

## Article

# The Effects of Various Silicate Coatings on the Durability of Concrete: Mechanisms and Implications

Jinfu Li <sup>1</sup>, Jiale Song <sup>1,\*</sup>, Shuheng Zhang <sup>1</sup>, Wei Liu <sup>1</sup>, Zhaokuan Cui <sup>1</sup> and Weiguang Li <sup>2,\*</sup>

<sup>1</sup> School of Materials Science and Engineering, Chang'an University, Xi'an 710064, China; lif0521@163.com (J.L.); tangruos8117414@163.com (S.Z.); liuweil017@chd.edu.cn (W.L.); 18209237953@163.com (Z.C.)

<sup>2</sup> School of Highway, Chang'an University, Xi'an 710064, China

\* Correspondence: jlsong@chd.edu.cn (J.S.); wgli@chd.edu.cn (W.L.)

**Abstract:** Silicate solutions can improve the durability of concrete conveniently and effectively. To horizontally compare the enhancement effects of different composite silicate solutions, three types of silicate surface treatment agents were prepared by using sodium silicate, potassium silicate, and lithium silicate as the main agents, along with urea, sodium polyacrylate, catalysts, and fluoro-carbon surfactants as the adjuvants. Furthermore, their effects on the durability of concrete were compared. The results showed that silicate surface treatment could reduce the content of  $\text{Ca}(\text{OH})_2$ , increase the content of hydrated calcium silicate (C-S-H), and improve the compactness and hydrophobicity of the hardened cement surface. Although the three surface treatments enhanced the durability of concrete, the effects differed based on the complexities and mixtures. The sodium silicate compounded with potassium silicate performed the best of all three, wherein the content of the C-S-H gel increased by 389.8%, the permeability decreased by 60.6%, the water contact angle improved to  $83.5^\circ$  and the chloride ion resistance and freeze–thaw resistance of concrete increased by 36.7% and 37.34%, respectively, compared with the control sample.

**Keywords:** surface strengthening; complex silicate; concrete; durability



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## 1. Introduction

Concrete is a heterogeneous, porous material with a highly hydrophilic nature and a microcrack structure, which is widely applied in foundation engineering [1,2]. During practical applications, harmful ions, including external water,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ , persistently infiltrate concrete through surface pores, leading to freeze–thaw damage, chloride ion erosion, and other problems [3]. Consequently, these jeopardizations diminish the durability of concrete, significantly shortening the service life of buildings and even posing a threat to the safety of people's lives and property. Thus, it is imperative to develop concrete protection that can delay the erosion process and enhance the service life of concrete.

In engineering practice, extensive efforts have been made in several aspects to protect concrete, such as reducing porosity and enhancing impermeability. To improve concrete impermeability, researchers have carried out a lot of work in reducing the water–cement ratio, adjusting aggregate gradation, and surface protection techniques [4–6]. Among them, the surface protection technique is an extremely effective and convenient method to improve the resistance of concrete to the penetration of corrosive substances. Currently, according to their chemical compositions, surface protective agents can be categorized into organic and inorganic types [7–10]. Notably, organic surface protective agents exhibit excellent film-forming properties. Medeiros et al. [11] observed that siloxane coatings can improve concrete durability. Unfortunately, when the water pressure is high, its ability to inhibit water intrusion is significantly reduced. Franzoni et al. [12] demonstrated that ethyl silicate can enhance wear resistance and carbonization resistance in concrete. However, the organic coating exhibits significant cracking after post-curing. Additionally, the instability

of organic chemical bonds, influenced by factors like sunlight exposure and air humidity, leads to the rapid loss of the original protective properties in organic coatings, limiting their overall durability [4,13]. Therefore, researchers have turned their attention to inorganic coating materials with more stable chemical bonds. Silicate materials can not only form a film after being coated on the concrete surface but also react with  $\text{Ca}(\text{OH})_2$  in the cement matrix to form inorganic calcium silicate hydrate (C-S-H gel). The information of inorganic coating can effectively prevent harmful substances and improve the corrosion and wear resistance of cement slurry [13,14]. Its waterproof effect is almost permanent. In addition, it is also environmentally friendly due to the water-based material. Currently, numerous studies on the application of silicate coatings have revealed that the permeability of the concrete matrix after silicate surface treatment is significantly reduced [15–17], leading to improved corrosion resistance. Nevertheless, most current studies concentrate on single silicate coatings, which tend to exhibit surface cracking and weak water resistance after post-curing, leading to suboptimal treatment outcomes [12].

To address these issues, researchers employed a compound modification strategy. Yu et al. [18] combined sodium silicate with lithium silicate, enhancing the permeability, curing properties, and resistance to pulverization of the mixture. Likewise, the combination of sodium silicate and potassium silicate improved the moisture absorption resistance of the mixed solution, effectively mitigating the increase in the alkalinity of the concrete surface [19]. These studies highlight the significant advantages of combination. Nevertheless, there is still a lack of systematic comparative studies to provide necessary theoretical support and explanation. Furthermore, the majority of existing research on silicate treatment agents primarily focuses on comparing their effects on improving concrete performance with other types of treatment agents. There is also a scarcity of cross-sectional studies on various composite silicate-based treatment agents.

Herein, building upon the original research [20,21], this work prepared a concrete surface treatment agent by pairing lithium silicate, sodium silicate, and potassium silicate while incorporating essential auxiliaries. Gel time measurement was utilized to characterize the reaction rate between silicate and calcium hydroxide in concrete. The effects of three composite silicate coatings on concrete durability were comparatively investigated by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), surface contact angle, rapid chloride permeability test, and freeze–thaw resistance test. Whereafter, the strengthening mechanism of composite silicate coatings on the concrete surface was explored, offering essential support for the development of protective coatings for concrete.

## 2. Materials and Methods

### 2.1. Materials

Ordinary Portland cement (Type P·O42.5 with a specific surface area of  $346 \text{ m}^2/\text{kg}$  and chemical composition detailed in Table 1) was procured from Anhui Conch Cement Company, Wuhu, China. Fine aggregate comprised natural river sand (with a fineness modulus  $M_f = 2.65$  and gradation outlined in Figure 1), procured from Shaanxi Sand and Stone Wharf Company, Xi'an, China. Coarse aggregate consisted of granite gravel (with a maximum particle size of 20 mm and apparent density is  $2710 \text{ kg}\cdot\text{cm}^3$ ) acquired from Shaanxi Sand and Stone Wharf Company. Sodium silicate (with a modulus of 2.25), potassium silicate (with a modulus of 2.4), and lithium silicate (with a modulus of 4.8) solutions were obtained from Yourui Refractory Co., Shandong, China.

