Article

Protective Mechanism of Silane on Concrete upon Marine Exposure

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Abstract: Due to the high chloride ion concentration in marine environments, chloride ions can penetrate into concrete, along with the transportation of water molecules, and thus, cause rebar corrosion. This is an important reason for the decrease in the concrete durability. In this paper, by means of the sol–gel synthesis method, a silane emulsion, a silane compound emulsion, and silane compound gel were prepared by using isobutyl triethoxysilane and ethyl orthosilicate (TEOS) as the main raw materials. These silane materials were coated on a concrete surface and then placed in the marine exposure sites of Wheat Island, in Qingdao, for one year. The results show that these silane materials can effectively inhibit the chloride ions transporting in concrete. Upon the increase of the exposure time, the protection ability of the silane emulsion declined gradually, while the silane compound emulsion had stable protective effects. In comparison with the permeability coefficient of chloride ions in the blank test block, the permeability coefficient of chloride ions in the test block coated with the silane emulsion, the composition of silane emulsion, and silane compound gel fell off around 20%, 30%, and 50%, respectively. The test results indicate that the three kinds of protective materials have good inhibition abilities against chloride ion transportation, on which the compound gel had the best effect.

Keywords: marine exposure; chloride ions; silane; concrete; micro; sol–gel

1. Introduction

With the fast development of construction in civil engineering nowadays, reinforced concrete structures are being built all over the world, in which marine concrete structures occupy a significant position due to the applications of marine resources playing an increasingly important role in the national economy [1–4]. The properties of concrete materials in marine environments are affected by chloride salt and sulfate attack, microbial corrosion, as well as the permeability and diffusivity of concrete materials [5–7]. This has drawn great attention from researchers. The intrusion of negative ions, such as chloride and sulfate ions, reduce the service life of concrete structures and cause great losses in the economy, restraining the development of marine engineering [7–9]. The effect of environment and concrete characteristics on the transposition of chloride into reinforced concrete has been studied by both researchers and engineers for several years [10–12]. Chloride ions can be absorbed by capillary action, diffusion, and penetration, and transported into the surface of steel bars in reinforced concrete [13]. Capillary absorption refers to the transport of liquid caused by the surface tension of capillary pores, which is related to the degree of air drying on the concrete surface. Due
to the difference in chloride ion concentration between the interior and the surface of the concrete, the chloride ion transport caused by this difference is a diffusion effect. In the case of high pressure, the chloride solution will penetrate into the lower pressure direction, which is called osmosis. The penetration depth of chloride in unprotected concrete may reach 40 to 100 mm after exposure to seawater after a period of several years, which greatly reduces the durability and safety of concrete structures [14]. In summary, diffusion is considered to be one of the most important modes of transport in many cases and causes a threat to the steel bars, eventually reducing their service life [15,16].

Water repellent treatment is most efficient to reduce the water absorption of concrete by capillary action [17]. As early as in the mid-1980s, the United States and other countries found that silane-based surface impregnation material is effective in terms of preventing salt damage. Nowadays, a broad array of organic and inorganic products are available on the market for the protection of concrete surfaces, such as bituminous seal, grease, epoxy resin, and vinyl resin, which block the concrete pores by forming a certain thickness on the concrete surface [18,19]. However, due to the covering of the concrete surface, the capillary pores are blocked. Delamination or blistering may occur on the sealer and coating systems of concrete, resulting in a weakened protective effect [20]. According to the survey results, permeable silane protective materials act as a barrier between the environment and the concrete [21–23]. These can not only prevent the penetration of the surrounding water molecules into the concrete, but would not block the capillary channel in the concrete [21,24–26]. Silanes, which are used for surface impregnations, are a group of silicones containing one silicon atom. The alkoxy groups (\(\text{CH}_3\text{O}\)) linked to the silicate atom (Si) bond to silicates present in the concrete. The organic alkyllic (\(\text{CH}_3\)) group point into the pore structure and are responsible for the hydrophobic characteristics [22,27,28]. Silanes react with the cement matrix and form a hydrophobic layer on the walls of the pores within the concrete [21]. They prevent or retard the entry of harmful substances such as water and chlorides. As a permeable waterproof material, silane has been reported, which has good waterproof effects without affecting the permeability of concrete. Because of the high volatility of silane monomers, researchers have prepared a series of composite emulsions by the sol–gel method [29,30]. Zhang et al. prepared two silane compound emulsions with different structures by continuously improving their testing scheme. This not only solved the problem of the high construction cost but also improved the silane content, as well as the waterproof performance of cement-based materials.

