K-5 Application of fluorosilicate as pretreatment in improving effectiveness of waterglass surface treatment on cement-based materials

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ABSTRACT: As a by-product from the phosphate fertilizer factories, only about 10% of the fluorosilicates can be recycled, leading to low economic benefits and water pollution. This study aims to investigate the potential application of sodium fluorosilicate pre-treatment in enhancing the performance of waterglass which is the most common inorganic surface treatment agents for cement-based materials. In this paper, the enhanced performance of sodium fluorosilicate was studied via the water absorption, water vapor transmission, and rapid chloride migration tests. Results showed that the early-age effect of waterglass on reducing permeability of cement mortar increased after application of sodium fluorosilicate pre-treatment. It also dramatically reduced the migration of chloride migration. In addition, its enhanced mechanism was analysed by Thermogravimetric analysis (TGA) Mercury intrusion porosimetry (MIP). The sodium fluorosilicate could not only accelerate the hardening of waterglass, but also react with cement hydrates, generating finer pore structure.

KEY-WORDS: Cement-based materials, surface treatment, permeability, sodium silicate, waterglass

INTRODUCTION

In reinforced concrete, the penetration of aggressive substances through the cover layer is critical for the corrosion of reinforcement and hence for the durability of the concrete structure. Among many protective methods aiming at enhancing the durability of concrete, surface treatment has been concerned as an effective and economic method.

Concrete surface treatment materials can be grouped into tree types [1]: (1) hydrophobic impregnation so to produce a water-repellent surface to prevent water ingress, such as siloxane-based water repellent agent; (2) impregnation so to reduce the surface porosity; and (3) organic coating to produce a continuous protective layer as a physical barrier on the concrete surface. Most popular 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 [2]. For hydrophobic impregnation, silane and siloxane are widely used around the world. 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. [3] reported that their capacity of inhibiting water penetration reduced significantly when the water pressure was higher than 120 kgf/m^2. It was reported that their capacity of provide protection would decreased at high water pressure and temperature [3]. Ultraviolet light would harm its effect. Waterglass (sodium silicate) as an inorganic surface treatment agent has been drawn more attention recently. Previous research found that it could significantly reduce the carbonation depth of concrete and its performance can be improved by post-treatment with cationic surfactants [4]. However, it was reported that penetration depth of sodium silicate was minimal and its prevention of chloride penetration was ineffective [5]. Some people also worried about the potential risk of alkali-silica reaction due to the introduction of and there the risk of freeze-thaw damage due to the blocking of channel or water vapor movement. Based on above concerns, it is necessary to develop a new method to improve the performance of waterglass treatment.

As a by-product from the phosphate fertilizer factories, only about 10% of the fluorosilicates can be recycled, leading to low economic benefits and water pollution. This study aims to investigate the potential application of sodium fluorosilicate pretreatment in enhancing the performance of waterglass. In the present paper, the performance of sodium fluorosilicate, waterglass, and combine treatment of sodium fluorosilicate and waterglass are evaluated on following aspects water absorption, water vapor transmission, and chloride migration. The pore structure and microstructre of surface layer was also characterized.

EXPERIMENTAL

A P. I. 42.5 Portland cement with a specific surface area of 336 m^2/kg was used. The chemical composition of used cement is given in Table 1. Natural river sand with a density of 2610 kg/m^3 was used as fine aggregate. The grade of the sand is shown in Table 2.

Table 1 Chemical composition of cement (*w*/%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Na_2O_{eq}	LOI
Percentage	21.91	5.30	3.67	64.5	1.51	0.62	0.19	2.03	0.59	2.49

Table 2 Grading of fine aggregate

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

Waterglasses ($Na_2O{\cdot}nSiO_2$) with modulus (n) of 2, and sodium fluorosilicate were used as surface treatment agents. The watergalss with n = 2 was obtained by adding 5.92g NaOH in 100g industrial grade waterglass with modulus of 3. Then the waterglass was mixed with water in the proportion of 1:4 by weight to make a solution. Sodium fluorosilicate with a concentration of 2 wt. % was used alone as a surface treatment agent, and pre-treatment agents for waterglass treatment.

All the mortars were prepared with sand-to-cement ratio of 1.5 and water to cement ratio (w/c) of 0.45. Cubic specimens of 40×40×40 mm was cast for d water absorption testing; cylinder specimens of Φ75×100 mm and Φ110×100 mm were made in PVC molds for water vapor transmission and rapid chloride migration (RCM) testing respectively.