**Table 1.** Chemical composition of P·O42.5 cement.

| Ingredient     | $\text{SiO}_2$ | $\text{Al}_2\text{O}_3$ | $\text{Fe}_2\text{O}_3$ | CaO   | MgO  | f-CaO |
|----------------|----------------|-------------------------|-------------------------|-------|------|-------|
| Percentage (%) | 21.40          | 4.62                    | 3.25                    | 64.70 | 2.78 | 0.85  |

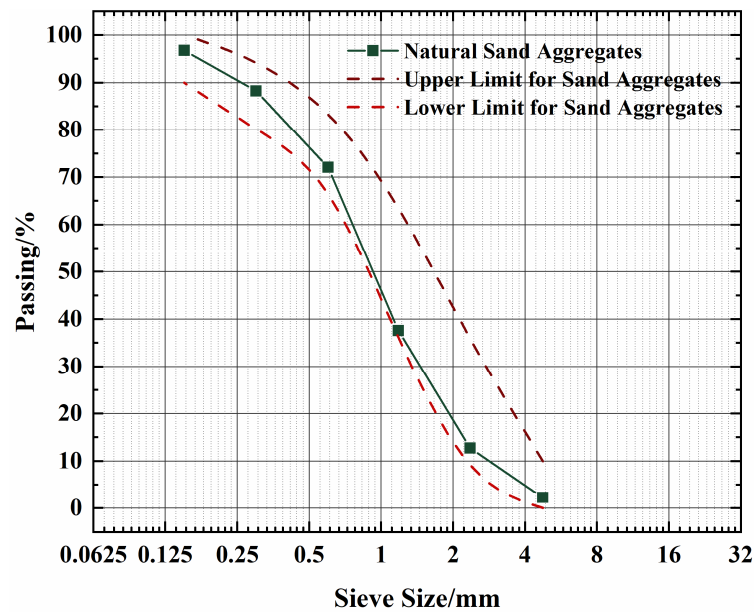


Figure 1. Gradation of sand.

## 2.2. Preparation of Three Compound Systems

Silicates were paired according to experimental design specifications. After thorough mixing, a complex system was created by sequentially adding surfactants, catalysts, defoamants, and film-forming additives. In this experiment, following the original work [20,21], the composite ratio providing the best permeability resistance was chosen from various proportioned composite systems within each group for a horizontal comparative study. The optimal composite scheme for silicate solid content in the three groups was determined as follows: Lithium silicate/sodium silicate (7:3, LN system), sodium silicate/potassium silicate (2:8, NK system), potassium silicate/lithium silicate (5:5, KL system), and KB system in the blank control group. In this experiment, the concentration of the above complex solutions was 20.0 wt%.

## 2.3. Preparation of Samples

With a water–cement ratio ( $w/c$ ) of 0.5, a mortar cube measuring 70 mm in length, width, and height was prepared for morphology, microstructure characterization, and impermeability tests. For air permeability testing, a mortar cylinder with a diameter of 100 mm and a height of 10 mm was prepared. For the carbonization resistance test, a cubic concrete specimen measuring 100 mm in length, width, and height was prepared. Cuboid concrete specimens, with dimensions of 400 mm (length), 100 mm (width), and 100 mm (height), were prepared for the freeze–thaw resistance test. For the chloride ion penetration resistance test, a cylindrical concrete specimen with a diameter of 100 mm and a height of 50 mm was prepared. All samples were compacted on a controlled shaking table, stored in the laboratory at  $20 \pm 1$  °C for 24 h, released, and subsequently cured in a standard curing room at  $RH \geq 98\%$  and  $T = 20 \pm 1$  °C until further treatment.

Following 26 days of standard curing, the sample underwent a 2-day drying process in an 80 °C oven, followed by cooling to room temperature. Subsequently, the molded surface of each sample was polished. In accordance with Table 2, a nylon brush dipped in a surface protective agent was utilized for coating until it achieved a mirror-wetted state. After a 1 h interval, it underwent an additional 4 coatings, resulting in a total coating amount of 900 g/m<sup>2</sup>. Following coating, all test surfaces underwent a 7-day room temperature curing period before proceeding to performance tests.

**Table 2.** Cutting surface treatment of mortar and concrete.

| Specimen | Surface Treatment                      | Treatment Number |
|----------|----------------------------------------|------------------|
| KB Group | No treatment                           | 0                |
| LN Group | Surface Protection Agent for LN System | 4                |
| NK Group | Surface Protection Agent for NK System | 4                |
| KL Group | Surface Protection Agent for KL System | 4                |

#### 2.4. Methods

Fourier transform infrared spectroscopy (FT-IR) of the sample was conducted using an ALPHA-II type infrared spectrograph from Bruker, Germany. The samples underwent analysis using the D8 AdvanceX X-ray diffraction spectroscopy instrument (XRD, Bruker, Germany). Scanning electron microscopy (SEM) images of the sample were captured using a scanning electron microscope, model S-4800 (SEM, Hitachi, Japan). The water contact angle of the sample was measured using the JC2000D1 contact angle (Shanghai Zhongchen Company, Shanghai, China) measuring instrument. The colloidal particle size of the compound solution was determined using the ZEN3600 Zeta potentiometer (Malvern, UK). The gel time of various compound silicate treatment agents was determined at room temperature following the guidelines of the China Building Materials Industry Standard JC/T 1018-2006 [22]. The chloride ion resistance and freeze–thaw resistance of the specimens were tested by GB/T 50082-2009 [23], the “Standard of Test Methods for Long-term Performance and Durability of Ordinary Concrete”.

For each test, 3 samples were tested to determine the mean values and corresponding standard deviations.

### 3. Results and Discussion

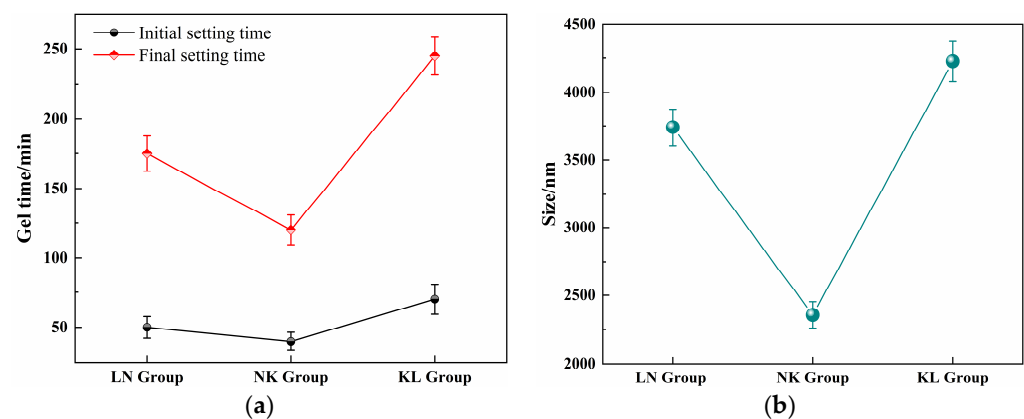
#### 3.1. Performance Analysis of the Compound Solution

