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Fundamental interaction of hydrophobic materials in concrete with different moisture contents in saline environment

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H I G H L I G H T S

- Enhancing the impermeability of concrete.
- Reducing chloride diffusion through concrete.
- Revealing the morphology and interaction mechanism of materials and concrete.
- The effect of initial moisture content on treatments.

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A B S T R A C T

The present paper investigates the performance and efficacy of four protective surface applied materials; sodium acetate, fluoropolymer, silicone resin and silane when applied to marine structures with different moisture contents. Materials were applied to fully dry and fully saturated concrete along with concrete with 2% and 4% moisture contents. The interaction mechanism of the materials with concrete and their microstructural and morphological assessments were conducted by running SEM, EDX and FTIR analyses to evaluate their performance in the presence of moisture. Also, their efficacy in protecting concrete from water ingress and chloride penetration was evaluated by operating the Initial Surface Absorption Test (ISAT) and Unidirectional salt ponding test respectively. Results demonstrated that moisture content imposes a vital effect on the interaction of the materials with concrete and their adhesion inside the pores, and consequently their efficacy in reducing both, water and chloride penetration.

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1. Introduction

The influence that chloride ions induce on the integrity and condition of any concrete structure, especially those in contact with seawater, is considered the main reason behind their deterioration [1]. The presence of chloride within concrete texture causes corrosion of embedded steel, which in turn expands through the whole texture of concrete, initiating spalling and delamination of concrete [2–6]. Accordingly, British and European standards concerns

were aroused by the complications generated by the presence of chlorides in concrete composition, and the chloride content has been limited to values that range between 0.2 and 0.4% in reinforced concrete and 0.1–0.2% in the case of prestressed concrete [1,7].

One of the main factors affecting the mechanism by which chloride passes through the pores of concrete is its moisture content, which results from the exposure of concrete to different environmental circumstances. Complete diffusion is believed to take place in saturated concrete like those soaked under water, and sorption is preponderant in concrete subjected to sea and oceanic atmospheres, concrete pavement in contact with de-icing agents, and dry concrete that is found in arid areas [8,9]. In the case of partially saturated concrete, capillary suction and diffusion of chloride ions are credited for the whole process of chloride transport [9,10]. In

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addition, it was proven by Conciatori et al. [11] that environmental conditions and the quantity of de-icing agents are the major elements in the process of chloride transport, eliminating the importance of concrete cover when concrete is in direct contact with saline water [11].

In order to increase the service life of concrete and reduce the cost of maintaining structures, more cost-effective solutions were followed which commence with the construction phase of these structures [12]. In view of that, decision makers and research administrators started to promote the use of surface applied protective materials to control and inhibit chloride ingress and water absorption into concrete structures [13]. Silane and siloxane materials were the most dominant options in protecting concrete, and since the 1980s, most of the research focused on testing these materials and enhancing their performance [14–19]. Conversely, some recent studies discussed the impact of those materials on the environment, and proved their harmful effect on natural resources and environment as their main constituent is made from the solvent and organic materials [20,21]. Moreover, silane/siloxane materials were found to be less effective when applied to saturated concrete [21–23]. Accordingly, researchers started to explore other options that do not impose any risks to the ecosystem and have a high affinity for water at the time of application [24]. Some alternative materials were either extracted from natural resources, like vegetable oils and animal blood and fats, or manufactured from low-risk chemicals, like silicate and crystalline materials [24–30]. Moreover, many researchers implemented the crystalline technology and other treatments in their research, and obtained some promising results in reducing water absorption and chloride diffusion in concrete [31–35].

In this study, the efficacy of four protective materials were tested to assess their performance when applied to concrete with different moisture contents. These materials are Fluoropolymer, Silicone resin, Sodium acetate, and solvent-based silane. More information about the materials are discussed in Section 3.1. The review of existing studies and literature indicated that no experimental investigations were run on the previously mentioned nature-friendly materials to study their performance in saline environments. Likewise, the effect of moisture content on the efficacy of applied materials was not discussed.

2. Research objectives

The significance of this study springs from the insufficient performance of most available materials and the necessity to compensate for their shortcomings. Therefore, the primary objectives of this research are:

1. Investigate the performance of three surface applied materials in protecting and waterproofing concrete in saline environments, and compare their performance to traditional silane.
2. Studying the influence of moisture content on the applied dosage and efficacy of the protective materials.
3. Establish a better understanding of the interaction mechanism and behaviour of the applied protective materials with concrete in the presence of different moisture contents.

3. Experimental work

3.1. Materials

Four protective materials were applied to the surface of concrete; Fluoropolymer, Silicone resin, Sodium Acetate and liquid Silane.

Fluorine is the main constituent of fluoropolymer, which gives it the ability to resist chemical attacks and repel water (hydrophobicity). The amalgamation of fluorine in polymers provides the attached polymer with lower surface energy that increases its hydrophobicity and decreases its friction coefficient and adhesion [36–38]. When fluoropolymers are applied on concrete, the fluorine part of the polymer has the ability to form a well-organised structure on the surface of concrete that results in a sheet, which is combined of strongly, bundled $-CF_3$ groups [36,39]. This gives the concrete the ability to repel water and reduces its water absorption, as it increases its hydrophobicity. Regardless of the role that fluoropolymers play in decreasing water absorption, some recent research found that fluoropolymers with long fluorinated side chains are hazardous to the environment and may cause cancer [40]. Accordingly, in this research, an environmentally-friendly fluoropolymer material with short fluorinated side chains was used with a hydrocarbon link between the fluorinated side chain and acrylic [41].

Silicone resin is a hydrophobic material that coats the internal walls of concrete pores with a film to repel water [2]. Little research has discussed this material, and for that reason, insufficient information about its performance against chloride or water penetration through concrete is known [2,41].

The Sodium acetate compound when first applied to concrete works on absorbing water that exists in the pores to form crystals. These crystals line the pores, without blocking them, allowing concrete to breathe and work on repelling penetrated water out of these pores. This material has an advantage over other commercially available and used materials, where it can be applied on wet surfaces and still works efficiently [41]. Fig. 1 shows a schematic model for untreated concrete and concrete treated with the sodium acetate solution, and how the material line the pores of the concrete.

For comparison purposes, a solvent-based silane with 100% active content was applied to concrete as well. One silicon atom is the main constituent of the pure silane compound, as shown in Fig. 2a. Alkoxy and Alkyl silanes are the main silane's derivatives that are used as hydrophobic surface applicants [42]. A typical alkyl alkoxy molecular structure is shown in Fig. 2b. When silane is applied to the concrete surface, it will penetrate through the pores and implanted in the pores. The organic alkylic OCH_3 group will overhang from pores' walls and make it water-repellent due to its fatty nature [14,42].

A concrete mix with water to cement ratio (w/c) of 0.46 was produced following the British standard BS 1881-125 [43]. All the previously mentioned protective materials were applied to concrete surface until refusal and following to the manufacturers' guidelines. The mix design of the used concrete mix is shown in Table 1.

3.2. Test specifications and specimens

190 cubes with the dimensions of $100\text{ mm} \times 100\text{ mm} \times 100\text{ mm}$ were cast; 180 cubes treated with the four protective materials and 10 control cubes. 95 cubes were tested for water absorption using the Initial Surface Absorption Test (ISAT), and the other 95 cubes were tested for Chloride penetration by using the Salt Ponding test. All treated cubes were conditioned before applying the protective materials; 40 cubes were fully dry, 40 cubes with 2% moisture, 40 cubes with 4% moisture, and 60 cubes were fully saturated. Cubes were fully immersed in water and their masses were measured after immersion at different intervals until the desired saturation level is achieved. Fig. 3 shows the testing protocol and the moisture content of the samples before applying the treatment. In the case of fully saturated cubes, they were tested twice; when they are still saturated and after drying them.