After curing for 6 days, top 25 mm ends of cylinders were cut off perpendicularly to its axis The cutting surfaces of cylinders and a lateral sides of cubic samples were marked and considered as treated surface. In samples SF and W2, the treated surfaces were brushed with surface treatment agents using a nylon brush every two hours for four times as shown in Table 3. In term of sample SF-W2, the same face was firstly brushed with sodium fluorosilicate every two hours for four times. And after 24 hours, waterglass treatment was applied on the treated surface for other 4 times. Then, all treated cylinders were placed back into the standard moist room at 20 ± 1 °C and RH ≥ 98% until testing.

Table 3. Surface treatment on cutting surface of the mortar and paste cylinders.

Specimen	Surface treatment	Treatment number
UNTR	no treatment	0
SF	2% sodium fluorosilicate solutions	4
W2	waterglass with modulus of 2	4
SF-W2	2% sodium fluorosilicate solutions + waterglass with modulus of 2	4+4

The water absorption test was conducted in accordance to ASTM C1585-13. Wet-cup method was used following ASTM E96-2005. The RCM testing time and voltage were chosen following Chinese Standard of GBT50082-2009. Mercury intrusion porosimetry (MIP) is based on the principle that mercury, a typical non-wetting liquid, can only intrude a porous material if a certain pressure is applied on the measured samples

RESULTS AND DISCUSSSION

Water absorption

Fig.3. shows the initial water absorption coefficients of mortar samples with sodium fluorosilicate and waterglass. It can be seen that water absorption coefficients of cement mortar decreased after surface treatment, and this effect generally increase with curing time. Sodium fluorosilicate treatment only affected the water absorption coefficients slightly. The initial water absorption coefficient was decreased by 3.9% after treatment, and 7.7% after 28 d of

treatment. For waterglass, it showed more obvious effect on resisting the ingress of water. Compared with control sample, its initial water absorption coefficient was reduced by 15.2% after treatment, and was further reduced by 41% after 28 d. The effect of combine treatment of sodium fluorosilicate and waterglass is even more significant than waterglass treatment alone. It allowed the initial water absorption coefficient dropped to half of untreated sample at 28 d. Since the effect of sodium fluorosilicate itself is negligible, the interaction between waterglass and sodium fluorosilicate should play an important role in its protective effect. Additionally, though all the samples showed better resistance to water ingress with increase of curing time, the decrease rate depended on the surface treatment method. It could find that the influence of sodium fluorosilicate pretreatment was reduced with time, but the effect of waterglass increased. This is because the sodium fluorosilicate accelerated the waterglass hardening at the beginning. Thus, the combined sodium fluorosilicate pretreatment and waterglass treatment reduced the permeability of concrete more efficiently at early ages.

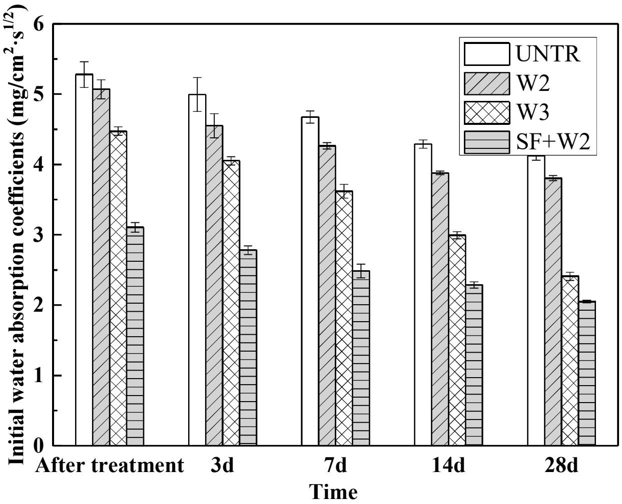


Fig.3. Effect of sodium fluorosilicate and waterglass on initial water absorption coefficients of cement mortars

Water-vapor transmission

Previous research showed that the migration of water-vapor related to the development of a moisture gradient which may result in shrinkage or expansion of the material, and has a good relationship with resistance to carbonation and thaw-freeze cycles [7, 8]. The slope of the mass loss in the steady state vs. time curve is defined as water vapor permeability coefficient, and showed in Fig. 4. After surface treatments, the vapor permeability coefficient of control sample, sodium fluorosilicate, waterglass and combine treatment samples were respectively 4.10×10^{-6}, 4.07×10^{-6}, 3.82×10^{-6} and 3.41 $g/mm^2\cdot h$. After 28 days of surface treatments, these vapor permeability coefficients were further decreased by 4.9%, 21.1% and 32.79% respectively. The combine treatments also showed most effective influence on prevent water vapor permeability. With the increase of curing time, the water vapor permeability coefficient decreased further in all samples. Similar with the water absorption result, the sodium fluorosilicate pretreatment not only improved the effect of waterglass treatment at early age, but also enhance its long-term effects. Without the sodium fluorosilicate pretreatment, the prevention of waterglass took more time to show up.