Gel time is a characteristic value that reflects the reaction speed between silicate and calcium hydroxide in concrete. An excessively short gel time indicates that the gel reacts too rapidly, resulting in the premature blockage of capillary channels and a reduction in penetration depth. Additionally, C-S-H gel rapidly forms on the surface of the concrete, obstructing surface pores and impeding the penetration of remaining silicate. This result leads to a protective coating that is too thin, rendering it ineffective. Conversely, an excessively long gel time not only indicates prolonged gel reaction time but also signifies an overly high concentration of silicate. This high concentration can lead to self-aggregation inside the concrete, forming orthosilicic acid, thereby impeding the reaction with  $\text{Ca}(\text{OH})_2$ .

Consequently, the gel time of different complex silicate compounds was tested, as illustrated in Figure 2a. The initial setting time of the three compound silicate groups appears similar, but there is a significant difference in the final setting time. The lithium silicate composite solution exhibits prolonged initial and final gel times, which is attributed to the smaller radius and higher charge density of lithium ions. In contrast, potassium silicate exhibits higher reactivity than sodium silicate. Theoretically, the final setting time of the KL group should be lower than that of the LN group. Surprisingly, the final setting time of the LN group is lower than that of the KL group. This discrepancy is attributed to the varying proportions of silicate compounds. The KL group generates a more extensive Si-O-Si colloidal network structure [24], hindering the interaction between potassium silicate and  $\text{Ca}(\text{OH})_2$  and resulting in an excessively long gel time for the KL group.

Varied gelling times among compound silicates result in diverse penetration depths, as detailed in Table 3. The KL group exhibits the lowest penetration depth. This result is attributed to its excessively long gel time, causing silicate self-aggregation on the concrete surface. This self-aggregation hinders the penetration of remaining silicate into the sample interior. To gain deeper insights into the internal conditions of the compound solution, a Zeta potential meter was employed to measure the colloidal particle size, as presented in Figure 2b. The silicate aqueous solution is fundamentally a colloidal solution consisting of

two components. One component involves the reaction between silicate and water, resulting in the generation of  $\text{Si(OH)}_4$ . The original silicate monomers condense to form dimers, and as the polymerization concentration reaches a certain level, monomers react with dimers to create trimers or higher polymers. This process ultimately produces larger spherical colloidal particles via a ring-closing reaction [25]. The second component comprises colloidal particles formed in the silicate aqueous solution, where  $\text{SiO}_2$  serves as the colloidal core. The colloidal core absorbs free  $\text{SiO}_3^{2-}$  and alkali metal ions in the solution, forming an adsorption layer. Together, the colloidal core and the adsorption layer constitute the second type of colloidal particle [26]. The KL group exhibits the largest particle size because of its heightened activity, leading to self-aggregation into larger particles that cannot penetrate into the concrete. In contrast, the NK group has the smallest particle size. Smaller particles are more adept at penetrating the interior through channels in the concrete matrix. They react with internal  $\text{Ca(OH)}_2$  to generate C-S-H gel, filling pores and cracks and aligning with the penetration depth results.



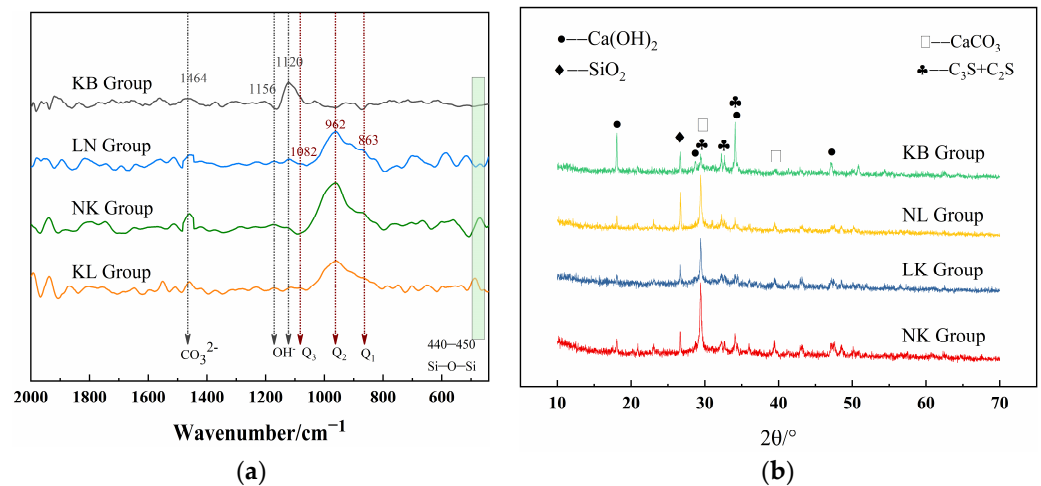
**Figure 2.** (a) Gelation time of composite silicate. (b) Colloidal particle size of different compound solutions.

**Table 3.** The permeability depth results for various compound silicates.

| Specimen | Treatment Number | Penetration Depth/mm |
|----------|------------------|----------------------|
| LN Group | 4                | 2.9                  |
| NK Group | 4                | 3.0                  |
| KL Group | 4                | 2.6                  |