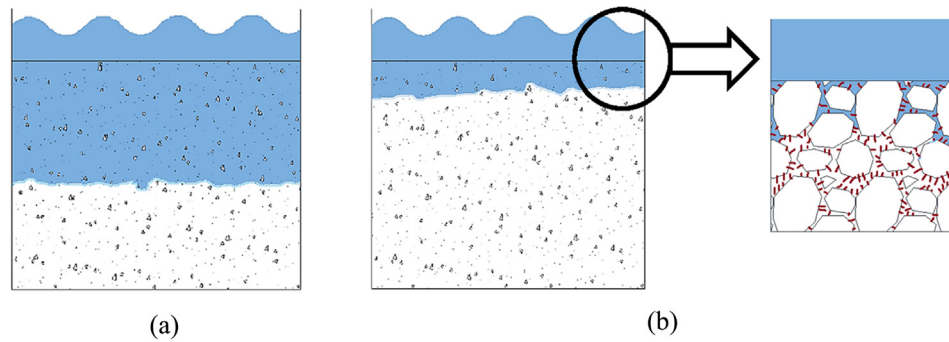


Fig. 1. Model for water absorption through concrete cube (a) untreated and (b) treated with Sodium acetate.

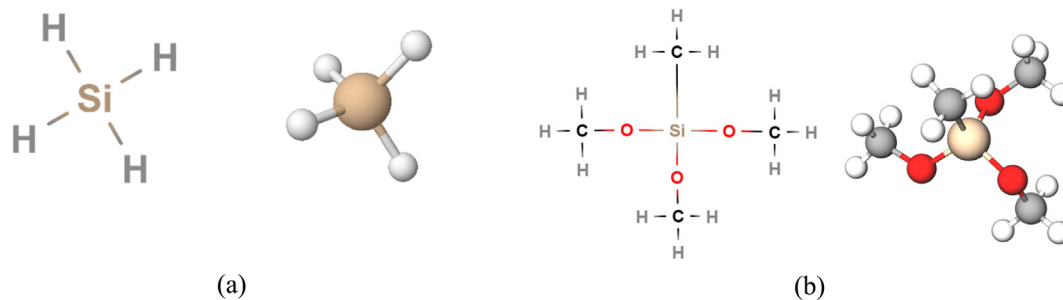


Fig. 2. The structural formula and 3D model of (a) a pure Silane compound and (b) Alkoxy Alkyl Silane.

Table 1
Concrete mix proportions.

Component	Quantity (kg/m ³)
Cement (CEM II/32.5 N; Sulphates <3.5%, Chlorides <0.10%, and initial setting time around 1.25 h)	457
Water	210
Fine aggregate (sharp silica sand, uniform grain size distribution between 1 mm and 300 μm)	660
Coarse aggregate (crushed stones with sharp edges and maximum size of 20 mm)	1073
Total	2400
Water/Cement ratio	0.46

After demoulding the concert samples, they were cured in a water tank with a temperature of 21 °C for 28 days. Once the curing period was finished, all concrete samples were dried in an oven at 105 °C until a constant mass was achieved (fully dry). The masses of cubes were measured after drying, and they were conditioned as follow:

Condition 1: 40 cubes were treated when they were assured to be fully dry.

Condition 2: 40 cubes were soaked in water until their moisture content (saturated surface dry) reached 2%.

Condition 3: 40 cubes were soaked in water until their moisture content (saturated surface dry) reached 4%.

Condition 4: 60 cubes were soaked in water until their moisture content (saturated surface dry) reached 6% (fully saturated). This was considered as fully saturated condition because concrete started to gain less than 0.01% moisture in 24 h.

Materials were applied to concrete surfaces when the required saturation level was achieved. The application process continued until refusal (when concrete starts to reject any further applied material) and following to the manufacturers' guidelines. After

the application of materials, part of the cubes in condition 4 was dried before testing, and the other part was tested without drying.

Concrete refusal for applied materials was measured by weighing the cubes before and after the application, to check the affinity of the applied materials to water and relate it to their performance when tested for water absorption and chloride penetration.

Scanning Electron Microscope (SEM), Energy-dispersive X-ray spectroscopy (EDX), and Fourier-transform Infrared Spectroscopy (FTIR) analyses were run on the tested materials to evaluate their morphology and their interaction with concrete. To achieve this purpose, materials were subjected to cryodesiccation (freeze-drying) to convert them from liquid state to solid state to facilitate their analysis procedure. Afterwards, the resulting powder samples, and treated concrete samples, were coated with a thin film of gold to make them conductive, before imaging them with the scanning electron microscope at 20 kV.

Water absorption of all samples was determined by using the ISAT test [44]. Also, the resistance of concrete for chloride diffusion was assessed by using the unidirectional salt-ponding test [21,45,46]. The specimens were ponded with a saline solution with 5% NaCl, and the test was run for 90 days. After finishing the testing period, powder samples from different depths of 5 mm, 10 mm, 15 mm, 20 mm, and 50 mm were collected, and the chloride content at each depth was measured by using Volhard's method, and with applying the following equation [47]:

$$CC = 3.545 * f * (V2 - V1)/m$$

where;

CC: chloride content percent (%).

f: molarity of silver nitrate solution.

V1: volume of the ammonium thiocyanate solution used in the titration (ml).

V2: volume of the ammonium thiocyanate solution used in the blank titration (ml).

m: mass of concrete sample (g).

