Preparation of novel and durable concrete skin

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Abstract
The performance of the conventional concrete skin was promoted by ultrasonic surface treatment (UST) in this study, and the newly formed dense and hard concrete skin was termed as ultrasonic hardening layer (UHL). The microstructure of UHL was scanned and analyzed, several durability-related indicators, such as water vapor penetration rate, surface, and interface hardness, were measured, and it was found that UHL could effectively improve the durability of concretes. The light reflectance of the UHL concrete surface was measured in the spectrum range of UV (200 nm) to NIR (2,500 nm), and it manifested 24.17% less mean reflectance than the conventional concrete skin. Therefore, UHL could serve as a promising road material due to its better melting capacity in cold-temperate zones.

KEYWORDS
concrete skin, durability, reflectance, surface treatment, ultrasonic

1 | INTRODUCTION

Concrete skin is defined as the surface layer that has a thickness of up to half of the maximum grain size of the aggregate in concrete,1–4 as a porous material, concrete skin plays an important role in improving the durability of concretes. Abrasion, particle erosion, frost heaving (freeze-thaw deterioration), and chemical corrosion (carbonation, chloride diffusion, and sulfate attack) generally start from the concrete surface.5–11 Therefore, it is a challenge for material researchers to prepare novel concrete skin for improving the durability of concretes.

Generally, four different types of surface treatment methods are applied to improve the performance of the conventional concrete skin12: (a) surface coating method: Organic paints, such as epoxy and silicone resins,13,14 acrylic,15,16 chlorinated rubber,14 coal tar,17 polyurethane,18 and polymer modified cementitious coatings19 are commonly used to form a continuous surface coating; (b) surface hydrophobic method: silane and siloxane are generally used to form a water-repellent surface20,21; (c) pore-blocking treatment: sodium silicate/potassium silicate and fluorine sodium silicate/fluorosilicate are widely used as permeable crystallization materials22,23; (d) biological method: calcium carbonate deposition is carried out by inducing microorganisms in cement-based materials, and consequently, pores and micro-cracks in concrete gradually become filled.24–27 However, organic materials have poor durability and fire-resisting ability,28 and the surface protection properties of inorganic materials have yet to be revealed.23,29 Moreover, biological treatments are very complicated,30 hence, the aforesaid methods need further treatments to improve the durability of concretes, thus incurring extra processing costs.

Discussion on this paper must be submitted within two months of the print publication. The discussion will then be published in print, along with the authors’ closure, if any, approximately nine months after the print publication.

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Some recent researches have addressed the performance of conventional concrete skin. Sadowski and Stefaniuk revealed a porosity skin structure of about 30–60 μm on the surface of the original concrete using micro-CT scanning. That is a disadvantage for the service performance of concrete. They presented a mechanical surface treatment method (grinding and shot blasting) to remove the skin of concrete, that dose decreased the porosity on the surface layer of concrete but also cause additional costs.

In this study, we present an ultrasonic surface treatment (UST) method to improve the microstructure of concrete skin with few additional costs, the durability of the conventional concrete skin was improved, and the newly formed dense and hard concrete skin was termed as an ultrasonic hardening layer (UHL). Additionally, the UHL makes a lower surface light reflectance, which may improve the melting capacity of concrete road materials in cold-temperate zones.

2 | MATERIALS, METHOD, AND EXPERIMENTS

2.1 | Materials

2.1.1 | Cement

PII 52.5 Onokazu cement with a specific surface area of 377 m²/kg was used in the present experiment, and its main chemical composition is presented in Table 1.

| Ingredient | CaO | SiO₂ | Fe₂O₃ | Al₂O₃ | Others |
|------------|-----|------|-------|-------|--------|
| Content (wt%) | 68.03 | 26.1 | 2.07  | 2.34  | 1.46   |

2.1.2 | Aggregates

ISO standard sand with a particle size of 0.08–2 mm was used as fine aggregates. Limestone gravel with a particle size of 5–15 mm was used as coarse aggregates.

2.2 | Method

2.2.1 | UST method

Before the final setting of cement, ultrasonic vibration was exerted on the concrete surface. Consequently, a highly dense layer with a colored cement matrix was formed on the concrete surface (termed as UHL).