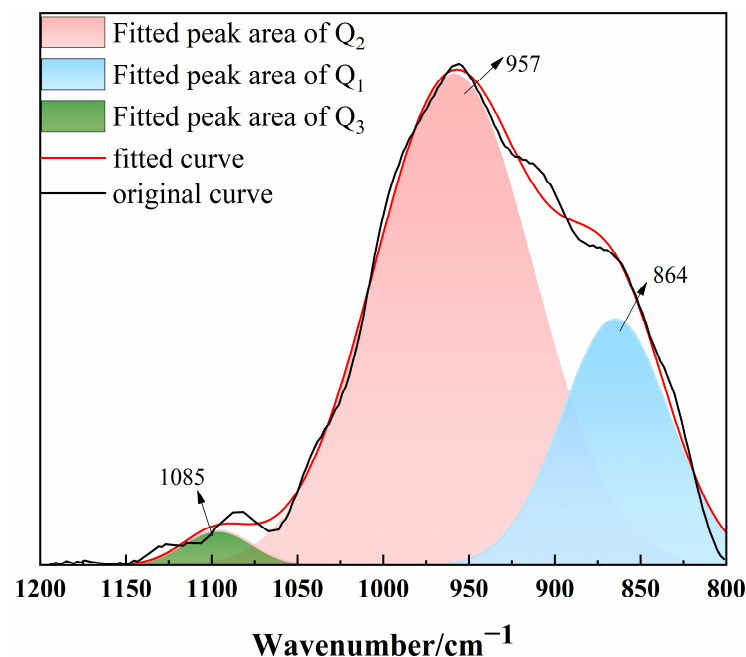
### 3.2. Analysis of Hydration Products

In Figure 3a, the FT-IR spectra in the range of  $2000\text{--}400\text{cm}^{-1}$  are shown before and after the surface treatment of the paste sample. In the untreated control group, the peaks at  $1156\text{ cm}^{-1}$ ,  $1464\text{ cm}^{-1}$ , and  $1120\text{ cm}^{-1}$  correspond to the stretching vibration of  $\text{CO}_3^{2-}$ , the asymmetric stretching vibration of  $\text{CO}_3^{2-}$ , and the stretching vibration of  $\text{OH}^-$ , respectively. After treatment, the  $\text{OH}^-$  stretching vibration peak basically disappeared, and a new peak appeared at  $960\text{ cm}^{-1}$ , indicating a reaction between the hydroxyl groups and silicate. Furthermore, peak splitting was performed. The symmetrical vibration peak at  $1082\text{ cm}^{-1}$ , labeled as  $\text{Q}_3$ , is usually the C-S-H gel after carbonization. The  $\text{Q}_1$  vibration peak at  $863\text{ cm}^{-1}$  represents the main component of unhydrated cement and is related to the Si-O stretching vibration. The stretching vibration peak of silicon-oxygen tetrahedral unit  $\text{Q}_2$  is at  $962\text{ cm}^{-1}$ , indicating that the cement is effectively hydrated, which reflects the content of the C-S-H gel [27–30].



**Figure 3.** (a) FT-IR spectra of mortar samples both before and after surface treatment. (b) XRD patterns of paste samples treated with various compound silicates on the surface.

In order to further study the impact of treatment on the interior of concrete, the area integration of these characteristic peaks was performed, as shown in Figure 4, and the corresponding integrated area is detailed in Table 4. In comparison, surface treatment resulted in a significant decrease in the characteristic peak areas of OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> and a significant increase in the Q<sub>2</sub> peak area. This phenomenon is caused by the reaction between Ca(OH)<sub>2</sub> and silicate, consuming OH<sup>-</sup> and forming a C-S-H gel. The C-S-H gel prevents CO<sub>2</sub> from entering the interior and reacting with Ca(OH)<sub>2</sub> to form CaCO<sub>3</sub>. Therefore, this reduces the OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> content and increases the C-S-H gel content. It is worth noting that the NK group shows the largest Q<sub>2</sub> peak area, indicating that the NK group reacts most fully with Ca(OH)<sub>2</sub> and has the highest C-S-H gel content. In addition, the red shift of the Q<sub>2</sub> vibration peak may be due to the increase in the degree of gel polymerization, resulting in a decrease in vibration frequency.



**Figure 4.** The fractional integration of Si-O vibration peaks in C-S-H gel.

**Table 4.** The integral area of extrinsic characteristic peaks for each group before and after sample processing.

|          | Ca(OH) <sub>2</sub> | CaCO <sub>3</sub> | Q <sub>1</sub> | Q <sub>2</sub> | Q <sub>3</sub> |
|----------|---------------------|-------------------|----------------|----------------|----------------|
| KB Group | 9.205               | 2.762             | 8.127          | 9.876          | 1.795          |
| LN Group | 1.832               | 5.537             | 13.348         | 41.351         | 1.631          |
| NK Group | 1.164               | 8.816             | 12.948         | 48.381         | 1.278          |
| KL Group | 3.738               | 4.513             | 14.068         | 36.151         | 1.865          |

The C-S-H gel characterizes the degree of hydration of cement and also reflects the degree of pozzolanic reaction. The XRD patterns of the clean paste specimens of different samples after curing for 28 d are shown in Figure 3b. The spectrum of the blank control group shows the diffraction peaks of Ca(OH)<sub>2</sub>, CaCO<sub>3</sub>, SiO<sub>2</sub>, C<sub>2</sub>S, and C<sub>3</sub>S [31,32]. The Ca(OH)<sub>2</sub>, C<sub>2</sub>S, and C<sub>3</sub>S peaks at  $2\theta = 32.3^\circ$  have the highest intensity, indicating that the 28-day cement is not fully hydrated and contains a large number of unreacted substances. These substances can provide the necessary reactants for subsequent penetration of the silicate solution. No new diffraction peaks appeared after treatment with three types of composite silicates. However, the peaks corresponding to C<sub>3</sub>S, C<sub>2</sub>S, and Ca(OH)<sub>2</sub> decreased significantly, and the peak corresponding to CaCO<sub>3</sub> increased. This suggests that complex silicates promote the Ca(OH)<sub>2</sub> reaction, leading to the formation of C-S-H gels. Furthermore, this accelerates the carbonization of the C-S-H gel, leading to the formation of CaCO<sub>3</sub> crystalline products and increasing the hardness of the cement surface layer. This result is consistent with the results of FT-IR analysis.

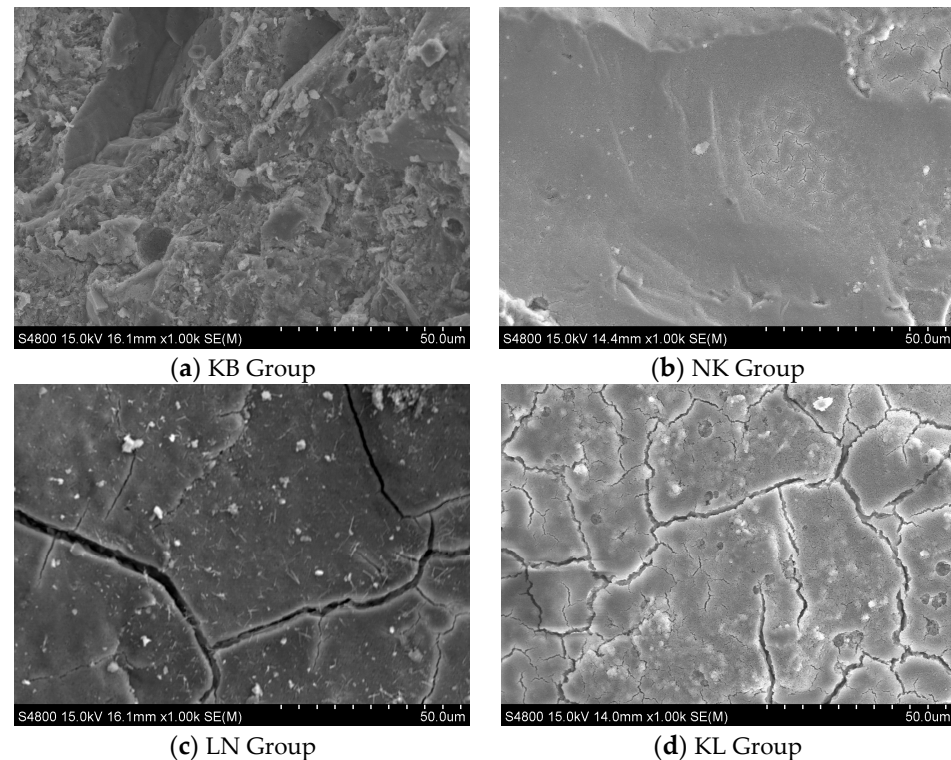
The XRD patterns of the three kinds of compound silicate-treated slurries' surfaces are further compared, and the peaks of Ca(OH)<sub>2</sub>, C<sub>2</sub>S, and C<sub>3</sub>S in the NK system are the lowest, while the peak of CaCO<sub>3</sub> is the highest, indicating that the NK system reacts most fully with Ca(OH)<sub>2</sub>. It removes a large amount of unreacted active substances on the concrete surface, promotes the cement hydration process, and fills the surface pores. The peak value of CaCO<sub>3</sub> in the KL system is lower than that of the other two systems, and the peak value of SiO<sub>2</sub> does not increase significantly, indicating that the type of alkali metal ions in the complex silicates will affect the activity of the surface strengthening reaction.