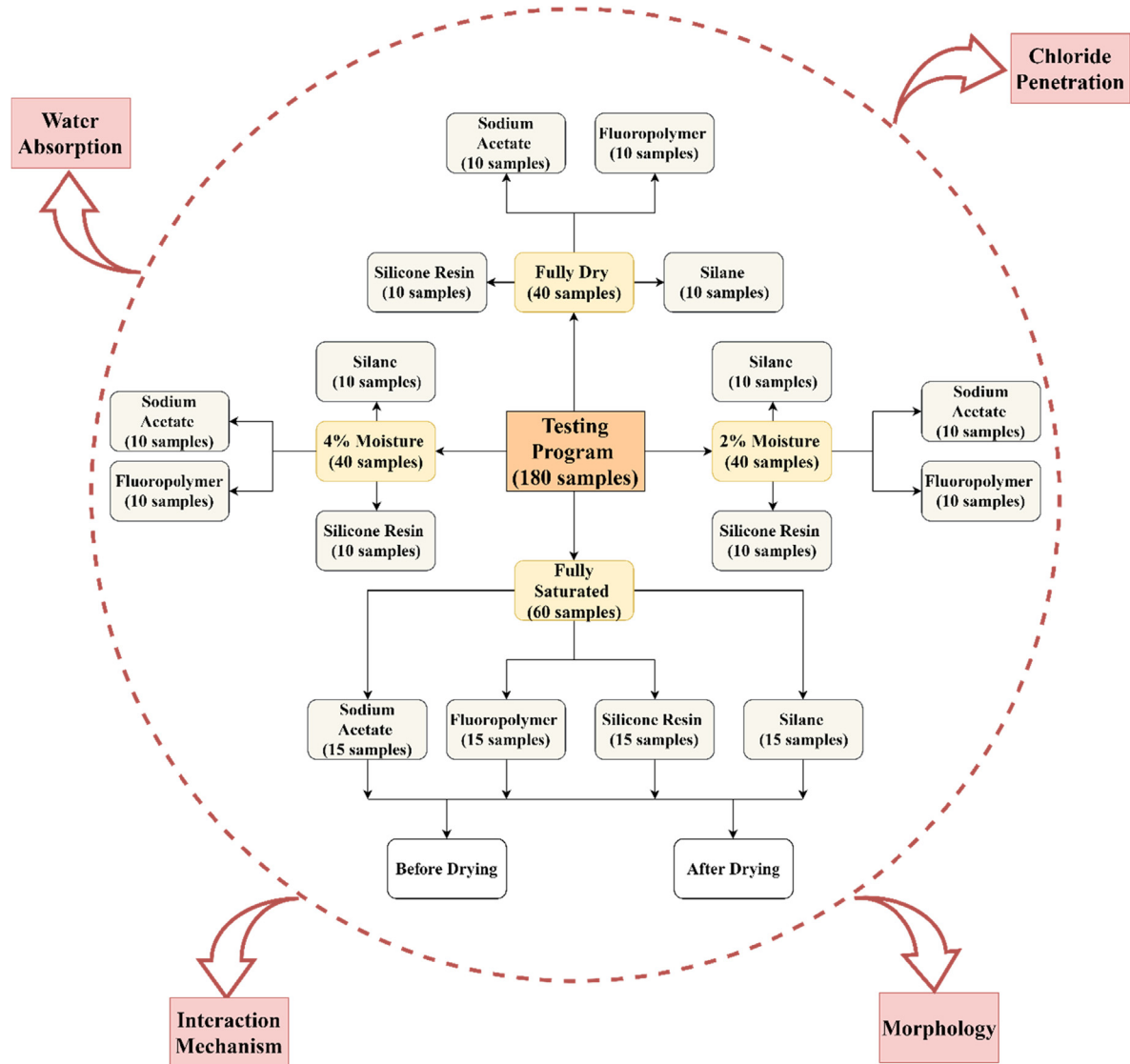


Fig. 3. Testing diagram of treated concrete and their saturation level.

4. Results and discussion

4.1. Material refusal

The effect of moisture content on the dosage of protective materials was assessed by measuring the amount refused by concrete. Table 2 outlines the amount of material rejected by preconditioned concrete.

It is evident that the wasted amount of applied materials increases with increasing the moisture content of concrete. However, Sodium acetate showed the least rejection rate, compared to other materials, when applied to concrete with high moisture content. This is due to its high affinity to water as it uses a certain amount of water to form its crystals. On the other hand, Silane showed an increase in the rejection rate by increasing the moisture content of concrete, and it reached more than 40% when applied to fully saturated concrete. However, when applied to fully dry concrete the rejection rate was the least of all materials, which is reflected on its performance in providing the optimal protection to concrete. Rejection rates for Fluoropolymer and Silicone resin were in the middle of the previously mentioned materials.

4.2. Morphology and interaction of materials

4.2.1. Microstructure and elemental composition analyses

The need for properly characterizing the applied treatments will help in explaining the way these materials work and their interaction with concrete. It is obvious that the morphology of the three materials differs from each other, as seen from their microstructure in Fig. 4. The utilization of the tested materials for the purpose of concrete protection, or even masonry structures [29], relies on the analysis of the materials themselves and the characteristics of their constituents.

Results from EDX analysis showed that the main elements composing Sodium acetate compound are Carbon, Oxygen, Sodium, and Silicon. These elements preliminary confirms that the active part of this compound is sodium acetate, which contains the former elements except Silicon [48]. This compound is believed to diffuse through the pore structure of concrete, links to the walls of the pores and starts forming its crystals in the presence of water. These crystals are characterised by being hygroscopic as they use water for their development; they trap water inside their crystalline structure and reduce the concrete's permeability [48]. The pres-

Table 2
percentage of material refusal corresponding to moisture content of concrete.

Preconditions	Material	Material rejected (%)
Fully dry	Sodium acetate	11.3
	Fluoropolymer	11.2
	Silicone resin	15.5
	Silane	8.2
2% moisture	Sodium acetate	17.2
	Fluoropolymer	23.7
	Silicone resin	21.6
	Silane	20.3
4% moisture	Sodium acetate	18.4
	Fluoropolymer	25.6
	Silicone resin	23.4
	Silane	28.4
Fully saturated	Sodium acetate	24.5
	Fluoropolymer	30.1
	Silicone resin	28.2
	Silane	40.5

ence of silicon in the elemental composition of this compound and the hydrophobic performance of the compound might indicate the formation of another type of crystals. It is suggested that an organosilicon composite might be present in the material, which is an organometallic compound with bonds of carbon and silicon [49,50]. The main characteristic of the organosilicon compounds is their high hydrophobicity, which gives them the advantage of being used for concrete protection. Furthermore, it is also believed that the presence of sodium and silicon in the composition of this compound will start a reaction with the calcium hydroxide, presents in concrete, and generates some amounts of silica crystals [51,52]. These silica crystals work on reducing the size of pores rather than blocking them allowing concrete to breathe and allowing for oxygen diffusion [53,54]. The microstructural analysis of sodium acetate, before applying to concrete, as shown in Fig. 4a on the left, revealed the presence of this material in dense and packed formation with amorphous and smooth surfaces, which contribute directly to increasing the material's hydrophobicity [55–57]. This would be seen in treated concrete (Fig. 4a on the right), as the sodium acetate material has made the internal structure of concrete denser and more compact, which would be reflected on its strength and rigidity. This aspect is discussed in details in Section 4.2.2.

Analysing the Fluoropolymer material under the EDX has revealed that Fluorine, Carbon and Oxygen are the main constituents forming its elemental structure. As discussed in Section 3.1, the presence of fluorine will provide the material with hydrophobic properties, which will contribute directly to concrete protection and waterproofing. A microstructural analysis for this material, as shown in Fig. 4b (on the left), reveals that it forms fine, smooth and 'needle-shaped' polymers with sizes less than 200 nm. Their shape, size and characteristic are suggested to give enough support for the material to be integrated easily within the concrete pores and attached strongly to their walls [54,58]. The interaction between fluoropolymer and concrete (Fig. 4b on the right) shows the integration of the material within the pores of the concrete and their dense distribution on the pores' walls. After the penetration of Fluoropolymer through the pores, its shape is recognised as 'rice-shaped' or 'pebble-shaped' clusters that are attached to the walls of pores and distributed over a wide area of them (Fig. 4b on the right). The small size of these clusters, their smooth surfaces and their high distribution within the pores allow them to act strongly against water and chemicals penetration.

EDX analysis of the Silicone resin material has shown that carbon, oxygen and silicon are the main elements of its composition. The structural analysis of this material, described in Fig. 4c on the

left, shows an attached sheet of resins that work together as one unit. The presence of the material in this state eases its connection to the pores as shown in Fig. 4c (on the right). When applied to concrete, a silicate gel will develop and initiates strengthening points in the internal parts of the pores [12,59]. Hydroxyl groups, formed from the by-products of cement, will possibly react with the silicon in the silicone resin, in the presence of hydrogen bonds, allowing silicone resin to link strongly with the pores all over the drying time. This would possibly guarantee the development of some hydrophobic properties [60].

Comparing the materials above with silane (Fig. 4d), the former works on entirely blocking the pores, not allowing concrete to breathe, because of the alkoxy group that forms its molecular structure [60]. This alkoxy group will generate a Silanol group, after its reaction with water, and congregate inside the pores and block them [60]. The aerogel microstructure of silane, as appears in Fig. 4d on the left, shows an obvious gel structure with multiple groves that increase the material's surface area. This gives the material the ability to extend its presence inside the pores and block them. Fig. 4d on the right reveals the presence of silane inside concrete in large-sized lumps, which are distributed all over the shown cross-section.