However, the effect of silane compound emulsions and silane compound gel on preventing chloride transporting into concrete in marine has not been fully investigated. In this work, in order to demonstrate the effectiveness of a chloride barrier with respect to the ingress of chloride ions by silane-based surface impregnation material, chloride penetration profiles were determined after the exposure of treated and untreated concrete samples to seawater for one year. Then, the exposed blocks were periodically retrieved from the sea for chloride ion titration and fitted the free diffusion coefficient of chloride according to Fick’s second law. In order to understand the protection mechanism from the micro, water contact angle, SEM, EDS, and FT-IR were measured on the blocks. Through this experimental study, we can more fully understand the protective effect and microscopic mechanism of silane protective materials on salt ions in different marine environments.

2. Experimental

2.1. Concrete Preparation

In the test, test blocks of concrete with a strength grade of C60 were used as the base material. The specific proportions of the concrete mixture are shown in Table 1.

The cement employed for testing was P·O·42.5 silicate cement. The formulations of concrete are shown in Table 1. Different dosages of the materials were weighed according to their proportions in the concrete mixture. Then, the concrete test blocks test blocks were prepared. The main mixing equipment was the horizontal-axis forced concrete mixer. After a 24-h molding process, the concrete test blocks were stripped and then placed into the standard curing room to be cured for 28 days.
2.2. Raw Materials and Preparation Technology of the Compound Gel

In the experiment, we mainly adopted constant temperature and high-speed stirring to composite two silane monomers with different molecular formulas, thus improving the content of silane in the protective materials. The specific raw materials are shown in Table 2.

Table 2. Materials for preparing the compound gel.

| Raw Materials          | Molecular Formulas        | Manufacturer                                      |
|------------------------|---------------------------|---------------------------------------------------|
| Isobutyl triethoxysilane (ITES) | (CH₃)₂CHCH₂Si(OC₂H₅)₃ | Quanzhou Sicong Chemical Co., Ltd., Quanzhou, China |
| Tetraethoxysilane (TEOS) | Si(OC₂H₅)₄               | Shanghai Aibi Chemistry Preparation Co., Ltd., Shanghai, China |
| Peregol O (PPG O)      | RO-(CH₂CH₂O)ₙ-HR         | Shanghai Aibi Chemistry Preparation Co., Ltd., Shanghai, China |
| Polyethylene glycol (PEG 2000) | HO(C₂H₄O)ₙ-H | Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China |
| Span80                 | C₇₄H₄₄O₆                 | Tianjin Ruijinte Chemical Co., Ltd., Tianjin, China |
| Distilled water        | H₂O                      | Qingdao University of Technology, Qingdao, China |

Firstly, the Span80 and the isobutyl triethoxysilane (ITES) monomer were mixed evenly via high-speed mixing by using a homogenizer to form an oil phase, and PPG O and distilled water were mixed evenly to form an aqueous phase. The aqueous phase was poured in a three-necked flask. Then, the flask was placed at constant temperature inside an oil bath pot. The oil phase was dripped into the aqueous phase while stirring to form a combined uniform oil-in-water structure. After a two-hour high-speed stirring at a constant temperature, TEOS was dripped slowly into the flask. Then, a three-hour high-speed stirring was conducted. Finally, the stirring temperature was increased appropriately and the mixture was exposed to the air. This facilitated the formation of the silane gel. The specific flow chart is shown in Figure 1.