### 3.3. Analysis of the Effect of Surface Treatment Agents on Morphology

Figure 5 shows SEM photos of 28-day samples treated with three different composite silicate systems. As shown in Figure 5a, the surface of the sample without surface strengthening treatment is rough, resulting from unhydrated cement particles (Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> crystals) as well as depicts a large number of pores and cracks. This structure can create a pathway for corrosive media to penetrate the concrete matrix. Figure 5b–d show the surface morphology of samples treated with three composite silicate solutions. Compared with the untreated surface, their surfaces show a denser structure, which is ascribed to the penetration of composite silicates into concrete through pores and cracks. The composite silicates would react with Ca(OH)<sub>2</sub> to form C-S-H gel and effectively fill these voids [12]. At the same time, a Si-O-Si cross-linked network shielding layer is formed by the reaction between polysilicic acid, being formed by hydrolysis and condensation of silicic acid (Si(OH)<sub>4</sub>) and silicate solution, with the hydroxyl groups on the surface of the mortar.

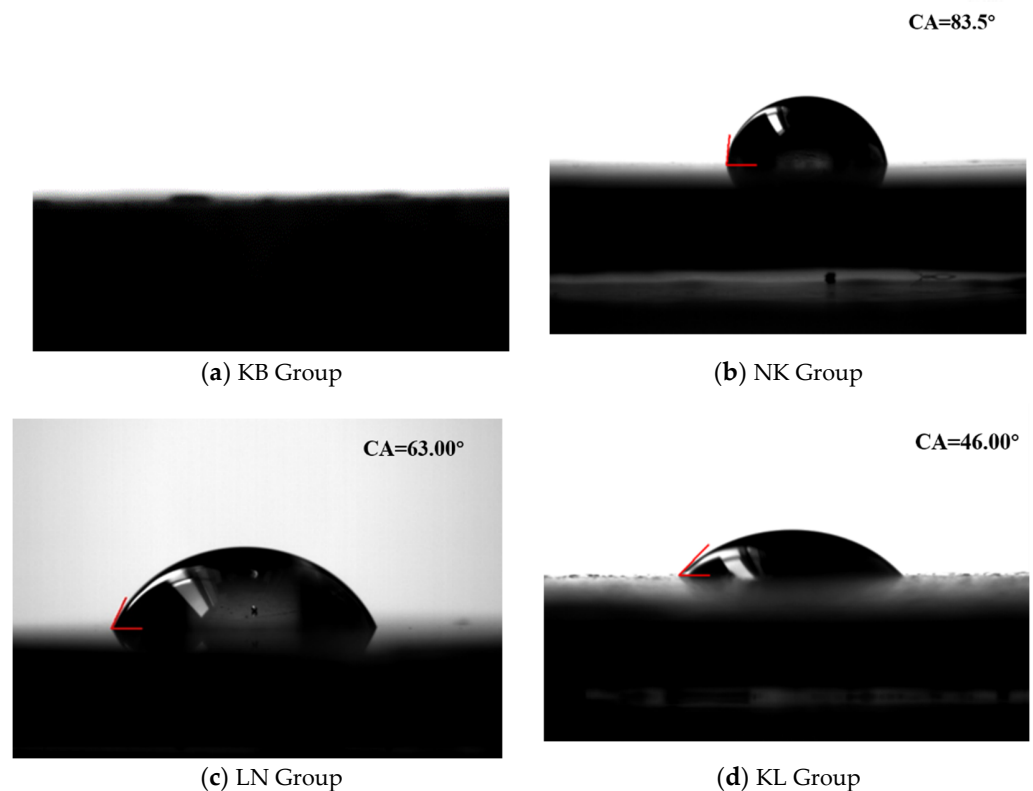
However, the micromorphology of different compound silicate coatings and the number and size of cracks are significantly different. This discrepancy stems from the disparate reactivity of alkali metal cations, thereby inducing pronounced disparateness in the degree of film-forming polycondensation reaction [33]. The NK system has the densest coating with almost no cracks on the surface, while the LN and KL systems present more cracks. This is attributed to K<sup>+</sup>, with the largest radius among the alkali metals Li, Na, and K, the highest degree of ionization, and the fastest hydrolysis to form Si(OH)<sub>4</sub>. Consequently, a proclivity for the agglomeration of polysilicic acid in systems with higher K<sup>+</sup> content. The more serious the problem [33], the worse the film-forming performance

of the coating. And the compounding of sodium silicate reduces the relative content of  $K^+$  in the solution, thereby improving the film-forming performance. Furthermore,  $Na^+$  can act as a catalyst during the film formation process [34] and improve the film-forming properties of the coating, leading to the dense surface of the NK group coating. Similarly, lithium silicate  $Li^+$ , characterized by the smallest atomic radius but high charge density, yields a minimal  $Si(OH)_4$  due to hydrolysis.  $Li^+$  combines with water molecules to form large volumes of hydrated ions, which sterically hinders the film formation of the coating. Although sodium silicate is introduced into the system to improve film-forming properties, the crack of lithium silicate remains inevitable; thus, compared with the NK group, the LN group has more cracks [35]. The introduction of lithium silicate to potassium silicate in silicic acid reduces the polymerization rate and agglomeration tendency of potassium silicate, improving film-forming properties. However,  $K^+$  will lose its coagulation effect at higher pH values [25], and the radius difference between  $Li^+$  and  $K^+$  is the largest. It is difficult to give full play to their respective advantages when the two are combined, resulting in a significant increase in the number of coating cracks. Thus, a notable escalation in the number of coating cracks occurs in the KL system.