4.2.2. Functional groups of the protective materials

FTIR spectroscopy was chosen to run a quantitative analysis on the protective materials and their interaction mechanism with concrete. This technique is well known for its high sensitivity, accuracy, and reliability in quantifying and analysing materials [61,62]. The FTIR spectra of the protective materials and their interaction with concrete are shown in Fig. 5a–d.

The interaction between sodium acetate and concrete is recognised with some characteristic peaks that range between 2966 and 2893 cm^{-1} , 1478 to 1395 cm^{-1} , 873 to 797 cm^{-1} and the peak at 1083 cm^{-1} . The sharpest band is found in 2966 to 2893 cm^{-1} range that may correspond to the –CH and –OH stretching vibrational bonds [63]. These peaks are caused by the non-harmonic resonances of the –CH and –OH bonds in the crystal of the acetic acid chain (CH_3COOH) forming sodium acetate [64]. The band range between 873 and 797 cm^{-1} mostly refers to the – CO_3 bond [65] and the strong – CH_2 rocking vibrational bond in the Si- CH_3 fragment of the material's molecular structure [63]. Also, it is believed that 1478 to 1395 cm^{-1} band may correspond to the stretching vibrations of the C–H bond [66,67]. Finally, the 1083 cm^{-1} refers to the stretching vibrational C–O bond in the –COOH carboxylic acid part [63].

After treating concrete with sodium acetate (Fig. 5a), an increase in the peaks' transmission (%) has been observed within the 2966 to 2893 cm^{-1} range (–CH and –OH). This increase in the intensity of the hydrogen bond could refer to the reaction between sodium acetate solution and concrete components in the presence of moisture, where sodium acetate dissociates in water at the beginning to form CH_3COO^- and Na^+ ions [63,64]. Afterwards, CH_3COO^- is believed to connect with concrete pores by reacting with sodium that already exists in concrete to form another type of sodium acetate crystals, which link strongly with concrete pores. This process has a strong influence in increasing the intensity of the C–H bond (Fig. 5a). In addition, it is noticed that the peaks at 1478 and 1395 cm^{-1} had become sharper when concrete was treated with sodium acetate, regardless of the reduction in their transmission, which might reflect the increase in the strength of the C–H bond after treatment. On the other hand, the detached Na^+ ions are suggested to react with the available moisture to form a sodium hydroxide (NaOH) product, which in turn participates in increasing the intensity of –OH bonds.

The observed reduction in the intensity of the C–O and – CO_3 bonds could result from the ionic reaction between the unreacted

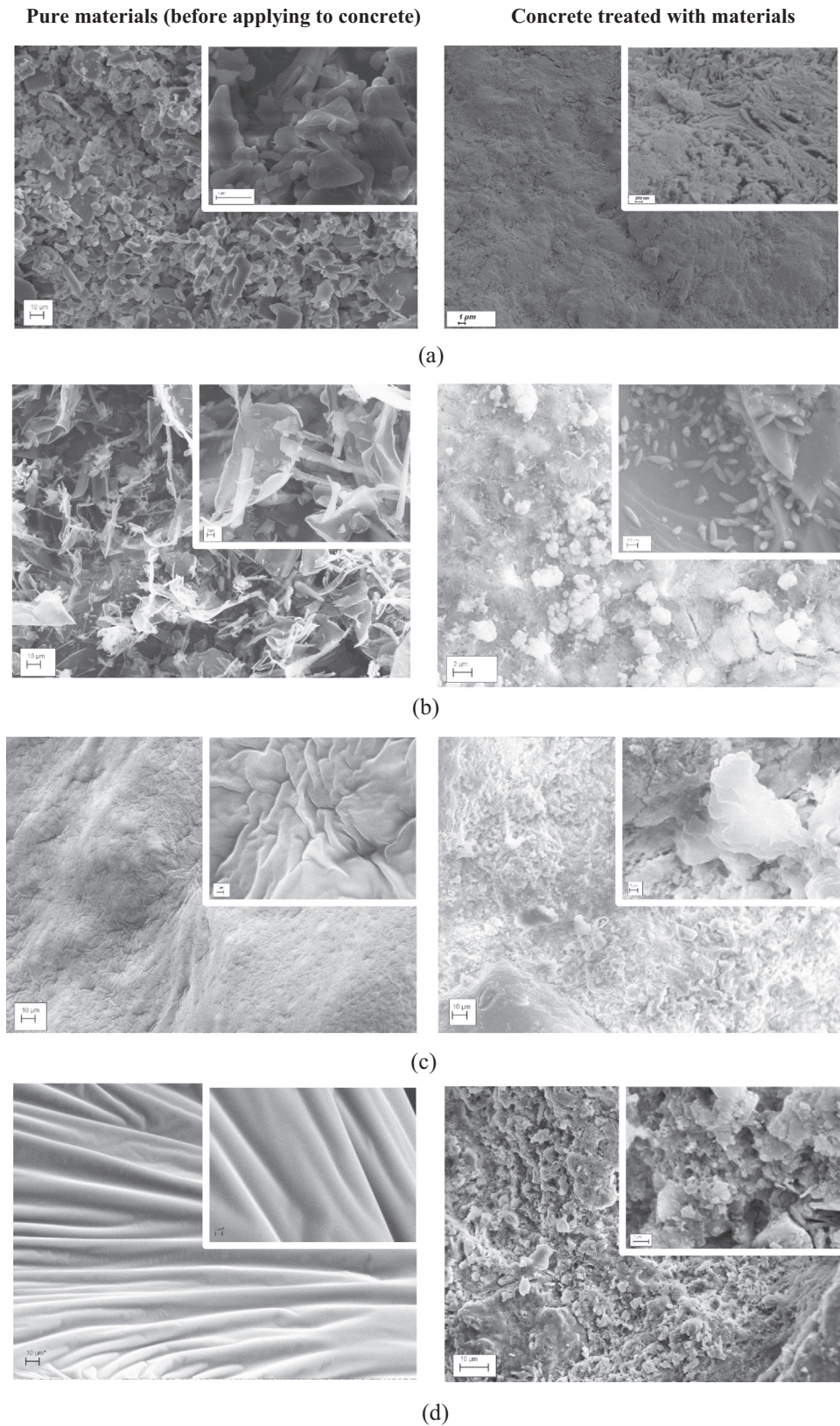
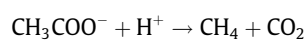


Fig. 4. SEM results for the applied protection and their integration with concrete: (a) Sodium acetate, (b) Fluoropolymer (c) Silicone resin, and (d) Silane.

CH_3COO^- and H^+ ions that form small quantities of volatile CH_4 and CO_2 gases as described in the following reaction [70,71]:



When it comes to the hydrophobicity of the sodium acetate solution, it is believed that a substitution process for the $-\text{OH}$ groups with CH_3 groups takes place, which results in increasing the intensity of the C–H peaks. With the presence of Silicon in

the used sodium acetate component (Section 4.2.1), CH_3 will bond with silicon after its penetration in concrete to form an organosilicon bond with some hydrophobic effect [72–74].