![Figure 1. Flow chart of TEOS/ITES compound gel.](image-url)
2.3. Marine Exposure Test

The cured concrete test blocks were taken out from the curing room and put in the oven for drying at 50–60 °C to evaporate the excessive water. The sample size was 100 mm × 100 mm × 100 mm. When the mass of the coupon remained unchanged, the surface to be tested was ground to be smooth, the surface dust was cleaned up, and the other surfaces were sealed with paraffin. The main component was solid alkanes, odorless and tasteless, and was a white or light yellow translucent solid. It was soluble in non-polar solvents, such as gasoline, and is insoluble in polar solvents, such as water and methanol. Paraffin becomes liquid after heating, solidifies into a solid at room temperature, and the sealing performance is good. In addition, the solid paraffin is very stable and it is difficult to react with other substances. Within 24 h, the uncoated paraffin paper has a water vapor permeability of 406 g/m², while the paraffin-coated paper is only 0.2 g/m² [31]. Here, the splash zone where the concrete test blocks would be severely corroded was selected for a one-dimensional experiment and the tidal zones and the full immersion zone were selected for a two-dimensional experiment. The specific coating means are shown in Figures 2 and 3. The marine exposure environment is complex and it can be generally divided into the splash zone, the tidal zone, and the full immersion zone. By selecting different environmental conditions for the marine exposure experiment of the concrete test blocks, one can analyze the inhibitory effects of the three different protective materials on the transportation of the chloride ions in the concrete under different environmental conditions. The concrete test blocks were placed in the marine exposure stations in Qingdao and fetched at regular intervals in batches after 3, 6, 9, and 12 months. The average values of each seawater environmental factor during the test period were: average temperature was 12.5 °C; maximum temperature was 35.0 °C; minimum temperature was −11 °C; annual average relative humidity was 71%; annual precipitation was 643 mm; salinity was 31.5 ‰; pH was 8.3; the dissolved oxygen concentration was 5.9 mL/L; and the seawater flow rate was 0.1 m/s. The tide was a regular half-day tide with an average tidal range of 2.7 m. The Mohr method was used to test the content of the free chloride ions in the concrete after its exposure for different periods—the formula is:

\[
w = \frac{c_{AgNO_3} \times 0.03545}{m \times V_3} \times 100\%
\]

where \(w\) = water-soluble chloride ion content in the concrete test block (%); \(c_{AgNO_3}\) = concentration of silver nitrate standard solution (mol·L\(^{-1}\)); \(m\) = weight of concrete test block powder (g); \(V_3\) = the volume of distilled water (mL) of the soaked powder sample; \(V_4\) = the filtrate volume (mL) extracted at each titration; \(V_5\) = volume of silver nitrate solution used per titration (mL).

Fick’s law was used for fitting the variation of the chloride ion content to analyze the diffusion coefficient of the chloride ions [32,33].
The cement paste test blocks with a water binder ratio of 0.5 and dimensions of 40 mm × 40 mm × 160 mm were cured under standard conditions for 28 days. Then, the coupon surfaces were coated with a silane emulsion, a compound emulsion, and a compound gel. Their coating amount was 400 g/m². The coated test blocks were left to rest for 72 h and then the contact angle was determined. The hanging drop method was used to determine the static contact angle. For each group of test blocks, the contact angle was measured at five positions (the contact status was photographed and recorded) and the average value was taken to define the final contact angle. The SL150 static contact angle meter was adopted to measure the contact angle.

2.5. Surface Morphology Observation (SEM)

The cement paste test blocks cured for 28 days were coated with three different kinds of protective materials and then left to rest for 72 h. An IGMA 300/VP field emission scanning electron microscopy (FESEM) (Zeiss, Oberkochen, Germany) was used to observe the surface morphology of the test blocks coated with the silane waterproof materials, as well as that of the test blocks without coating, for comparison.