**Figure 5.** SEM images of various compound silicate surface-treated mortar samples after 28 days.

To further study the surface-wetting conditions of different samples, the water contact angle after treating the sample surface is shown in Figure 6. The surface water contact angle of the blank control group was  $0^\circ$ , indicating that the surface of the concrete material was completely hydrophilic. After being treated with three kinds of compound silicate systems, the water contact angle significantly increases, indicating that the hydroxyl groups on the surface of the specimen are consumed during the film formation process to improve the impermeability of concrete. Among these systems, the NK system exhibits the most substantial water contact angle, which may be attributed to the thorough completion of the silicate reaction in the NK system, resulting in the densest surface of the test piece with almost no cracks.



**Figure 6.** Water contact angles of samples treated with various silicate surfaces.

### 3.4. Permeability

The water vapor permeability test can verify whether the concrete surface is dense or not. The gas permeability index is one of the indicators that characterize the impermeability and durability of concrete. Studies have shown that gas permeability is related to carbonation resistance, internal humidity, etc. [4]. The smaller it is, the more difficult it is for harmful gases such as  $\text{CO}_2$  to enter the inside of the concrete. The changes in methanol volatilization over time after the specimens that treated with different compound silicate systems are shown in Figure 7. The results showed that the methanol vapor volatilization after 2 h had a linear relationship with time. After 7 h, the NK group, LN group, and KL group, compared with the blank control group, were reduced by 60.6%, 53.8%, and 46.5%, respectively. This is mainly because the internal filling and external shielding of concrete by silicate synergistically reduce the volatilization of methanol gas. Among them, the NK system has the best effect, but it has not yet reached complete sealing. This may be explained by the fact that the water inside the specimen does not evaporate in time enough, which makes the silicate particles remaining on the surface of the matrix dispersed twice and difficult to polymerize [36]. Smaller pores and cracks are formed on the surface of the substrate, resulting in the coating not fully achieving the absolute barrier effect. In addition, the different  $\text{CO}_2$  concentrations inside and outside the coating lead to a gradient distribution of curing degree and cause stress cracking of the coating [37]. Since the penetration distribution of gas in the concrete matrix is more sensitive, the newly generated microcracks and holes provide transmission channels for the volatilization of methanol gas, so the volatilization of methanol gas cannot be completely isolated. Meanwhile, the methanol volatilization amount of the three sets of curves increased significantly after 2 h. This may be due to the increasing pressure inside the vessel caused by the prolonged experimental time. The larger pressure continues to squeeze the surface defects, resulting in the continuous expansion of newly created microcracks and pores. The generation and expansion of these defects lead to the increase in methanol vapor overflow, which eventually leads to the reduction in the density of the specimen.

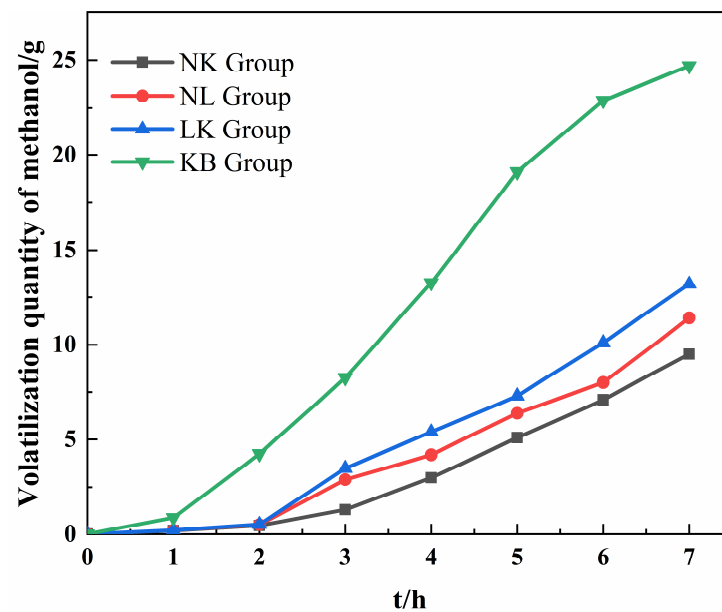


Figure 7. Methanol volatilities of samples treated with various silicate surfaces.

### 3.5. Durability

The chloride ion resistance test and freeze–thaw resistance test can visually show the impact of the coating on the durability of the specimen. As shown in Table 5, the three types of compound silicates reduced the 6 h electric flux value of the concrete after treating concrete surfaces with different strengths. The 6 h electric flux values of the C30 concrete surface were treated by the NK group, LN group, and KL group, respectively. Compared with the blank group, the electric flux decreased by 36.7%, 33.4%, and 30.4%, respectively, and the electric flux 6 h after treating the C50 concrete surface decreased by 19.0%, 15.4%, and 10.2%, respectively. These results indicate that the C-S-H gel produced by the reaction of complex silicate with  $\text{Ca}(\text{OH})_2$  can adsorb free  $\text{Cl}^-$  between the layers, in the lattice or on the surface of the C-S-H gel and convert it into bound  $\text{SiO}_2 \cdot 2\text{MCl}$  (M represents Li, Na, and K). The bound  $\text{SiO}_2 \cdot 2\text{MCl}$  can fill the void and block the erosion of water and other harmful ions. At the same time, it can also assist the circular nano- $\text{SiO}_2$  cross-linked network shielding layer produced by silicate self-condensation to synergistically resist  $\text{Cl}^-$  infiltration into the concrete interior [35]. As shown in Figure 8, the NK group has the best resistance to chloride ion penetration compared to the other two compound silicates. After treating the C30 concrete surface, the 6 h electric flux dropped from 3327 C to 2107 C, a decrease of 36.7%, and the chloride ion penetration resistance level was medium. After treating the C50 concrete surface, the 6 h electric flux dropped from 2040 C to 1653 C, reduced by 19.0%, and the chlorine penetration resistance level dropped from medium to low. It shows that the same compound silicate has different strengthening effects on concrete with different strengths. The ability of silicate to resist chloride ion penetration is closely related to the strength grade of concrete, and the strength grade of concrete determines the strengthening effect of silicate.

