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# Effects and mechanisms of surface treatment of hardened cement-based materials with colloidal nanoSiO$_2$ and its precursor

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## HIGHLIGHTS

- Effects of colloidal nanoSiO$_2$ (CNS) and tetraethoxysilane (TEOS) of surface-treatment of cementitious material were studied.
- Effects of surface treatment of mortar with CNS and TEOS were attributed to the pozzolanic reactivity and filler effect.
- CNS and TEOS were able to fill pores larger than 50 nm, while TEOS was more effective in filling pores finer than 50 nm.

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## ABSTRACT

A dense surface structure of cement-based material is important for its resistance to the impacts of environment. Effectiveness and mechanisms of colloidal nanoSiO$_2$ (CNS) and its precursor, tetraethoxysilane (TEOS), on surface-treatment of the one-month-old cement mortar by brushing technique were studied in this work. It revealed that CNS decreases the water absorption ratio of mortar when cured at 50 °C and/or in sealed condition, but its effect is negligible when samples are cured at 20 °C. A greater reduction of water absorption ratio is found in TEOS-treated mortar at 20 °C or 50 °C and under sealed or unsealed condition. Pozzolanic reaction between CNS/TEOS and Ca(OH)$_2$ was observed by XRD, IR and EDS techniques. In addition, filler effects as revealed by SEM/EDS techniques were ascribed to for the densification of the exposed hardened mortar. Pore size distribution analysis conducted on mercury intrusion porosimeter showed that TEOS is more effective than CNS in filling pores finer than 50 nm, while CNS is found effective in filling capillary pores coarser than 50 nm.



## 1. Introduction

During the service life of cement-based material, the influences of environment would lead to the decrease of its quality by the migration of harmful substances inward/outward of its surface [1]. It has been well-recognized that the densification of the surface of hardened cement-based material will result in a significant improvement of the quality of the entire structure [1–3].

To make this happen, some surface treatment methods, which can be grouped into three types, are often used. Among them are: (1) surface treatment with hydrophobic agents, such as silane- or siloxane-based water repellent products, which make the pores in the concrete structure water-repellent [4,5]; (2) surface impregnation of sealing agents, such as alkali silicate, which makes the surface structure less porous [6]; and (3) surface coating with organic film-forming agent [1]. The surface-treatment methods are effective in ceasing the migration of substances in and out of the surface of hardened cement-based materials to some extent, but their shortages are apparent in some way. For example, the weathering of the organic treatment materials would lead to the failure of the protection [1]. The cohabitation of old structure with new cement-based materials would temporarily protect the inner structure, however, an incompatibility of the properties of the new and old cementitious materials, especially the difference in the volume stability, would easily lead to the cracking or detachment of the newly-applied protection layer and inevitably result in the failure of the protection [7].

It has been well-recognized that by introducing pozzolanic material into cement-based materials, additional C–S–H gel could be formed through its reaction with the hydration product of calcium hydroxide (CH) of cement. This mechanism is ascribed to for the surface-treatment of hardened cement-based materials with sodium silicate, which produces more C–S–H gel, and alters the properties of the gel as well [8]. However, the production of sodium hydroxide during the process would possibly increase the

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risk of alkali-silicate reaction that is detrimental to the properties of the bulk structure (as see in Eq. (1)).

$$Ca(OH)_2 + Na_2SiO_3 + H_2O \rightarrow C{-}S{-}H + NaOH \quad (1)$$

Thus, when using the pozzolans to make the surface structure of hardened cement-based materials denser and durable, they should not bring adverse side effect to the bulk structure. Such kind of alternatives should not only be favorable for the improvement of the pore structure, but also improve the quality of C–S–H gel [9]. It has been recognized that the pozzolanic reaction is highly-correlated to the calcium ion concentration, the alkalinity of the solution, and the reactivity of the pozzolans [10]. In the case of surface-treatment of hardened cement-based materials with pozzolans, a limited amount of CH and a low concentration of the $Ca^{2+}$ in the pore solution are the characteristics that may hinder the pozzolanic reaction [9], and thus the alternative for surface treatment of hardened cement-based materials should have a very high pozzolanic reactivity and can penetrate into the fine pores.

As a siliceous material, nano$SiO_2$ has been intensively studied in cement and concrete [11]. It exhibits a very fine particle size (about several to one hundred nanometers) and an extremely high pozzolanic reactivity. Our previous work showed that the pozzolanic reaction rate constant of nano$SiO_2$ with a mean particle size of 4 nm is about one order of magnitude bigger than that of silica fume [12]. Moreover, our research found that the hydration products of nano$SiO_2$ are more compact than that of silica fume [13], which could be beneficial for the resistance to harsh environment. In addition, the nanosized particle size feature of nan$SiO_2$ would be favorable for its penetration into the pores. Kupwade-Patil et al. used nanoparticles for treatment of reinforced concrete to reduce the corrosion of ion bars, whose results supports the sealing effect of nanoparticles on concrete [14].