2.6. Infrared Spectrum Analysis

The cement paste test blocks with a water binder ratio of 0.5 were cured for 28 days, and the well-molded surface was coated with the compound emulsion. This was followed by 72 h of rest. The coated surface was ground to produce a powder, and the powder was sampled and dried. A BRUKER TENSOR 27 infrared spectrometer (Billerica, MA, USA) was adopted for the spectral analysis. A pure KBr tablet was selected as the infrared base background and the mixture of the sample powder and KBr with a mass ratio of 1:200 was used to measure the infrared spectrum of the sample.

3. Marine Exposure Experiment Results

3.1. Results and Analysis in the Full Immersion Zone

3.1.1. Variation of the Chloride Ion Content in the Concrete

As shown in Figure 4a–d, the content of chloride ions in the concrete generally varied, following the same trend, under different testing periods. Moreover, it gradually decreased upon the increase of the penetration depth. Among these concrete test blocks, the blank coupon had the highest chloride ion concentration, while the test blocks coated with the compound gel had the lowest. By comparing Figure 4a–d, it can be found that the initial chloride ion concentration of the blank coupon gradually increased, while the test blocks coated with the compound gel were relatively stable, with an chloride ion concentration of about 0.2%. At 3–6 months, after the surface depth of 10 mm, the chloride ion concentration of the compound gel treated block began to stabilize, and the content was significantly lower than the blank test block. During the period from September to December, the chloride ion content increased significantly, and the stable penetration depth shifted back. In comparison, compound gels exhibit better stability. By contrast, the silane emulsion and the compound emulsion had poorer stability, and the compound gel had good stability.
Figure 4. Ion content in the concrete test blocks coated with different protective materials under different immersion periods in the full immersion zone.

3.1.2. Fitting Results of the Chloride Diffusion Coefficients in the Concrete

Table 3 shows the chloride diffusion coefficients. As can be seen, for an exposure time of three months, the three different kinds of silane-based protective coatings had better protective effects compared with the blank coupon. To be specific, the chloride diffusion coefficients for the silane emulsion, compound emulsion, and compound gel decreased by 58%, 60%, and 80%, respectively. Moreover, the compound gel had the best protective effect. When the exposure time was prolonged to six months, the protective effect of the compound gel was clearly enhanced. The chloride diffusion coefficients decreased by 65% compared with that of the blank test block, and it increased by 15% to 20% compared with the other two kinds of protective materials. When the exposure time was extended to nine months, the hydrophobic films formed by the protective materials appeared to be damaged. The protective effects of the three kinds of protective coatings all decayed significantly and the chloride diffusion coefficients decreased by about 30% compared with those for the three-months samples. When the exposure time was prolonged to 12 months, due to the enrichment of the chloride ions on the concrete surface and the damage of the hydrophobic films, the inhibitory effects of these three kinds of protective materials on the transportation of the chloride ions in the concrete were decreased and the concentration of the chloride ions in the concrete generally showed an increasing trend. Notably, the hydrophobic film formed by the compound gel and the concrete-based material was more stable and more uniform relative to those formed by the other two protective materials with a concrete-based material. For this reason, the concentration of the chloride ions in the concrete coated with the compound gel was relatively stable. The chloride diffusion coefficients decreased by 48% when compared to that of the blank coupon. Moreover, the compound gel still had a certain protective effect on the concrete.
Table 3. Permeability coefficient of the chloride ions in the full immersion zone ($\times10^{-12}$ m$^2$·s$^{-1}$).

| Exposure Time (Month) | Chloride Diffusion Coefficients/($\times10^{-12}$ m$^2$·s$^{-1}$) |
|-----------------------|---------------------------------------------------------------|
|                       | Blank | Silane Emulsion | ST Compound Emulsion* | ST Compound Gel |
| 3                     | 7.85  | 3.35           | 3.15                   | 1.62           |
| 6                     | 3.56  | 2.01           | 1.85                   | 1.32           |
| 9                     | 2.75  | 2.12           | 1.69                   | 1.42           |
| 12                    | 2.50  | 2.06           | 1.62                   | 1.21           |

* ST Compound Emulsion: Composite emulsion of isobutyltriethoxysilane and TEOS.

