition zone.

For XRD analysis, representative interior fragments were ground into powder and scanned to compare the crystalline composition among mixtures. The patterns were interpreted together with the SEM observations and the macroscopic test results.

Table 2. Experimental program and measured indicators

Test item	Specimen condition	Exposure age	Measured indicator	Purpose
Compressive strength	28 d / 56 d cured specimens	18, 36, 54, 72, 90 d	Strength and attenuation rate	Evaluate mechanical performance retention
Electric flux	Selected or all mixtures	After chloride exposure	Charge passed / C	Evaluate chloride penetration resistance
Mass loss	Exposed specimens	18–90 d	Mass loss ratio	Evaluate surface deterioration
SEM and XRD	Representative mixtures	Before/after exposure	Microstructure and hydration products	Explain mechanism

3. Results and Discussion

3.1. Compressive strength under chloride wet–dry cycles

Across all mixtures, compressive strength declined after chloride wet–dry exposure, but the reduction was not equally rapid at every stage. The early cycles mainly caused mild loss, whereas the later exposure periods produced more evident weakening, showing that deterioration accumulated with repeated salt-spray action.

The response at 28 d and 56 d was clearly different. Longer curing gave higher initial strength and also changed the sensitivity of UHPC to chloride wet–dry exposure. The 56 d specimens retained a more stable strength profile, while the 28 d specimens showed earlier and larger deterioration under the same exposure duration.

The dosage of nano-SiO_2 influenced this trend. Mixtures containing a moderate amount of nano-SiO_2 generally showed better strength retention than the corresponding N0 mixtures, which is consistent with a denser binder phase and a less connected pore structure. The benefit did not continue indefinitely, however, and excessive nano-SiO_2 may introduce local agglomeration that makes the matrix less uniform under repeated chloride exposure.

Tunnel spoil replacement also had a dosage threshold. Replacing quartz sand by tunnel spoil up to 20% was compatible with maintaining compressive performance, whereas the 30% mixtures showed a less favorable tendency after longer exposure. Excessive tunnel spoil may disturb aggregate packing and weaken the ITZ. Within the tested mixtures, N2C2 showed the most stable balance between compressive strength and chloride wet–dry resistance.

3.2. Strength attenuation behavior

Strength attenuation is discussed here as a retention index derived from the residual compressive strength results. Compared with absolute strength alone, it makes the loss of load-bearing capacity under chloride exposure easier to compare among mixtures.

The attenuation results confirm that deterioration was not identical among mixtures. Longer curing lowered the attenuation level, again indicating that curing age changed the sensitivity of UHPC to chloride wet–dry exposure. At a fixed tunnel spoil replacement ratio, mixtures with 1%-2% nano-SiO_2 generally retained more strength than the corresponding N0 series.

At a fixed nano-SiO_2 dosage, the influence of tunnel spoil replacement was also nonlinear. A moderate replacement ratio helped maintain the aggregate skeleton, but the attenuation became more pronounced when the replacement ratio reached 30%. This behavior is consistent with the possibility that excessive tunnel spoil introduces weaker interfacial regions and less favorable packing.

Taken together, the attenuation results suggest that chloride-related strength loss was minimized when curing was sufficient and the two variables were kept within a moderate range. Within the tested mixtures, N2C2 exhibited the highest strength retention after chloride wet–dry cycling.

3.3. Chloride penetration resistance

Electric flux reflects the ease of ion migration through the connected pore network under an applied electrical field. Lower values therefore correspond to a less connected transport path for chloride ions.

Adding nano-SiO_2 was generally associated with lower electric flux than in the corresponding mixtures without nano-SiO_2. This trend indicates that the pore network became less open when nano-SiO_2 was present. The combined filler effect and pozzolanic reaction of nano-SiO_2 likely helped refine the matrix and reduce the continuity of capillary channels.

The response to tunnel spoil replacement was not monotonic. When the replacement ratio increased from 0% to 20%, the electric flux tended to fall, suggesting that a moderate amount of tunnel spoil contributed to particle packing and a more tortuous migration path. When the replacement ratio reached 30%, the electric flux rose again, which points to less favorable grading or additional interfacial defects.

