



# Interactions between inorganic surface treatment agents and matrix of Portland cement-based materials



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## HIGHLIGHTS

- In cement paste, magnesium fluorosilicate may not be limited on the reaction with  $\text{Ca}(\text{OH})_2$ .
- Carbonation plays an important part in waterglass treatment.
- Sodium fluorosilicate can improve the effectiveness of waterglass treatment.

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## ABSTRACT

Magnesium fluorosilicate, waterglass, sodium fluorosilicate, and combination of waterglass and sodium fluorosilicate were used as surface treatment agents and their interactions with the Portland cement hydrates were studied. Thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FT-IR) were employed to analyze the phase changes in the hardened cement pastes after surface treatments. A scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDX) analysis was adopted to examine the changes in morphologies and chemical compositions. The TGA and FT-IR results showed that the inorganic surface treatments could reduce the content of  $\text{Ca}(\text{OH})_2$  in the surface layer of hardened cement, whereas the amount of calcium silicate hydrate (C-S-H) and silica gel increased. Combined treatment with waterglass and sodium fluorosilicate could generate more gel products, and made the sample surface denser than other treatments used in this work, because sodium fluorosilicate could accelerate the hardening of waterglass, and both waterglass and sodium fluorosilicate could react with cement hydrates respectively.

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## 1. Introduction

Durability of Portland cement-based materials is a major concern for reinforced concrete structures, which is governed by the ingress of aggressive substances, such as chloride, sulfate and carbon dioxide. Among many protective methods aiming at enhancing the durability of concrete, surface treatment has been concerned as an effective and economic method.

Surface layer of concrete usually refers to a 30 mm thick layer below the surface, generally thinner than protective layer [1]. Many properties of concrete are affected by the quality of surface layer which can improve by surface treatments [2]. The protective surface treatments are generally classified into three categories as literatures [3–5]: (a) surface coatings which form a continuous polymer film to create a physical barrier, (b) hydrophobic impreg-

nation which can produce water-repellent capillary surface while leave the pores open [6,7], and (c) pore blocking surface treatment agents which have partial or total pore-filling effect and thus reduce the surface porosity.

Most surface coatings and hydrophobic impregnation are organic polymers. Although organic polymers can significantly improve the durability of concrete, they have some drawbacks, such as poor fire resistance, possibly leading to crack and detachment, and hard to remove after losing effectiveness [6,8]. Many coatings would greatly reduce the air permeability of concrete which could result in detachment of coatings from the matrix [9]. For hydrophobic impregnation, silane and siloxane are widely used around the world [6,7]. Although silane and siloxane can prevent the ingress of water into concrete, their effects on the air permeability and carbonation are negligible. In addition, Medeiros et al. [10] reported that their capacity of inhibiting water penetration reduced significantly when the water pressure was higher than  $120 \text{ kgf/m}^2$ . The author [11] also found that silane

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and siloxane did not have significant impact on the resistance to chloride diffusion. Furthermore, the aging resistance of organic polymers is poor, and they should not be used in long-life structures. Dhir et al. [12] showed that silane and siloxane would decompose and lose their protective effects when the temperature was higher than 45 °C. Levi et al. [13] found that the effects of silane and fluorinated polymers would reduce to 10% and 50% respectively after exposure to ultraviolet (UV) light.

Since inorganic surface treatment agents have better aging resistance, they draw more attention recent years. Silicate-based solutions, e.g. waterglass, potassium silicates and fluorosilicates are most common inorganic surface treatment agents [14]. Some studies demonstrated that waterglass treatment could reduce the water absorption and chloride diffusion, especially after post-treatment of cationic surfactant (alkyl quaternary ammonium salts) [14,15]. Franzoni et al. [16] found that abrasion resistance of concrete was increased by waterglass treatment. However, there are some different results. Dai et al. [4] showed that waterglass hardly penetrated into concrete substrate. Ibrahim et al. [17] reported that waterglass treatment could not significantly improve the resistance to ingress of water and chloride ions. In addition, reaction of waterglass and  $\text{Ca}(\text{OH})_2$  would generate  $\text{NaOH}$ , which would increase the likelihood of alkali aggregate reaction [8,18].

Recently, researches showed that magnesium fluorosilicate, waterglass, and sodium fluorosilicate had the capacity to enhance the resistance of concrete to water permeability, air permeability and carbonation [19,20]. However, limited works focused on mechanisms of these inorganic surface treatments. In this paper, the mechanisms of these inorganic surface treatment agents, particularly the interactions of the surface treatment agents with cement hydrates, are investigated using thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) examination, and scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDX) analysis.

## 2. Materials and methods

### 2.1. Materials

A P.I. 42.5 Portland cement with a specific surface area of 336  $\text{m}^2/\text{kg}$  was used. Its chemical compositions are shown in Table 1. Natural river sand with a density of 2610  $\text{kg}/\text{m}^3$  was used as fine aggregate. The grading of the sand is shown in Table 2.