3.2. Results and Analysis in the Tidal Zone

3.2.1. Variation in the Chloride Ion Content in the Concrete

Figure 5a shows the variation of the chloride ion content in the concrete test blocks after exposure in the tidal zone for three months. As can be seen, when the surface depth was deeper than 8 mm, the rate of decrease in chloride ion concentration slowed down and tended to stabilize. The initial concentration of the blank test blocks reached 0.38%, while that of the concrete test blocks coated with silane protective material was only 0.2%, and it decreased by nearly one-half. Thus, it can be seen that the silane protective coatings have an excellent effect in preventing the penetration of the chloride ions. With the extension in exposure time (Figure 5b–d), the concentration of chloride ions increased gradually. Among these protective materials, the protective ability of the silane emulsion began to be damaged first, then the concentration of the chloride ions increased from an initial concentration of 0.23% to 0.38%. The compound gel had the best protective effect, and the initial concentration of the chloride ions was only 0.24% after exposure for up to 12 months.

Figure 5. Ion content in the concrete test blocks coated with different protective materials upon different immersion periods in the tidal zone.
3.2.2. Fitting Results of the Natural Permeability Coefficient in the Concrete

Table 4 shows the chloride diffusion coefficient in the concrete test blocks in the tidal zone under different testing periods. When the exposure time was three months, the chloride diffusion coefficient for the compound gel was reduced by about 78%, and those for the compound emulsion and the silane emulsion were reduced by 68.5% and 54%, respectively. Obviously, the overall protective effect in the tidal zone was degraded compared to that in the full immersion zone. This is mainly due to because the drying and the watering cycles in the tidal zone are more significant than those in the full immersion zone [34], which shows higher requirements for the durability of the concrete test blocks [35]. With the extension in exposure time, the protective effects of the protective coatings began to show a decreasing trend. Among them, the silane emulsion was damaged most seriously, and the chloride diffusion coefficient was reduced by 30%, and the protective effect of the compound emulsion was reduced by 36.9%. The protective effect of the compound gel was the most stable, and was only reduced by 24.4%. Based on the test data, it can be seen that the hydrophobic film formed by the compound gel on the surface of concrete was the most stable, and that the damage-degree of the silicon oxygen bond was lower. Therefore, the compound gel has good protective effects in terms of inhibiting the penetration of the chloride ions into the concrete over a long time, which is of great significance for enhancing the durability of the concrete.

Table 4. Permeability coefficient of the chloride ions in the tidal zone (×10^{-12} m^2·s^{-1}).

| Exposure Time (Month) | Chloride Diffusion Coefficients/(×10^{-12} m^2·s^{-1}) |
|----------------------|----------------------------------------------------------|
|                      | Blank | Silane Emulsion | ST Compound Emulsion * | ST Compound Gel |
| 3                    | 8.52  | 3.92            | 2.72                    | 1.89            |
| 6                    | 5.82  | 3.12            | 3.01                    | 1.51            |
| 9                    | 3.72  | 3.31            | 1.82                    | 1.41            |
| 12                   | 2.72  | 1.98            | 1.92                    | 1.35            |

* ST Compound Emulsion: Composite emulsion of isobutyltriethoxysilane and TEOS.