Fig. 5 presented the results of chloride migration coefficient of surface treatment cement mortars. All three inorganic surface treatments could prevent the ingress of Cl^- into mortar substrate. The chloride migration coefficient of untreated sample was $25.4 \times 10^{-12} m^2/s$ after treatment, and it reduced by 46.6 % at 28 d. For mortar samples treated with sodium fluorosilicate and waterglass, their chloride migration coefficients were similar with control sample after treatment, while they further decreased by 52.5% and 56.5% at 28 d. Unlike their effect on water and vapor permeability, both of them did not show obvious effect on mitigating the chloride migration. This result is consistent with previous results [5, 9]. It is notice that the combine treatment significantly improved the resistance of chloride migration right after the treatment, and its effect also became stronger with curing. Its chloride migration coefficient was 59.4% and 19.3% of control samples after treatment and 28 days respectively. This result indicated that combine treatment has bigger advantage in enhance quality of the surface layer than waterglass treatment.

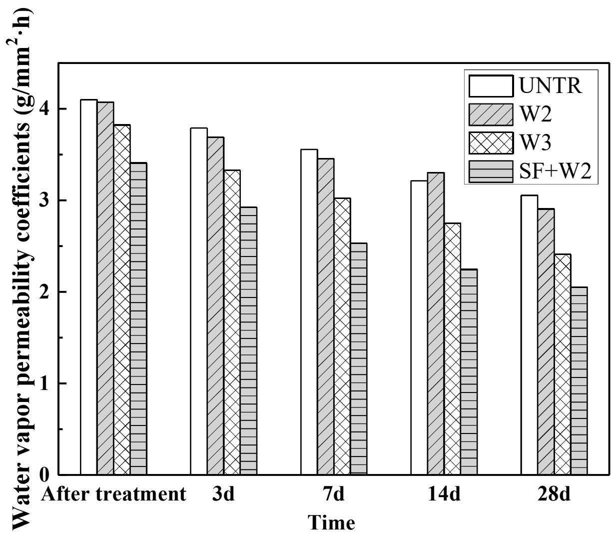


Fig. 4. Effects of sodium fluorosilicate and waterglass on the water vapor transmission coefficient of cement mortars

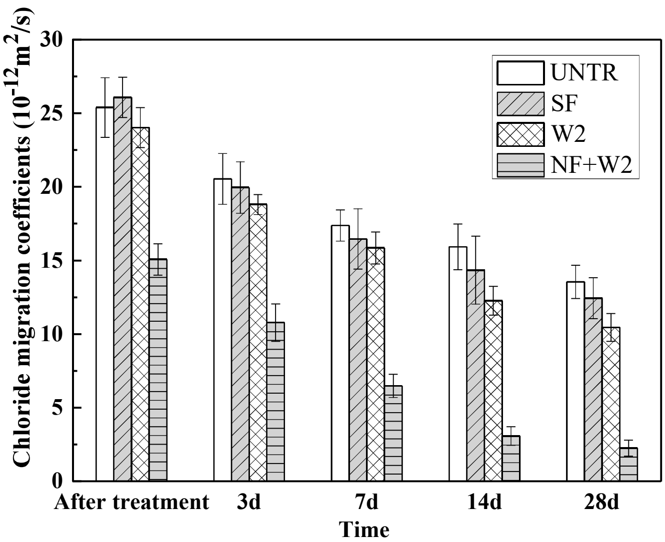
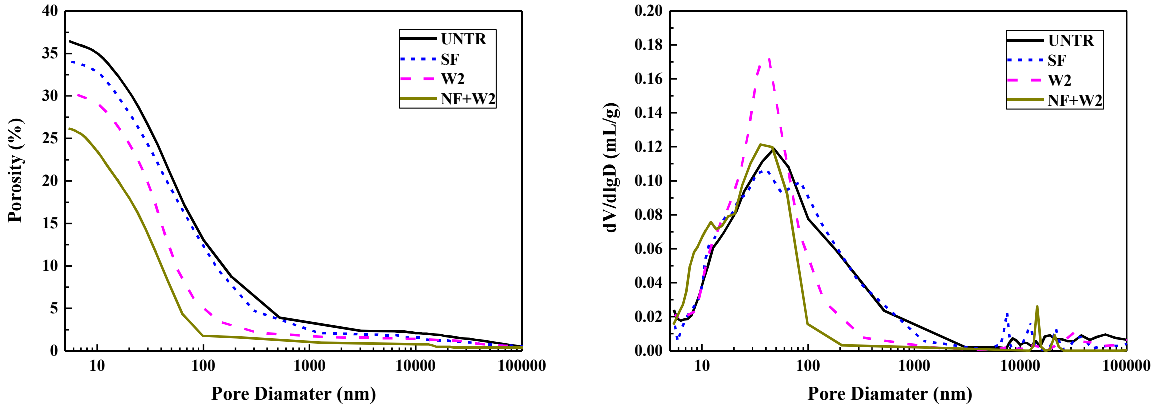