The FTIR analyses of the fluoropolymer material and concrete impregnated with fluoropolymer are shown in Fig. 5b. The fluoropolymer material has a number of distinctive bands; the

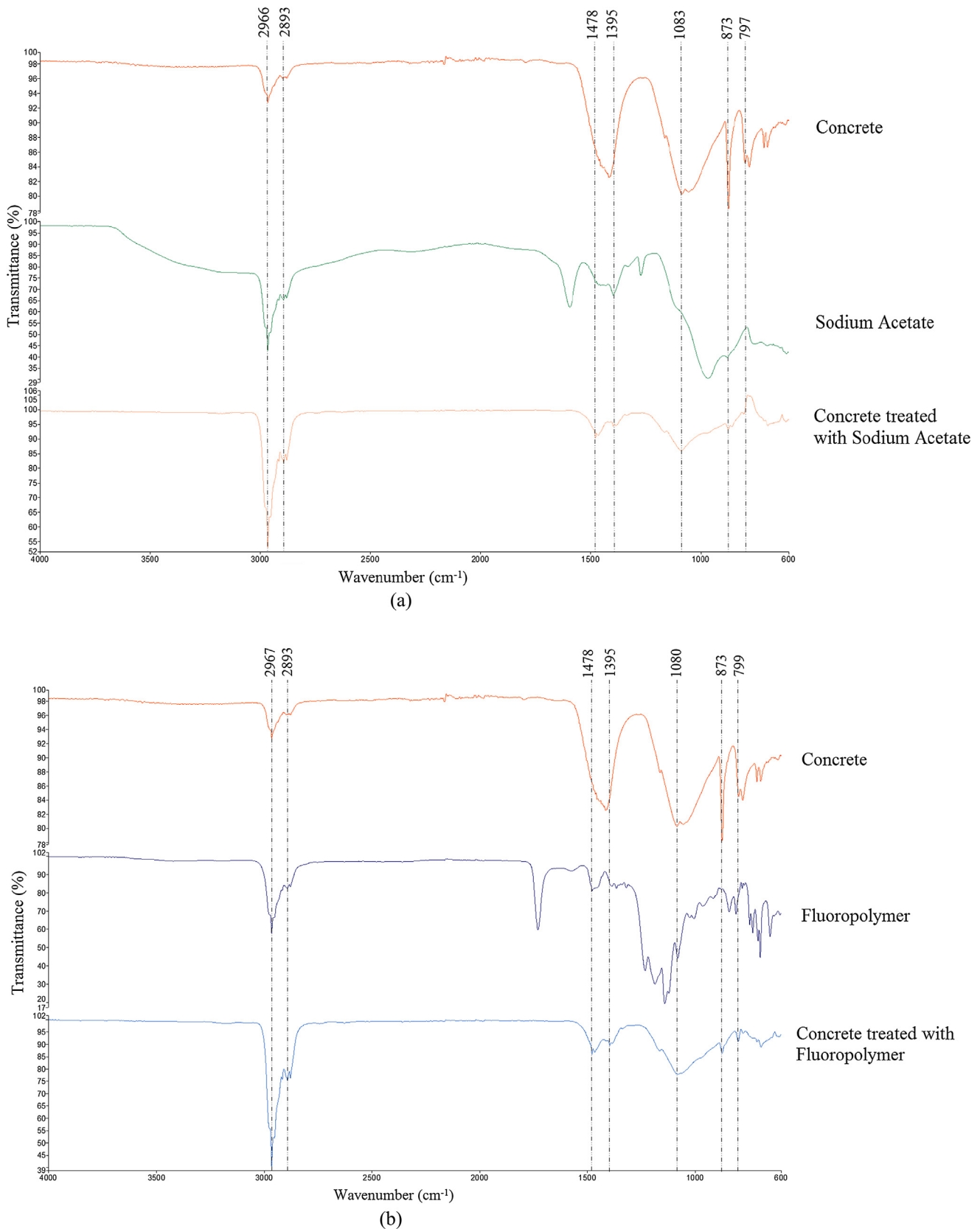


Fig. 5. FTIR analysis for the interaction between concrete and (a) Sodium Acetate, (b) Fluoropolymer, (c) Silicone resin and (d) Silane.

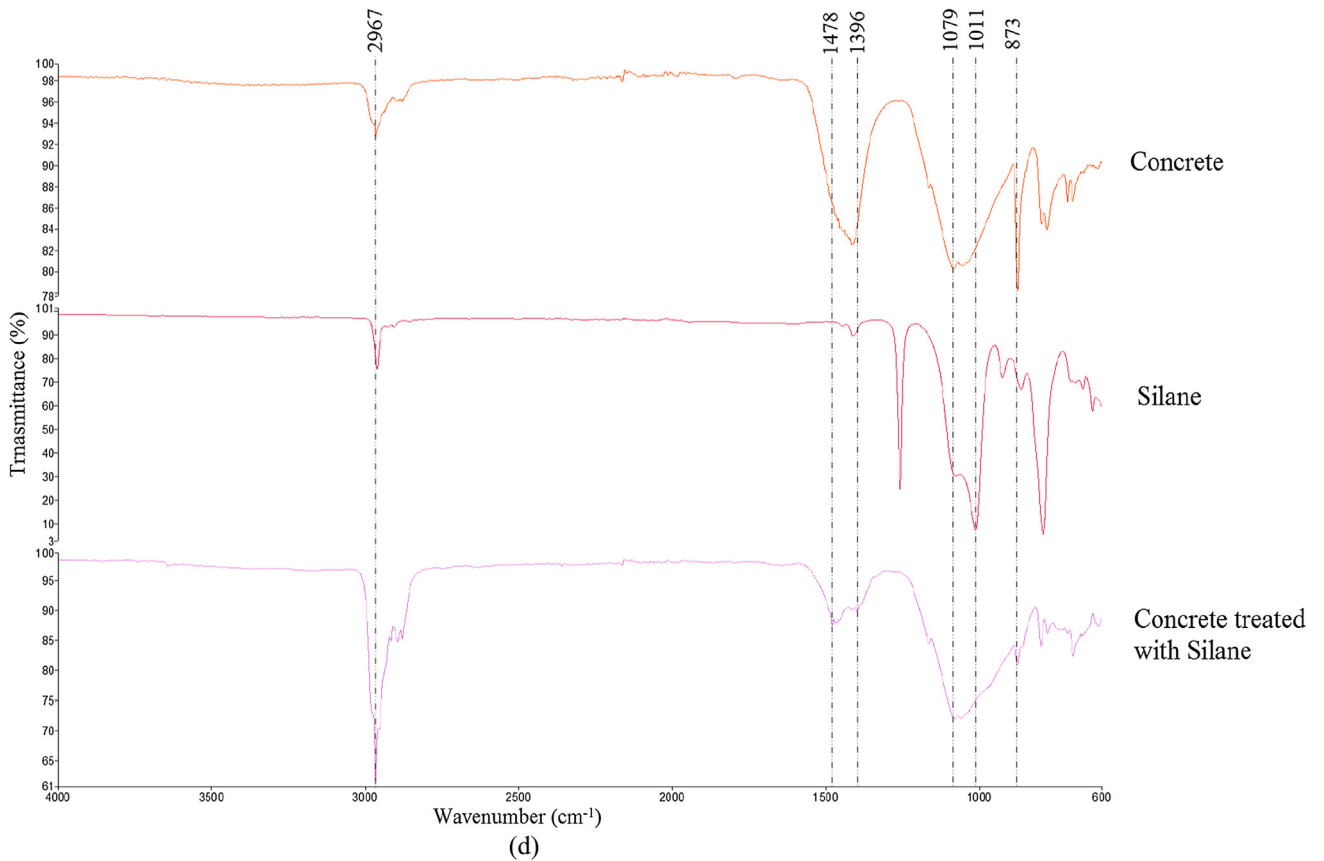
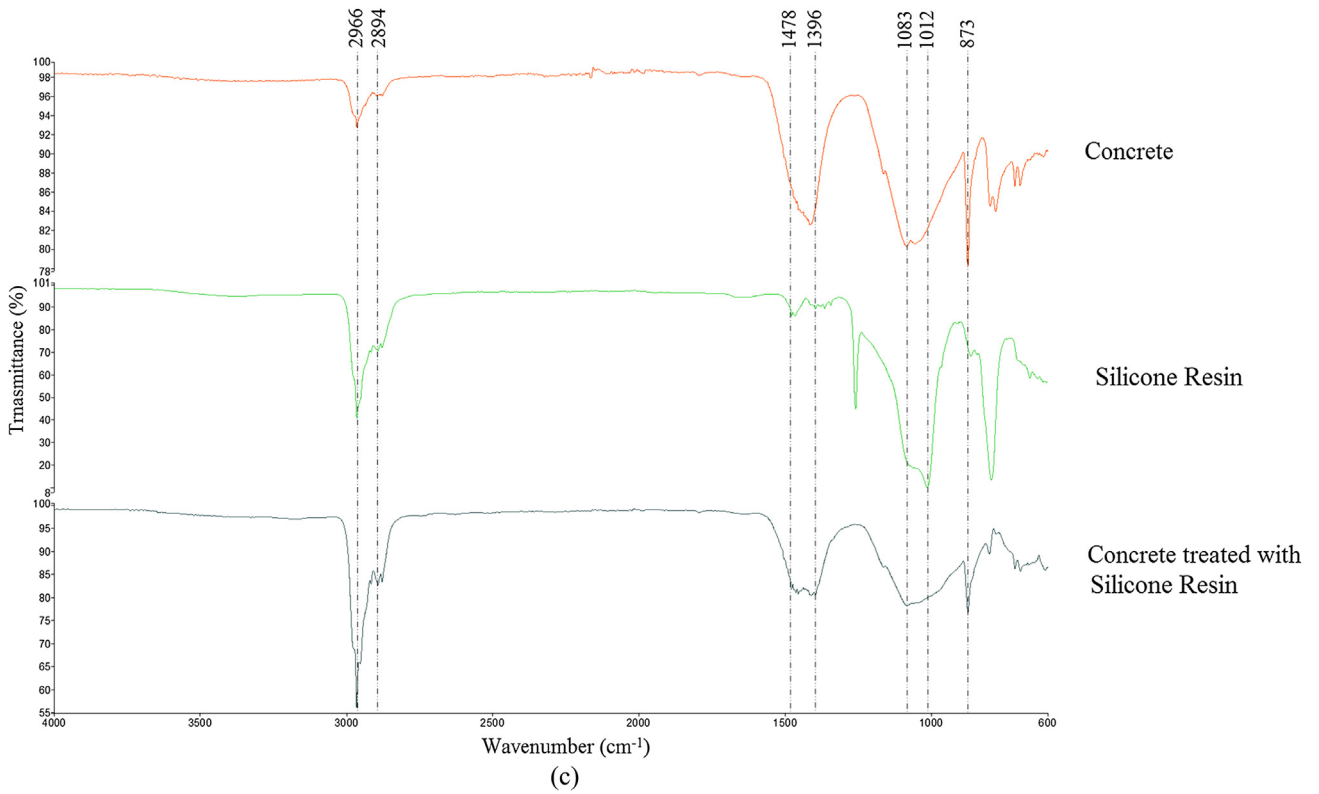