For manufacturing of nano$SiO_2$ in industry scale is pretty mature and the sol–gel technique is commonly used. In this technique, nano$SiO_2$ is produced by the condensation and polymerization of $SiO_2$ monomers that formed through hydrolysis of trimethylethoxysilane or tetraethoxysilane–the commonly used precursors for the synthesis of nanosilica in controlled acidic or alkalic environment. Eq. (2) can be used to summarize the nanosilica synthesis process [15].

$$n\mathrm{Si}(OC_2H_5)_4 + 2nH_2O \rightarrow n\mathrm{SiO}_2 + 4nC_2H_5OH \quad (2)$$

Not only nano$SiO_2$, Sandrolini and his co-workers' results showed that tetraethoxysilane was also pozzolanic reactive [16], which exhibited the potential for surface-treatment of hardened cement-based materials.

Realizing both the importance of surface-treatment of cement-based materials and the properties of nano$SiO_2$, it would be possible to apply this fine and pozzolanic-reactive silicious material for the surface treatment of hardened cement-based materials by exploring its in situ pozzolanic reactivity and filler effect in the surface pores. To facilitate the penetration of the pozzolan into pores, in this work, a colloidal nano$SiO_2$ (CNS) with the mean particle size of 10 nm and its precursor of tetraethoxysilane (TEOS) were applied onto the surface of the hardened cement mortar by brushing technique and their effects and mechanisms on surface-treatment were investigated and compared.

## 2. Materials and methods

### 2.1. Materials

Ordinary Portland cement complying to Chinese standard GB 175-2007 was used in this work and its physiochemical properties are listed in Table 1.

Commercially available CNS with a mean particle size of 10 nm and solid content of 30% was used. Morphologic graph shown in Fig. 1 indicates that CNS is round in shape and is well dispersed. Chemical grade tetraethoxysilane (TEOS) was used and its content was 30% by mass.

### 2.2. Methods

#### 2.2.1. Sample preparation

Mortar samples with water-to-cement ratios of 0.4 and 0.6 and a cement-to-sand ratio of 1/3 were prepared in this work. The fineness modulus of the river sand was 2.8. Raw materials were dry-mixed for one minute and then wet mixed for another two minutes. After mixing, mortars were cast in 4 cm × 4 cm × 16 cm rectangular molds and covered with plastic sheet and cured for 1 day at ambient environment (about 25 °C/60%RH) before being demolded and stored in curing chamber at 20 ± 1 °C and RH 95% until surface treatment.

#### 2.2.2. Surface treatment

The one-month old mortar samples were cut into small pieces with dimensions of 4 cm × 4 cm × 1 cm. The slices were then dried at 60 °C for 1 day before being surface-treated with CNS and TEOS by brushing technique. The surface was treated for three times at a time-interval of 20 min. A saturated wet condition was achieved after each brushing.

**Table 1**
Physiochemical properties of cement.

| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $SO_3$ | CaO | MgO | LOI | Total | Density, g/cm$^3$ | Fineness, m$^2$/kg | 28-day compressive strength, MPa |
|---|---|---|---|---|---|---|---|---|---|---|
| 21.1 | 4.7 | 3.5 | 3.3 | 62.9 | 2.8 | 1.1 | 99.4 | 3.1 | 390 | 50.1 |

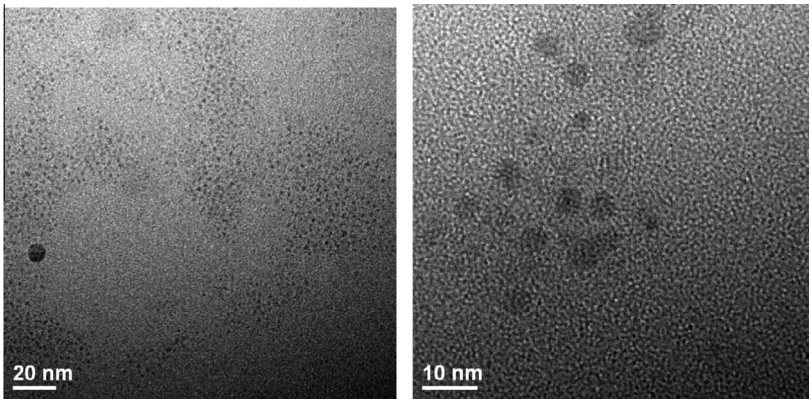


**Fig. 1.** TEM image of CNS-10 nm.