Fig.5. Effects of sodium fluorosilicate and water-glass on the chloride migration coefficient of cement mortars

Pore structure

Fig. 6 hows the porosity and pore size distribution of 10 mm surface layer of mortar with different inorganic surface treatments at 28 d. It can be seen from Fig. 6(a) that the total porosity decreased after surface treatment. Among all the surface treatment, the sodium fluorosilicate had little effect on reducing the porosity of surface layer as a surface treatment agent. However, it can find that it showed great influence on the porosity as a pretreatment agent. The total porosity of surface layer treated with waterglass was 30.45%, while sodium fluorosilicate pretreatment made it reduce to 26.2%. In addition, according to Fig. 6(b), waterglass and combine treatment can efficiently fill surface pores with diameter higher than 100 nm, and thus change the pore structure in surface layer. This may attributes to their protective effect on cement mortar.

In order to further analyze the MIP results, the pores can be classified into five categories, including gel micro-pores (<10 nm), meso-pores (10–50 nm), middle capillary pores (50–100 nm), large capillary pores (100–5000 nm), and macro-pores (>5000 nm) [10]. These values are summarized in Table 3. It can be seen that the volume fractions of micro-pores and meso-pores pores in mortar surface increased after surface treatments, especially waterglass and combine treatments. On the other hand, the total fraction volume of large capillary pores decreased by 21.3%, 56.7% and 83.5% after sodium fluorosilicate, waterglass and combine treatments respectively. Mehta et al [11] thought that the pores larger than 100nm were related to the permeability of concrete. Thus, the greatly reduction in volume of large capillary is important to the resistance of concrete to water penetration.



a) Porosity b) Differential pore size distribution

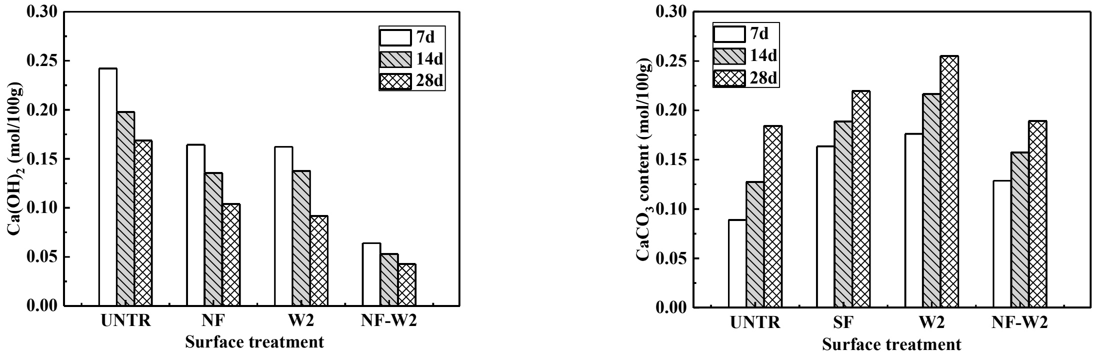
Fig. 6. Effects of sodium fluorosilicate and waterglass on porosity of surface layers at 28 d

Table 4. Pore structure characteristics of mortar surface layer with different surface treatments

Sample	Total porosity/%	Critical-pore diameter (nm)	Pore size distribution/%			
			<50nm	50-100nm	100nm-1μm	>1μm
UNTR	36.46	65.51	41.20	22.19	29.37	6.44
SF	34.04	56.35	47.81	24.40	21.93	6.22
W2	30.45	33.83	68.55	20.19	11.04	4.48
NF-W2	26.18	35.55	68.39	24.84	2.25	3.67