Fig. 5 (continued)

sharpest band is found at 2967 cm^{-1} that refers to the C–H stretching vibrational bond [64,76,77]. Another distinctive small peak could be spotted at 2893 cm^{-1} that also refers to the C–H stretch-

ing vibrational bond [64,76,77]. Both bands are observed to increase after treating concrete with fluoropolymer, which might refer to the formation of strong carbon bonds between concrete

and fluoropolymer, as fluoropolymer could strongly adhere to hydrated cement particles. Likewise, the 1478 and 1395 cm^{-1} bands are mostly associated with the C–H stretching vibrational bonds, which are observed to be distinguished with small peaks when concrete is treated with Fluoropolymer [66,67]. The formation of these small peaks might also indicate the creation of carbon bonds between the applied fluoropolymer and concrete pores. Furthermore, the transmission (%) of the 1083 cm^{-1} peak, which might correspond to the strong stretching vibrational C–F bond [63,75], has been observed to increase by more than 4% when adding Fluoropolymer to concrete. Accordingly, the increase in the intensity of this peak could be linked with the hydrophobic effect that fluoropolymer gives to concrete; fluorinated side chains are assembled together to form a tight $-\text{CF}_3$ groups that provide concrete with hydrophobicity [36].

In the IR spectra of silicone resin and its interaction with concrete (Fig. 5c), two sharp distinctive peaks are noticed at 2966 cm^{-1} and 2893 cm^{-1} bands, and two broad peaks at 1478 cm^{-1} and 1395 cm^{-1} . All of them are believed to belong to the C–H stretching bonds, and they have shown an increase in their transmission (%) after treatment [64,67,68,78,79]. This increase in intensity was accompanied with an increase in the intensity of the 1083 to 1012 cm^{-1} bands (become broader) in treated concrete, which belong to the Si–O–Si absorption bond [77,78]. The increase in the intensity of the C–H and Si–O–Si bands might refer to the high activity of silicone resin, which leads to the breaking of the hydrogen bonds in the material after impregnation into concrete and in the presence of moisture inside the pores. This will participate in consuming the calcium hydroxide that resulted from the hydration process, contributing towards the enhancement of the interfacial properties of the material and its adhesion with concrete [78].

Fig. 5d shows the IR spectra of Silane and its interaction with concrete. The 2967 cm^{-1} sharp peak presents the most distinctive band in the spectra, which corresponds to the $-\text{OH}$ stretching vibrational bond [63]. After applying silane to concrete, the band has shown an increase in its intensity going with another increase in the intensity of the 1079 to 1011 cm^{-1} bands, which belong to the Si–O–Si bonds [64,78,79]. This increase in the transmission (%) of those bands might refer to the reaction between silane and moisture inside the pores, which leads to the formation of silanol groups by the hydrolysis of alkoxy groups in silane [79]. Finally, a linkage between concrete and hydroxyl groups in silane will take place after the drying of the pores, creating a strong bond between them.

4.3. Water absorption

The ability of treated and untreated concrete samples to resist water absorption was assessed by the ISAT, and outcomes from this test are outlined in Fig. 6.

As expected, fully saturated concrete showed the least water absorption rate when tested before drying (Fig. 6d). This is due to the presence of water that fully occupies the pores, not allowing more water to be absorbed, which shows a 'pseudo-performance' for the treatment. Accordingly, samples were dried after applying the materials to show the right performance of these materials when applied to fully saturated concrete. After drying, a high increase in water absorption can be noticed (Fig. 6e), which reflects the right performance of applied materials. Sodium acetate has provided the optimal protection under all preconditions except the fully dry condition, which might refer to its need for a certain amount of water to form its active crystals, as explained in Section 4.2.2. It is also noticed that sodium acetate has shown better performance for saturated concrete after drying, which denotes its high affinity to water and its ability to work well in the presence

of water. Moreover, reflecting the rejection rate of this material, once applied to saturated concrete, on water absorption outcomes, it shows that the presence of its high active content (around 75%) in concrete enhanced water impermeability, compared to other materials especially silane. Sodium acetate uses a certain amount of water to create hydrogen bonds with concrete that allows the material to link properly in the pores, and at the same time, the material will create hydrophobic organosilicon crystals that work on fending off excess water [68–74]. A similar drop in water absorption was noticed previously in the work of Reiterman and Pazderka [13] when applying protective materials with similar technology to concrete [31].