3.3. Results and Analysis in the Splash Zone

3.3.1. Variation of Chloride Ion Content in the Concrete

Figure 6 shows the variation in the chloride ions in the concrete in the marine splash zone. By comparison with Figures 4 and 5, it can be found that the content of the chloride ions in the splash zone was significantly higher than the one in the other two zones and that the highest value was close to 0.7%. The main reason for this lies in the fact that the concrete in the splash zone was exposed to the environmental drying and watering alternation for a long time. The oxygen supply in the splash zone is sufficient and the corrosion is more serious [36,37]. Moreover, it is usually about five to ten times higher compared to that in the full immersion zone. With the increase in penetration depth, the chloride ion concentration in the concrete without the protective treatment decreased to a maximum of 0.4%. As shown in Figure 6a, when the surface layer depth was greater than 8 mm, the chloride ion content tended to be stable through the test piece treated with the silane-based impregnating material. The chloride ion content of the blank test block was significantly higher than that of the treated test block. As the exposure time increased, as shown in Figure 6b–d, the depth value at which the chloride ion content tended to be stable increased from 12 to 16 mm. The main reason for the above phenomenon can be summarized as follows: the concrete in the splash zone is greatly influenced by the drying and watering cycles and the chloride ions can enrich the concrete surface continuously [38,39]. Moreover, it can enter inside the concrete via capillary absorption, penetration, and diffusion [40]. Moreover, the high pressure produced by the shock waves can help the water molecules to enter into the concrete and the water molecules can act as a carrier for the chloride ion transportation and carry large amounts of chloride ions into the internal part of the concrete [41]. When the concrete dries up, the water in
the pore channels evaporates outward and the chloride ions remain in the concrete. This leads to an increase in the chloride ion concentration in the concrete and to its subsequent serious corrosion. After a protective treatment via the use of protective materials, the protective materials can react with the concrete surface to form hydrophobic films and to inhibit the penetration of water molecules into the concrete when the marine water wets the concrete test blocks. As a result, the amount of the carrier that can penetrate into the concrete decreases and the concentration of chloride ions into the concrete also is reduced accordingly [42]. Thus, the protective materials can achieve their purpose of inhibiting the chloride ions into the concrete and alleviate the accompanied corrosion damage [43].

![Graphs showing ion content in concrete test blocks coated with different protective materials](image)

**Figure 6.** Ion content in the concrete test blocks coated with different protective materials under different immersion periods in the splash zone.

### 3.3.2. Fit Results of the Chloride Diffusion Coefficients in the Concrete

In order to more intuitively analyze the influences of the three kinds of protective materials on the concentration of the chloride ions in concrete, the chloride ion diffusion coefficient was calculated via the fitting method [32], as shown in Table 5. Combined with Tables 3 and 4, it can be seen that the environmental characteristics in the splash zone caused the most serious chloride ion corrosion. When the exposure time was three months, the chloride diffusion coefficients of the untreated concrete test blocks reached $13.99 \times 10^{-12} \text{m}^2\cdot\text{s}^{-1}$, which was about 50% higher than that of the untreated concrete test blocks in the full immersion zone or in the tidal zone, and about 60% higher than that of the concrete test blocks upon protective treatment in the splash zone. When the exposure time was extended to six months, the chloride diffusion coefficients of the concrete test blocks treated with the compound gel, the compound emulsion, and the silane emulsion decreased by about 60%, 52%, and 31%, respectively. Afterwards, with the extension in exposure time, the chloride diffusion coefficients of the concrete coupon treated with the silane emulsion tended to be stable, at about 30%, and that of the concrete coupon treated with the compound emulsion decreased to 37%. For the concrete coupon
treated with the compound gel, the chloride diffusion coefficients upon a 12-month exposure decreased by about 50% compared with that of the concrete coupon treated with the silane emulsion after an initial exposure time. Thus, it can be deduced that the compound gel has excellent protection effects and a longer aging time.