Ultrasonic vibration acting on the concrete surface disintegrated the coarse C-S(A)-H gel network formed during the initial setting period of the cement and subsequently, formed a refined gel network. The ultrasonic action caused a vibration/compaction effect on the surface of the cement slurry, squeezed out the free water, and lowered the water/cement ratio of the surface layer.

The formation of UHL was not dependent on the shape or volume of the mold attached to the concrete surface; hence, UHL can be obtained on any types of cementitious materials and molds.

In our experiment, two types of molds were fabricated for cement paste sheets and concrete specimens (Figure 1). The ultrasonic vibration intensity on molds was 1 kW/m² and the duration of UST was 30 min.

2.2.2 | Laser confocal microscopy scanning

An Olympus OLS4100 laser confocal microscope working with laser wavelength of 405 nm and a resolution of 120 nm with ×50 and ×100 objectives was used for morphology scanning.
2.2.3 | Scanning electron microscope scanning

A FEI Inspect F50 scanning electron microscope (SEM) with a resolution of 3.0 nm @ 10 kV was used for microstructure scanning.

2.2.4 | Micro-CT scanning

A nonaVox3000 X-ray microcomputed tomography (micro-CT) was used for porosity scanning. The scanning slice thickness was 4.323 μm. The porosity was calculated in line with the volume fraction of closed pores in each slice.

2.3 | Experiments

2.3.1 | Water vapor penetration experiment

Cement paste sheets (thickness = 3 mm) with water/cement ratios of 0.28, 0.30, 0.32, and 0.34 were produced by the UST method (Figure 1a). All specimens were cured in a standard maintenance room for 28 days.

Water vapor penetration experiments were executed according to the ASTM E96 standard, and penetration cups with a cup-mouth of 83 mm were used. The temperature and the relative humidity of the test room were set to 25°C and 50%, respectively. The test duration was 216 hr, and the changes in specimen weight were measured every 24 hours with a balance (accuracy = 0.001 g). The water vapor transmission rate was calculated by Equation (1).

\[
WVT = \frac{G}{t.A} \tag{1}
\]

WVT = Water vapor transmission rate (g/h.m²), 
G = Weight change (g), 
t = Time during which G occurred (h), 
A = Test area (cup mouth area) (m²).

2.3.2 | Surface and interface hardness measurement

Cubic concrete and mortar specimens with UHL were produced by the UST method, and for comparison, conventional concrete samples without UHL (termed as contrast specimens) were also prepared. The concrete mix mass proportion was: cement:sand:gravel:water = 1:2.0:3.88:0.47; the mortar mix mass proportion was: cement:sand:water =1:3:0.5. All samples were cured in a standard maintenance room for 28 days and then cut into two halves and polished.

A Vickers micro-hardness tester with a measurement range of 5–3000 hv was employed to measure the matrix hardness on the surface and also at the aggregate-matrix interface. The test force was 0.01 kgf and loading time was 10 s.

2.3.3 | Surface reflectance measurement

A SHIMADZU UV-VIS-NIR spectrophotometer was used to measure the surface reflectance of the investigated concrete specimens with UHL in the spectrum range of 200–2,500 nm.

3 | RESULTS AND DISCUSSION

3.1 | Apparent morphology of UHL

The concrete surface treated with the UST method had a darker surface in comparison to contrast specimens (Figure 2). Moreover, the laser confocal scanning on the surface of the UHL reveals that the cement matrix was mainly composed of a gel phase. Due to the dense microstructure of UHL, there was no space for crystal development. However, in contrast specimens, hydrated calcium silicate crystals were easily developed (Figure 3). The difference in crystal content can explain the reason for the dark color of UHL. As lower crystal content can significantly reduce the reflection of light on the crystal surface, UHL has a darker surface in comparison to the conventional concrete skin.

3.2 | Micro-structure of UHL

Colored skin layers with a thickness of 5 mm (Figure 4a) and 2 mm (Figure 4b) were observed on cross section of concrete and mortar specimens, which is the UHL structure.

In UHL, aggregates were closely bonded to the cement matrix; hence, no clear surface defects were observed at the interface section. On the contrary, severe defects were detected in contrast specimens (Figure 5).