Increasing moisture content above 2% showed an obvious negative effect on the performance of silane; exploring the sequence of water absorption for concrete treated with this material through Fig. 6a–e, shows the deficiency of this material to provide proper protection when the moisture content is higher than 2%. This refers to the activation process of silane inside the pores; it either needs to be applied on concrete with small amounts of water or on dry concrete surfaces to activate the silanol groups that provide the material with its hydrophobic properties [79]. Silane mainly depends on the penetration depth it can achieve when applied to concrete, and this penetration depth is a fundamental requirement for an effective protection [80]. In the presence of high amounts of water inside the pores (>2%), the penetration depth of silane would be nominal and insignificant which affects its efficacy in protecting concrete. Another reason for the reduction in silane's efficacy when applied to concrete with high moisture content (>2%), is the presence of Alkoxy groups that are attached to its silicon atoms and provide silane with its fatty nature. These Alkoxy fatty groups are supposed to react with silicate in concrete to establish a stable bond with concrete. In the presence of high amount of water in concrete, and with the hydrophobic properties of the Alkoxy groups, the bonding between silane and concrete would be difficult [1]. Most of the marine structures are damp all the time due to their continuous contact with water, which makes their treatment with liquid silane an economic waste (matching results in Table 2 with Fig. 6a–e).

Fluoropolymer and silicone resin have shown a converging performance with better efficacy for silicone resin. They both had an average performance between sodium acetate and silane in reducing water absorption. However, silicone resin has shown a higher affinity to moisture than fluoropolymer due to its interaction mechanism with concrete that depends on the presence of certain amounts of moisture for better adhesion inside the pores, as discussed in Section 4.2.2. In the presence of moisture in concrete, silicone resin works on breaking the hydrogen bonds, increase the rate of consuming calcium hydroxide and link its silicates on the walls of the pores with strong carbon and silicon bonds. On the other hand, fluoropolymer showed its optimum efficacy when applied to dry concrete, with a gradual reduction in its efficacy when moisture content increases inside the pores (Fig. 6a–e). This refers to the low surface energy of the fluorinated side chain of the material, which decreases its adhesion to applied surfaces in the presence of water [81,36–38].

4.4. Chloride penetration

The concentration of the free chloride in concrete at different depths and with different pre-conditions are shown in Fig. 7a–e. As expected, the chloride content reduces with increasing the depth from the exposed surface for all the preconditioned samples. When observing the chloride content on the surface of all samples (0–5 mm), it is witnessed that their values show some anomaly for some of the exposure conditions, especially when concrete is treated with silane. This refers to the carbonation of some concrete

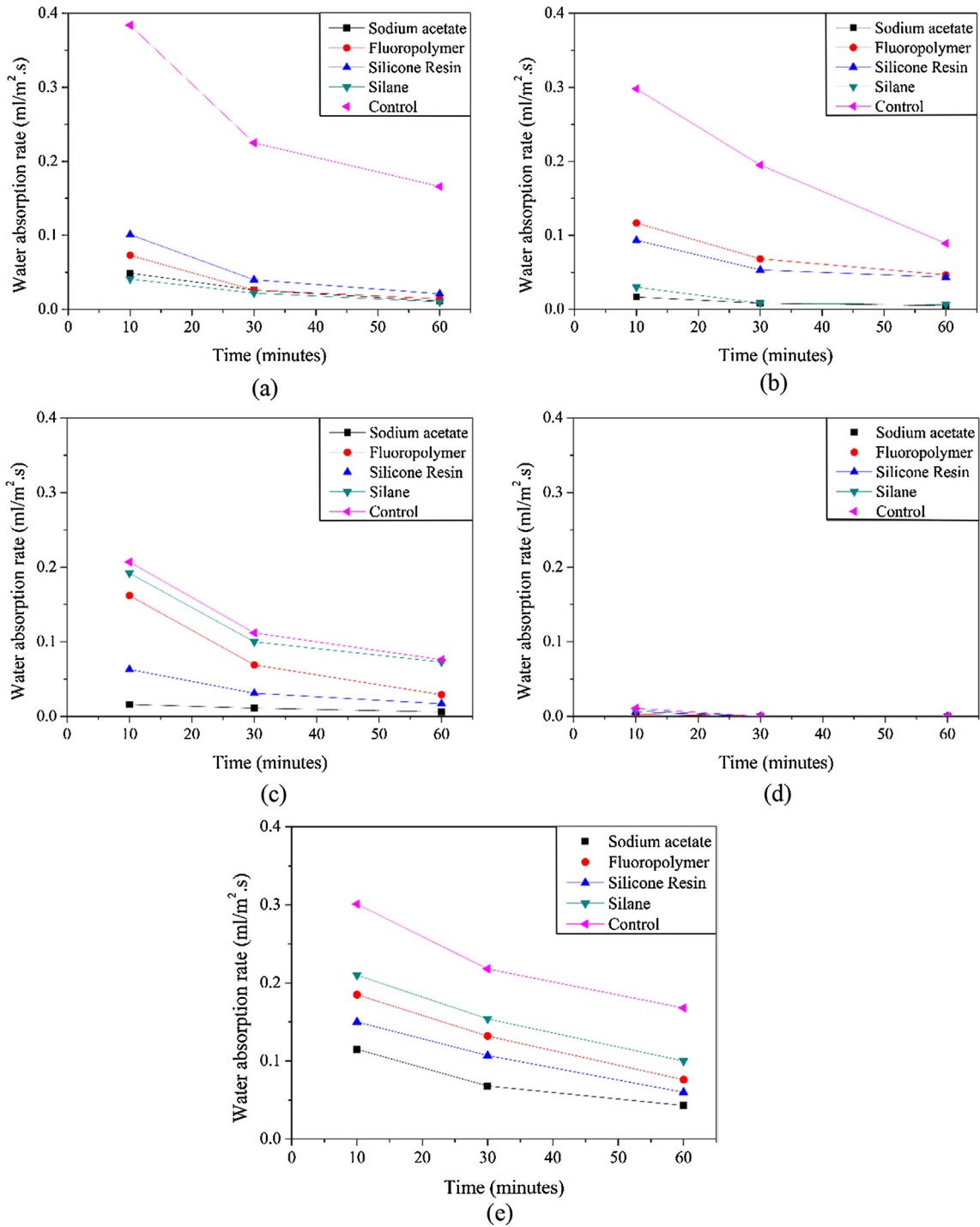


Fig. 6. Water absorption rates for treated and untreated concrete after preconditions: (a) fully dry, (b) 2% moisture content, (c) 4% moisture content, (d) fully saturated (before drying), and (e) fully saturated (after drying).

surfaces that liberates some constrained chlorides [82]. Adding to that, silane could contribute to accelerating the carbonation rate of concrete in laboratory conditions [83].