Table 5. The 6 h electric flux data for concretes of different strengths.

| Strength Class | 6 h Electric Flux (C) |          |          |          |
|----------------|-----------------------|----------|----------|----------|
|                | KL Group              | NK Group | LN Group | KB Group |
| C30            | 2361                  | 2107     | 2216     | 3327     |
| C50            | 1831                  | 1653     | 1725     | 2040     |

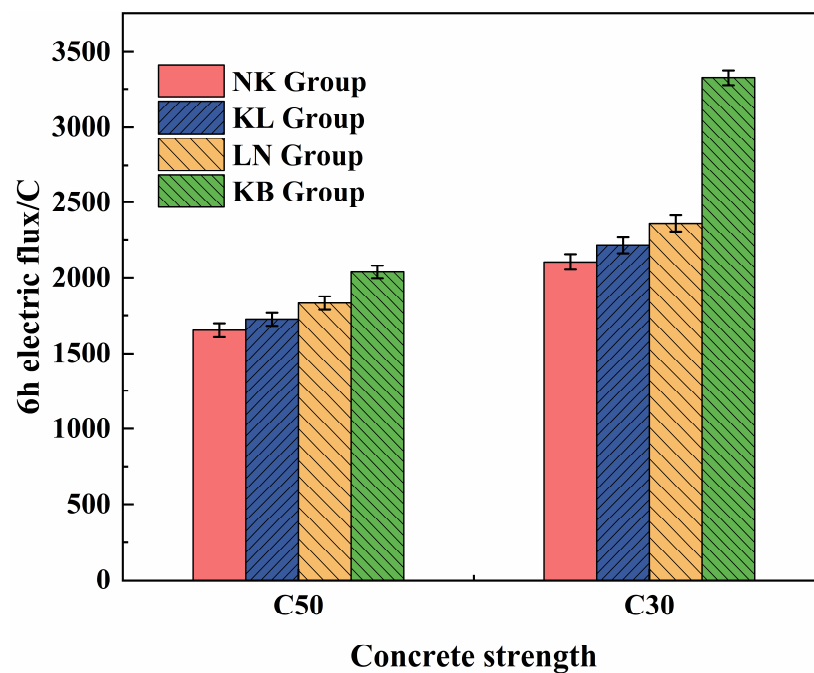


Figure 8. Six-hour electric flux data for different concrete strengths.

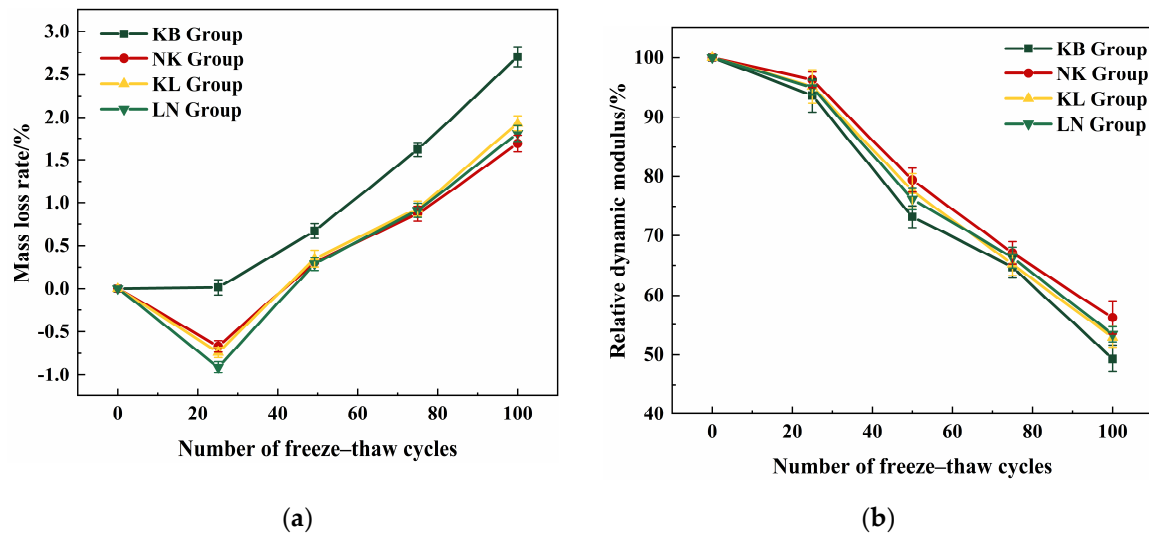
The freeze–thaw cycle test results of concrete are shown in Figure 9, Tables 6 and 7. The quality of the C30 concrete specimen decreased after 25 freeze–thaw cycles. After being treated with three types of compound silicates, the quality of the surface of the specimen was improved. This is because silicate treatment of the C30 concrete surface increases the density of the surface layer, and the formed  $\text{SiO}_2$  cross-linked network shielding layer blocks the penetration of water. Even if the concrete is saturated with water for 4 days, it has not reached a completely saturated state. After 25 freeze–thaw cycles, the surface pores and cracks further expanded, increasing the penetration of water, so the mass change rate was greater than that of the blank group specimen. However, as the number of freeze–thaws further increases, the freezing expansion of water causes more cracks and greater internal damage to the concrete. The relative dynamic modulus of concrete decreases more dramatically than in the early stages, and the mass loss also increases rapidly. On the C30 concrete surfaces of the NK group, LN group, and KL group, after 100 freeze–thaw cycles, the mass loss rates of the specimens in the blank group were reduced by 37.4%, 33.0%, and 28.5%, respectively, and the relative dynamic modulus by 12.3%, 8.2% and 7.3%, respectively. It reveals that the frost resistance of concrete is improved after silicate treatment of the concrete surface. On the one hand, silicate increases the compactness of the surface layer of concrete and accelerates the hydration reaction of cement, thus reducing the volatility of water inside concrete. The successful barrier of moisture improves the impermeability of concrete. On the other hand, silicate also reduces the number and size of capillary pores on the surface of concrete.

Table 6. The mass change rate (%) of C30 concrete specimens after undergoing freeze–thaw cycles.

| Specimen | Number of Freeze–Thaw Cycles |       |      |      |      |
|----------|------------------------------|-------|------|------|------|
|          | 0                            | 25    | 50   | 75   | 100  |
| NK Group | 0                            | −0.67 | 0.31 | 0.87 | 1.69 |
| LN Group | 0                            | −0.91 | 0.29 | 0.91 | 1.81 |
| NK Group | 0                            | −0.74 | 0.35 | 0.93 | 1.93 |
| KB Group | 0                            | 0.16  | 0.67 | 1.62 | 2.7  |

**Table 7.** Relative dynamic modulus of C30 concrete specimen after freeze–thaw cycle (%).

| Specimen | Number of Freeze–Thaw Cycles |      |      |      |      |
|----------|------------------------------|------|------|------|------|
|          | 0                            | 25   | 50   | 75   | 100  |
| LN Group | 100                          | 95.1 | 77.6 | 65.2 | 53.9 |
| NK Group | 100                          | 96.2 | 79.4 | 67.1 | 56.2 |
| KL Group | 100                          | 94.9 | 76.2 | 66.3 | 52.4 |
| KB Group | 100                          | 93.6 | 73.2 | 64.7 | 49.3 |

**Figure 9.** (a) The mass loss rate of specimens following freeze–thaw cycles. (b) The relative dynamic modulus of specimens after freeze–thaw cycles.