SEM images in Figure 6a confirm that the dense microstructure of UHL was mainly composed of gels with few pores, on the contrary, a loose and porosity microstructure composed of gels and crystalline phases was observed on contrast specimen, as shown in Figure 6b. The microstructure of the UHL means a better penetration resisting ability and erosion resistance ability.
FIGURE 2  Morphologies of concrete samples with UHL (left) and contrast specimens (right)

FIGURE 3  LCMS scanning pictures on the surface of concrete specimens, (a) UST treated and (b) contrast

FIGURE 4  Cross sections pictures of concrete specimens treated with UST method, (a) concrete and (b) mortar
Moreover, laser confocal microscopy scanning (LCMS) on cross section revealed that a highly dense gel phase skin formed on UHL. The thickness of the skins were over 100 μm. As shown in Figure 7a,b.

3.3 | Porosity scanning and analysis

X-ray micro-CT scanning on concrete and mortar UST specimens indicated a relatively lower porosity layer with
a thickness over 1 mm under surface, which means the UHL has a dense layered structure, as shown in Figure 8a,b. Furthermore, the enlarged graph (in red box) showed much low porosity (<0.1%) layers on the surface with a thickness of 150–200 μm, which is in line with the gel phase skin revealed in LCMS scanning.

Differ to the porosity concrete skins that Sadowski and Stefaniuk 32 revealed on raw concrete surface, the skins that on UST specimens surface were much dense, consequently, it will improve the permeability and erosion resistance of concrete, and improve the durability.

### 3.4 Water vapor transmission rate of UHL

The water vapor transmission (WVT) rates of UHL and contrast specimens are presented in Figure 9. It is clear that UHL had lower WVT rates than contrast specimens, and it can be attributed to the existence of fewer pernicious pores (size >100 nm, as shown in Figure 6) in UHL. The WVT rates of contrast specimens increased monotonically with the increasing water-cement ratio, and it can be
ascribed to the increase in porosity with the increasing water content in the slurry. Moreover, for UHL specimens, the relationship between WVT and the water-cement ratio was not linear, which means there was an optimal water-cement ratio for the UST method in a WVT test.

3.5 | Surface and interface hardness of UHL

The surface and interface hardness values of UHL and contrast specimens are presented in Figure 10. The surface hardness of UHL specimens was found to be 3.5 times that of contrast specimens (Figure 10a); thus, it indicates that UHL had better abrasion resistance. In Figure 10b, the hardness values of the cement matrix (in UHL and contrast specimens) around aggregates are plotted against the distances to aggregates. The hardness of cementitious materials gradually increases with the increasing distance between the matrix and aggregates, and a weak interface transition zone (ITZ) (range of 70 μm) was noticed in contrast specimens.25,26 The interface hardness values of UHL specimens were noticeably higher than those of contrast specimens. The hardness of UHL specimens (against the distance between the cement matrix and aggregates) changed along a nearly horizontal line; hence, no clear ITZ was detected.

FIGURE 10A  Surface Vicker’s hardness of UHL and contrast specimens

FIGURE 10B  Interface Vicker’s hardness of UHL and contrast specimens

FIGURE 11A  Graph of surface light reflectance against wavelength
The higher surface and interface hardness of UHL specimens can be ascribed to the existence of fewer pores and hydration crystals in the cement matrix.

3.6 | Surface light reflectance measurement

The surface light reflectance values of the investigated concrete samples against light wavelength are plotted in Figure 11a. Concrete samples with UHL had a lower surface reflectance than contrast specimens in the spectrum range of UV (200 nm) to NIR (2,500 nm). The mean light reflectance values of the investigated samples are presented in Figure 11b, and UHL manifested 24.17% less mean reflectance than the conventional concrete skin. Therefore, UHL can absorb more heat than the conventional concrete skin and could serve as a promising road material due to its better melting capacity in cold-temperate zones. This phenomenon can be ascribed to the existence of fewer hydration crystals in the cement matrix of UHL.

4 | CONCLUSION

The main observations of the present research are presented below:

- A novel and durable concrete skin (termed as UHL) was produced by the UST method.
- The microstructure of UHL was dense and less porous and consisted of lower crystal content than the conventional concrete skin.
- UHL had a lower water vapor transmission rate than the conventional cement matrix; hence, it manifested improved resistance to chemical erosion and frost heave damage.
- UHL had an excellent erosion resisting ability due to its higher surface and interface hardness.
- The UHL surface had a lower light reflectance than the conventional concrete in the spectrum range of UV (200 nm)–NIR (2,500 nm).
- UHL can effectively improve the durability of concretes, and it could serve as a promising road material due to its better melting capacity in cold-temperate zones.

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