Table 5. Permeability coefficient of the chloride ions in the splash zone (×10⁻¹² m²·s⁻¹).

| Exposure Time (Month) | Blank Chloride Diffusion Coefficients/(×10⁻¹² m²·s⁻¹) | Silane Emulsion | ST Compound Emulsion * | ST Compound Gel |
|-----------------------|------------------------------------------------------|-----------------|------------------------|----------------|
| 3                     | 13.99                                                | 5.82            | 5.62                   | 3.01           |
| 6                     | 6.45                                                 | 4.36            | 3.03                   | 2.32           |
| 9                     | 4.95                                                 | 3.35            | 2.96                   | 2.45           |
| 12                    | 4.56                                                 | 3.06            | 2.82                   | 1.99           |

* ST Compound Emulsion: Composite emulsion of isobutyltriethoxysilane and TEOS.

3.4. Contact Angle Determination Test

According to the marine exposure experiment, it can be found that the compound emulsion has good inhibitory effects on the penetration of the chloride ions. Since the water molecules are the carriers of the chloride ions penetrating into the concrete, it is necessary to further study the effects of protective coatings on the water molecules, based on the surface of the cement-based material. Figure 7 shows the surface contact angle before and after treatment by silane materials on test blocks.

![Figure 7](image_url)

Figure 7. Angle of the water-to-concrete surface after different coating treatments on the test blocks (°).

Under the action of the capillary surface tension, the capillary suction phenomenon occurs on the concrete materials [44,45]. The contact angle, as a test indicator, can intuitively represent the test blocks surface tension. With an increase in the contact angle, the hydrophobic ability also gradually increased [46]. As shown in Figure 7, the contact angles of the net paste test blocks treated with different protective materials were significantly different. Figure 7a shows a picture of the control coupon without protective treatment. The average value of the contact angle was 57.9°. Figure 7b
presents the photo of the coupon coated with a silane emulsion. The average value of the contact angle was 108.3°. Figure 7c,d are the photos for the test blocks coated with the compound emulsion and the compound gel, respectively. Their contact angles were 120.2° and 131.5°, respectively. From the contact angle determination test, it can be found that protective coatings can reduce the surface tension and slow down the rate of the water molecules into the concrete, thus reducing the content of the chloride ions into the concrete.

Through the exposure test, we can find that the effect of the silane emulsion and the composite emulsion was reduced, to some extent, with the extension of time. We chose the splash zone with more severe corrosion as an example to test the contact angle. The results are shown in Figure 8. Compare the contact angles of different treatments. It can be found that although the contact angle had a certain decrease, the contact angle of the test piece treated by the composite gel was slower. This shows that the stability of the composite gel was better than the other two.

![Figure 8. Angle of the water-to-concrete surface after different coating treatments on the test blocks (°) in the splash zone.](image)

In order to further understand the binding mechanism of the compound emulsion and the cement-based material, an SEM observation and an infrared spectrum analysis were carried out. The results are reported in the following section.

3.5. SEM and Infrared Spectrum Analysis

Figure 9 shows the SEM surface morphology of the control coupon (a) and the net paste test blocks treated with the silane emulsion (b), the compound emulsion (c), and the compound gel (d) under a magnification of 1500 times. The surfaces of the control group and of the silane emulsion group presented a granular morphology, which mainly corresponds to the products of the cement hydration process [47,48]. Since the content of silane in the silane emulsion was relatively low, its permeability was stronger than that of the compound emulsion. Hence, the impact of the silane emulsion on the surface morphology of the net paste coupon was relatively low. The surface of the test piece coated with the composite emulsion and the composite gel was covered with a silane-based lamellar structure, which can effectively fill the capillary channels and prevent the penetration of water molecules and ions.
Figure 9. Surface morphology of the concrete test blocks treated with different protective materials (1500×).  

Figure 10 shows the surface morphology of the SEM of a concrete test block after 12 months of exposure to the splash zone. The compactness of the surface of the silane emulsion and the composite emulsion were significantly reduced, and the surface sealing effect of the composite gel was relatively stable.  