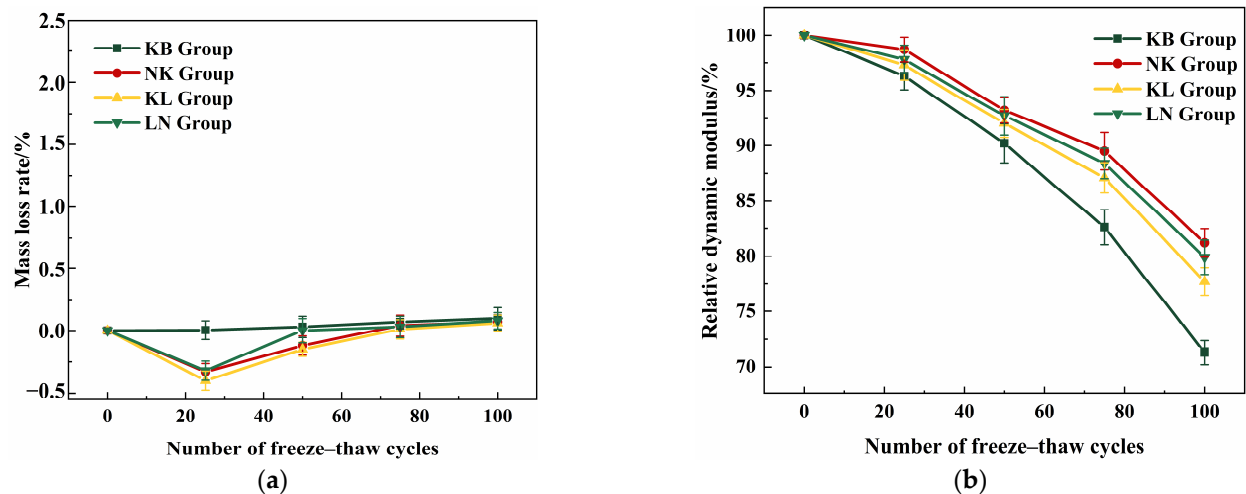
As shown in Figure 10, Tables 8 and 9, after 100 freeze–thaw cycles on the C50 concrete surfaces of the NK group, LN group, and KL group, compared with the KB group specimens, the mass loss rate was reduced by 30%, 20%, and 10%, respectively. The relative dynamic elastic modulus increases by 8.8%, 7.1%, and 4.2%, respectively. This indicates that silicate treatment of the C50 concrete surface can improve the freezing resistance of C50 concrete. However, the mass loss rate and relative dynamic modulus improvement effect are not as good as C30. This is because the ability of C50 concrete to resist external erosion is much greater than that of C30 concrete, and the silicate has a certain solubility. With the increase in the number of freeze–thaw cycles, the soluble ions in the silicate continue to dissolve, forming holes on the surface of the coating. The formation of these holes will cause water to penetrate into the concrete more easily, increase the internal damage of concrete, and thus reduce the frost resistance of concrete. Compared with Figures 9a and 10a, after silicate treatment of the surface of C50 concrete, it also shows a similar law to that of C30 concrete, and the mass of the specimen increases slightly after 25 freeze–thaw cycles.

**Table 8.** The mass change rate (%) of C50 concrete specimens following freeze–thaw cycles.

| Specimen | Number of Freeze–Thaw Cycles |       |       |      |      |
|----------|------------------------------|-------|-------|------|------|
|          | 0                            | 25    | 50    | 75   | 100  |
| NK Group | 0                            | −0.33 | −0.12 | 0.04 | 0.07 |
| LN Group | 0                            | −0.32 | 0     | 0.03 | 0.08 |
| KL Group | 0                            | −0.4  | −0.15 | 0.04 | 0.09 |
| KB Group | 0                            | 0     | 0.03  | 0.07 | 0.1  |

**Table 9.** The relative dynamic modulus (%) of C50 concrete specimens following freeze–thaw cycles.

| Specimen | Number of Freeze–Thaw Cycles |      |      |      |      |
|----------|------------------------------|------|------|------|------|
|          | 0                            | 25   | 50   | 75   | 100  |
| NK Group | 100                          | 98.7 | 93.2 | 89.5 | 81.2 |
| LN Group | 100                          | 97.8 | 92.7 | 88.4 | 79.9 |
| KL Group | 100                          | 97.3 | 92.0 | 87.1 | 77.7 |
| KB Group | 100                          | 96.3 | 90.2 | 82.6 | 74.6 |

**Figure 10.** (a) The mass loss rate of specimens after freeze–thaw cycles. (b) The relative dynamic modulus of specimens following freeze–thaw cycles.

#### 4. Conclusions

This study investigated the impact of three composite silicate coatings on concrete durability and explored their mechanism on the concrete surface. The primary components include three silicate solutions and additives. Composite solution properties were assessed via gel time and particle size analyses. The composite solution's impact on concrete microstructure was analyzed using SEM, XRD, surface contact angle, and FT-IR. The protective effectiveness of the composite coating on concrete was evaluated via chloride ion resistance and freeze–thaw tests. According to the analysis of the experimental results, the following conclusions are obtained:

1. When different types of silicates were used for compounding, the gelation time and colloidal particle size of the solutions were quite different. The NK group has the shortest gel time, the smallest colloid particle size, and the deepest penetration depth.
2. The hydration process of cement was accelerated after the treatment of the compound solution, resulting in an observable decrease in the content of  $\text{Ca}(\text{OH})_2$  in the sample and a significant increase in the content of the C-S-H gel. The NK group had the highest gel content, which was 389.8% higher than the blank group, and its hydration was more complete.
3. Surface treatment can improve porosity and surface morphology. Compared with the blank group, the air permeability of the NK group, LN group, and KL group decreased by 60.6%, 53.8%, and 46.5%, respectively.
4. After treatment with the compound solution, the chloride ion resistance and freeze–thaw resistance of concrete were improved. Generally speaking, the improvement effect of C30 concrete is greater than that of C50 concrete.

The surface treatment of composite silicate solution enhances the durability of concrete to extend the service life of concrete pavement by improving its surface condition. However, as a surface treatment agent, the effect of composite silicate solution on the skid resistance

and wear resistance of concrete surfaces still needs further research to clarify its impact on the safety performance of pavement.

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