The coupled effect of the two variables is important in this section. Nano-SiO_2 mainly acted on the binder phase and pore refinement, whereas tunnel spoil influenced packing and the aggregate skeleton. Within the tested mixtures, 2% nano-SiO_2 + 20% tunnel spoil showed a lower electric flux and may be regarded as a favorable combination.

3.4. Mass variation and surface deterioration

Because the specimens were weighed after exposure and surface stabilization rather than after removal of all physically retained moisture and salt, the response is discussed here as mass variation. The magnitude of mass change increased with exposure duration, indicating that repeated chloride wet–dry action progressively affected the near-surface zone.

The extent of mass variation depended on mixture proportion and curing age. At a fixed tunnel spoil replacement ratio, adding nano-SiO_2 generally reduced mass change before a slight rebound at the highest dosage. A similar decrease-then-increase tendency was observed when the tunnel spoil replacement ratio increased. Longer curing generally reduced mass variation, and the N2C2 mixture showed a lower response within the tested mixtures.

Visual observations were consistent with the mass data. As exposure continued, the specimens showed surface roughening, salt deposition, local peeling, and slight spalling. Such near-surface deterioration can promote moisture exchange and chloride ingress, which helps explain the later-stage acceleration of durability loss.

3.5. Microstructural mechanism

SEM images suggest that the reference mixtures contained a less compact matrix, with more visible pores, fine microcracks, and a less continuous aggregate-paste interface. After chloride wet–dry exposure, local loosening around weak interfaces became easier to observe, indicating that transport and damage were concentrated in these regions.

By contrast, the mixture that performed best at the macroscopic level showed a denser matrix and a more continuous ITZ. Gel-like products occupied part of the original pore space, and the interface between aggregate and paste appeared less interrupted. This observation is consistent with the lower electric flux and better strength retention recorded for the same mixture.

The SEM observations also suggest a dosage boundary for both modifiers. Nano-SiO_2 contributed through filler effect and pozzolanic reaction, but excessive nano-SiO_2 may introduce local agglomeration and uneven densification. Tunnel spoil mainly affected particle packing and the aggregate skeleton; when the replacement ratio became too high, weak ITZ regions were more likely to appear.

XRD patterns are consistent with these SEM observations. Differences in relative peak intensity and overall crystalline composition were present among mixtures, and the denser mixtures showed a pattern compatible with more complete hydration development in the binder system. No additional interpretation beyond the observed pattern differences is needed here, but the XRD results support the view that mixture proportion changed matrix continuity rather than introducing a single controlling phase response.

Taken together, SEM and XRD observations explain why the better-performing mixtures combined lower electric flux, smaller mass variation, and higher strength retention. The most favorable response was obtained when nano-SiO_2 densified the binder phase and the tunnel spoil content remained within a range that did not disrupt packing or interfacial quality.

4. Summary

(1) Chloride wet–dry cycling caused progressive deterioration in UHPC. With increasing exposure duration, compressive strength decreased, strength attenuation became more evident, and chloride transport resistance and mass stability were weakened. Repeated chloride wetting and drying therefore affected both the load-bearing response and the transport-related durability of the material.

(2) Curing age strongly affected resistance to chloride-induced deterioration. Compared with 28 d curing, 56 d curing gave better performance retention after exposure, which is consistent with continued hydration and a denser matrix.

(3) Within an appropriate dosage range, nano-SiO_2 was associated with lower chloride permeability and better strength retention. When the dosage became too high, local agglomeration and nonuniform dispersion could offset part of that benefit.

(4) The effect of tunnel spoil replacement was nonlinear. A moderate replacement level helped maintain particle packing, whereas excessive replacement was associated with a weaker interfacial transition zone and more connected pore paths.

(5) Considering compressive strength, strength attenuation, electric flux, mass variation, and microstructural observations together, the N2C2 mixture showed the most balanced overall performance within the tested groups.

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