In addition, a spot scanning and a map scanning of the coupon surface were carried out. The obtained silicon content on the coupon surface is listed in Table 6. Compared with the blank group, the silicon content on the surface of the test blocks treated with protective materials increased noticeably. It can be determined that the lamellar substance on the coupon surface belonged to the silane protective materials.
As the results show, there was no alkyl absorption peak at 3000 cm$^{-1}$ in the infrared spectrum of the pure compound emulsion, while an alkyl absorption peak appeared at 3000 cm$^{-1}$ in the infrared spectrum of the compound emulsion coated on the net paste coupon [49]. Because in the emulsion, the silane was encapsulated inside the water molecules, there were no exposed alkyl groups. The coupon surface coated with the compound emulsion reacted with the cement-based material, and the alkyl group was exposed. This drove the hydrophobic alkyl to form a protective layer on the coupon surface, thus preventing the penetration of water molecules and slowing down the chloride ion erosion [50,51].

### 3.6. Infrared Spectrum Analysis

Infrared spectroscopy was performed on the surface of the pure composite emulsion and the sample coated with the composite emulsion. This allowed further observation of the binding mechanism of the composite emulsion to the surface of the cement-based material. The results are shown in Figure 11. As the results show, there was no alkyl absorption peak at 3000 cm$^{-1}$ in the infrared spectrum of the pure compound emulsion, while an alkyl absorption peak appeared at 3000 cm$^{-1}$ in the infrared spectrum of the compound emulsion coated on the net paste coupon [49]. Because in the emulsion, the silane was encapsulated inside the water molecules, there were no exposed alkyl groups. The coupon surface coated with the compound emulsion reacted with the cement-based material, and the alkyl group was exposed. This drove the hydrophobic alkyl to form a protective layer on the coupon surface, thus preventing the penetration of water molecules and slowing down the chloride ion erosion [50,51].

![Figure 11. Spectra of the pure compound emulsion and the net paste coupon surface coated with the compound emulsion.](image)

| Coating Method        | Silicon Content (at.%) | Spot Scanning | Map Scanning |
|-----------------------|------------------------|---------------|--------------|
| Blank                 | 3.98                   | 4.75          |              |
| Silane emulsion       | 9.56                   | 9.23          |              |
| Compound emulsion     | 12.65                  | 11.78         |              |
| Compound gel          | 14.26                  | 13.58         |              |

### 4. Conclusions

In summary, the performances of different silane materials, which resist the chloride ion erosion in practical marine environment, were investigated via chloride ion titration and chloride diffusion coefficients fitting. The mechanisms of protective materials inhibiting chloride ion penetration were explored via the microscopic tests. Some conclusions can be drawn, as follows:

- In the early stage of marine exposure, the three kinds of protective materials had a good ability to resist the chloride ion erosion. With an extension in exposure time, the protective effect of the three protective materials showed a downward trend, to some extent. The compound gel displayed the best stability. Under marine exposure durations, the chloride diffusion coefficients of the concrete test blocks coated with the compound gel were reduced to about 50%. This confirms its excellent ability to resist chloride ion erosion;
Via the contact angle determination tests, it can be found that the use of coating protective materials on the coupon surface can effectively reduce the coupon surface tension and increase the contact angle. This makes the coupon surface transform from a hydrophilic surface to an hydrophobic surface. Therefore, coating the coupon surface with protective materials can effectively inhibit the transportation of water molecules into the concrete and reduce the content of chloride ions that are carried by the water molecules into the concrete;

According to the microscopic test results of the SEM and infrared spectrum analysis, the protective coatings can react with the cement-based materials when they are coated on the surface of cement-based material, and drive the hydrophobic alkyl to form a lamellar protective layer on the coupon surface. This fills the capillary pores and effectively inhibits the entrance of water molecules and ions into the capillary channels of the concrete.

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