The following inorganic protective treatments were used: magnesium fluorosilicate solution with a concentration of 30 wt.%, two waterglasses ( $\text{Na}_2\text{O}\cdot n\text{SiO}_2$ ) with modulus ( $n$ ) of 2 and 3, and sodium fluorosilicate. The waterglasses with  $n = 2$  was obtained by adding 5.92 g  $\text{NaOH}$  in 100 g industrial grade waterglass with modulus of 3. The chemical compositions and physical properties of these waterglass solutions are shown in Table 3. Both the waterglass were mixed with water in the proportion of 1:4 by weight to make surface treatment agent solutions. Sodium fluorosilicate with a concentration of 2 wt.% was considered, because it performed best in improving the efficiency of waterglass treatment [19–22].

### 2.2. Mixture proportions and sample preparation

Mortar cylinders with 50 mm diameter and 100 mm length were prepared for morphology and microstructure characterizations with water to cement ratio ( $w/c$ ) of 0.45 and sand to cement ratio ( $s/c$ ) of 1.3. Paste cylinder (110 mm diameter and 100 mm length) with same  $w/c$  was prepared for TGA and FT-IR analyses. All the samples were compacted on a controlled vibration table, and then covered with plastic films. The samples were kept in a laboratory at  $20 \pm 1$  °C for 24 h, and then cured in a standard moist room at  $20 \pm 1$  °C and  $\text{RH} \geq 98\%$  until treatment.

**Table 1**  
Chemical compositions of the P.I. 42.5 Portland cement.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{SO}_3$	$\text{Na}_2\text{O}_{\text{eq}}$	LOI
Percentage (wt.%)	21.91	5.30	3.67	64.5	1.51	0.62	0.19	2.03	0.59	2.49

**Table 2**  
Grading of sand.

Size (mm)	5	2.5	1.25	0.63	0.315	0.16
Cumulative retained of sand (wt.%)	8.0	21.2	36.7	56.5	89.0	98.6

**Table 3**  
Chemical composition and physical properties of the waterglass.

Modulus	$\text{Na}_2\text{O}$ (wt. %)	$\text{SiO}_2$ (wt. %)	Baume degree ( $^\circ\text{Bé}$ )	Density ( $\text{kg}/\text{m}^3$ )
3	9.05	26.5	38.4	1369
2	12.9	25.0	44.1	1440

**Table 4**  
Surface treatment on cutting surface of the mortar and paste cylinders.

Specimen	Surface treatment	Treatment number
UNTR	No treatment	0
MF	30% magnesium fluorosilicate solutions	4
W2	Waterglass with modulus of 2	4
W3	Waterglass with modulus of 3	4
SF	2% sodium fluorosilicate solutions	4
SF-W2	2% sodium fluorosilicate solutions + waterglass with modulus of 2	4+4

### 2.3. Surface treatments

After curing for 6 days, both ends of each cylinder were cut off perpendicularly to its axis. The remaining parts with 50 mm thickness were dried in an room at  $20 \pm 2$  °C and  $\text{RH} = 55 \pm 5\%$  for 24 h before surface treatment. The cutting surface near to the cast surface was considered as treated surface. In samples MF, W2, W3 and SF, the treated surfaces were brushed with surface treatment agents using a nylon brush every two hours for four times according to Table 4. In term of sample SF-W2, the same face was firstly brushed with sodium fluorosilicate every two hours for four times. And after 24 h, waterglass treatment agent with modulus of 2 was applied on the treated surface for other 4 times. Then, all treated cylinders were placed back into the standard moist room at  $20 \pm 1$  °C and  $\text{RH} \geq 98\%$  until testing.

### 2.4. Methods

#### 2.4.1. Thermogravimetric analysis

Thermogravimetric analysis (TGA) analysis was performed on the paste samples after 7, 14 and 28 days of surface treatment. According to previous research, the penetration depth of the inorganic surface treatment agents in mortar was about 5 mm [20]. Thus, 1 mm thick surface layer below the treated face of each cylinder was ground into powder by a computer numerical control (CNC) machine. The collected powders were dried in an oven at 60 °C for 24 h, and then they were sieved through a 125  $\mu\text{m}$  sieve and the fine powders were analyzed. The powders (about 10 mg per each sample) were heated at 10 °C/min from 20 to 1200 °C in a nitrogen atmosphere in a TGA instrument (Netzsch STA 409PC). The amounts of  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  were quantified using the software of the TGA instrument according to the temperature ranges for dehydration of  $\text{Ca}(\text{OH})_2$  (450–550 °C) and decomposition of  $\text{CaCO}_3$  (550–1000 °C) respectively.

#### 2.4.2. Fourier transform infrared spectroscopy

The samples for Fourier transform infrared spectroscopy (FT-IR) were the same as those prepared for TGA. The FT-IR spectra were obtained by Thermo Scientific IS10 FT-IR workstation and conventional KBr disc method. Approximately 1 mg of powder was ground together with 100 mg of IR-grade KBr for 5 min and pressed into a thin disc. Each sample was tested at a resolution of 2  $\text{cm}^{-1}$  with 32 scans. The blank KBr pellet was tested at the same time as reference. The relative absorbance spectra over the range of 1400–400  $\text{cm}^{-1}$  were subjected to a deconvolution analysis using the Peakfit 4.12 software with Gaussian peak shape and variable

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