Thermogravimetric analysis

The TGA quantified amounts of $Ca(OH)_2$ and $CaCO_3$ in the surface layers of samples after t surface treatments are shown in Fig. 7. The results in Fig. 7(a) shows that all the studied surface treatment agents can reduce the amount of $Ca(OH)_2$ as compared to the reference sample (UNTR). Samples treated with waterglass and sodium fluorosilicate have comparable but lower amount of $Ca(OH)_2$ than that of untreated sample. Dramatic reduction in $Ca(OH)_2$ were observed in SF-W2 sample indicating that combination of sodium fluorosilicate and waterglass has a synergetic effect with respect to reduction of $Ca(OH)_2$ content. It could be seen from Fig. 7(b) that the combined treatment slightly increased $CaCO_3$ content, while the $CaCO_3$ content was significantly increased in the pastes treated with waterglass and sodium fluorosilicate. The $CaCO_3$ content of sample W2 were increased by 97%, 70% and 38% compared with that of the control sample at 7, 14 and 28 days. Less amount of but similar trend was fond in sodium fluorosilicate treated sample. This result indicated that them could react with $Ca(OH)_2$ and made carbonation in surface layer more easily during storage, because of the reaction with CO_2 from the ambient environment. Though the mechanism needs more investigation, watergalss treatment could accelerate the carbonation of $Ca(OH)_2$ most pronounced, which might contribute to its effect on reducing porosity and small influence on chloride migration.



a) $Ca(OH)_2$ b) $CaCO_3$

Fig.7. Effect of sodium fluorosilicate and waterglass treatments on $Ca(OH)_2$ (a) and $CaCO_3$ (b) content.

CONCLUSIONS

The effects of sodium fluorosilicate treatment, waterglass treatment and combine treatment of sodium fluorosilicate and waterglass on permeability and microstructure of cement mortars were investigated. The sodium fluorosilicate had little influence on the water permeability, vapor permeability and chloride migration when acts as a surface treatment agent independently. However, it shows potential on improve the performance of waterglass treatment. The waterglass surface treatment could not only significantly reduce the content of $Ca(OH)_2$, but also increased the content of $CaCO_3$ and gel products. The sodium fluorosilicate could accelerate the hardening of waterglass and show impact on the chemical composition and morphology of surface layer. It reduced the $Ca(OH)_2$ and accelerated the carbonation, while could not significantly increase the total gel content. The pore blocking effect of the combined treatment of waterglass and sodium fluorosilicate was much significant odds. The combined treatment could not only significantly reduce the content of $Ca(OH)_2$, while did not significantly increased the content of $CaCO_3$.

REFERENCES

[1] X. Y. PAN, et al. *A review on concrete surface treatment Part I: Types and mechanisms.* Constr. Build. Mater. 132 (2017): 578-590.

[2] Y. DANG, et al, *Accelerated laboratory evaluation of surface treatments for protecting concrete bridge decks from salt scaling.* Constr. Build. Mater. 55(2014): 128-135.

[3] MEDEIROS M, HELENE P, *Efficacy of surface hydrophobic agents in reducing water and chloride ion penetration in concrete.* Mater. Struct. 41(2008): 59-71.

[4] D.A. KAGI, K.B. REN, *Reduction of water absorption in silicate treated concrete by post-treatment with cationic surfactants.* Build. Environ. 30(1995): 237-243.

[5] J. G. DAI, et al., *Water repellent surface impregnation for extension of service life of reinforced concrete structures in marine environments: the role of cracks.* Cem. Concr. Compos. 32(2010): 101-109.

[6] L. BERTOLINI, *Corrosion of steel in concrete: prevention, diagnosis, repairs.* 2013: John Wiley & Sons.

[7] ASTM International, Standard test method for measurement of rate of absorption of water by hydraulic-cement concretes. ASTM (2004) C1585.

[8] P HOU et al. *Characteristics of surface-treatment of nano-SiO2 on the transport properties of hardened cement pastes with different water-to-cement ratios.* Cem. Concr. Compos. 55(2015): 26-33.

[9] L JIA, C SHI, X PAN, J ZHANG, L WU, *Effects of inorganic surface treatment on water permeability of cement-based materials*. Cem. Concr. Compos. 67 (2016): 85–92.

[10] J.B. AGUIAR. *Carbonation of surface protected concrete*. Constr. Build. Mater. 49 (2013): 478–483.

[11] X ZHANG, et al. *Studies on forecasting of carbonation depth of slag high performance concrete considering gas permeability*. Appl. Clay Sci., 79 (2013): 36–40.

[12] M. BRAHIM, et al., *Use of surface treatment materials to improve concrete durability.* J. Mater. Civ. Eng., 11(1999):36-40.

[13] METHA PK, Concrete, Microstructure, Properties and Materials, McGraw-Hill, London, (2006).

[14] D. MANMOHAN, P. K. METHA. *Influence of pozzolanic, slag, and chemical admixtures on pore size distribution and permeability of hardened cement pastes*. Cem. Concr. Aggre. 3 (1981): 63-67.