Referring to the fully dry condition (Fig. 7a), silane has shown the least chloride content compared to other materials and control. This could be linked with the rejection rate of silane in Table 2, as more than 91% of its active content has been integrated within the pores of the concrete. When silane is applied to dry surfaces, Alkoxy groups that are bonded with silicon atoms in silane will react with the silicate, which already exists in concrete, and adhere strongly in the pores [1]. With increasing the moisture content of

concrete before treatment, the protection efficacy of silane decreases until it reaches its minimum when applied to fully saturated concrete (the same reason discussed in Section 4.3). Adding to that, the continuous impact of aggressive chemicals over a long period will participate in breaking the hydrophobic Si-O-Si bonds of the applied silane and reduces its efficacy, especially when it is applied to wet surfaces [82,84]. On the other hand, sodium acetate and silicone resin were less efficient than silane when applied to dry concrete, due to their interaction mechanism with concrete that needs the presence of moisture inside the pores, as discussed previously in Sections 4.2.2 and 4.4. Furthermore, their efficacy

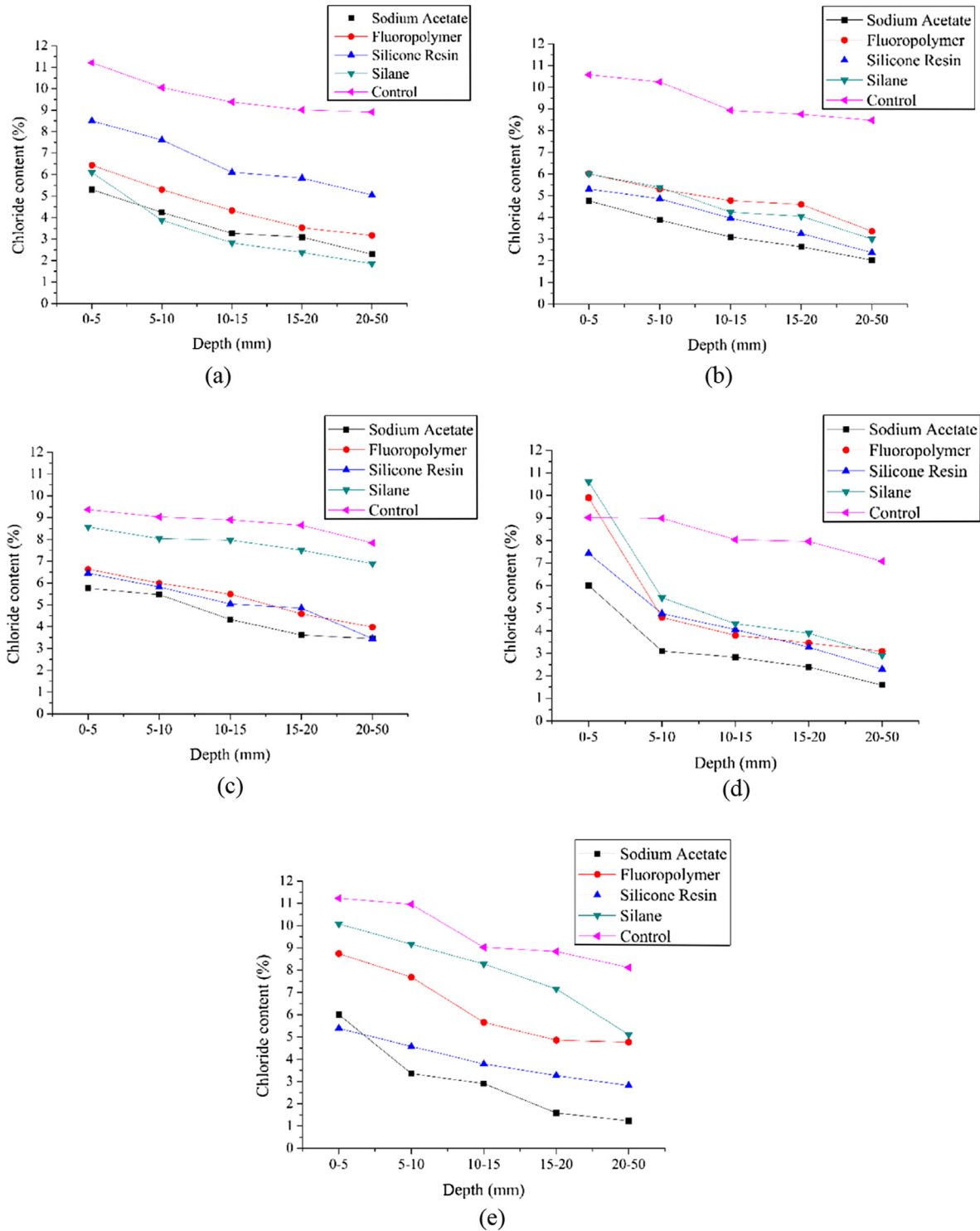


Fig. 7. Chloride profiles for treated and control preconditioned concrete: (a) fully dry, (b) 2% moisture content, (c) 4% moisture content, (d) fully saturated (tested before drying) and (e) fully saturated (tested after drying).

starts to increase by increasing the moisture content in concrete (Fig. 7b–e). In contrast, Fluoropolymer has shown the best performance when applied to dry concrete, and its efficacy declined with increasing the moisture content of concrete. Water forms a barrier between concrete and the applied Fluoropolymer that weakens the adhesion of Fluorine to concrete [81,36–38].

When referring to fully saturated concrete (before drying) (Fig. 7d), it could be seen that the chloride content for all samples is less than for fully dry, partially saturated and fully saturated

(after drying) concrete. Chloride transport in fully saturated concrete depends mainly on ion diffusion, which is the same transport process that takes place in submerged marine structures. Accordingly, the low amount of chloride in saturated concrete is attributable to the formation of a protective layer on concrete surface that decreases chloride permeability. This occurs with increasing ion diffusion due to the reaction between the saline solution and concrete, resulting in coatings of $Mg(OH)_2$ (Brucite) and $CaCO_3$ (Aragonite) [82,85]. After drying fully saturated concrete, the chloride

content is witnessed to increase, as the penetration of chloride through the pores is backed by capillary absorption of the saline solution following direct contact [85].

5. Summary and conclusions

Based on the performance evaluation of three surface applied protective materials; sodium acetate, fluoropolymer, and silicone resin, their mechanism, morphology and interaction with concrete have been investigated and compared with a commercially available silane. The effect of concrete moisture content on the efficacy of the treatment has been investigated in terms of water absorption and chloride penetration. An increase in the moisture content of concrete resulted in an increase in the rejection of concrete to the applied materials especially silane. Sodium acetate has shown the least rejection rate with increasing the moisture content of concrete followed by silicone resin, fluoropolymer and silane, respectively. The increase in water absorption and chloride penetration of treated concrete was associated with the rejection rate of the materials and their affinity to water, where sodium acetate has provided the maximum protection when applied to fully saturated concrete followed by silicone resin. On the other hand, silane provided its maximum efficacy when applied to fully dry concrete followed by fluoropolymer. The elemental composition, microstructural analysis and functional groups of the materials have revealed their interaction mechanism with concrete and their bonding inside the pore structure of concrete. Sodium acetate dissociates inside the pores in the presence of water to form crystals with a hydrophobic effect (with organosilicon bonds) that connect strongly with the pores and increase their hydrophobicity. In contrast, and due to the low surface energy of the fluorinated side chain of fluoropolymer, the presence of water inside concrete will prevent fluoropolymer from adhering to the pores. Silane was found efficient if only applied to dry concrete or to concrete with low moisture content ($\leq 2\%$) because of the presence of the hydrophobic Alkoxy groups in its composition. On the other hand, silicone resin has displayed a reasonable efficacy when applied to wet concrete, as it works on breaking the hydrogen bonds and on consuming the calcium hydroxide resulted from the hydration process, which increases its adhesion to concrete.

Microstructural analysis of materials has revealed the presence of sodium acetate in the pores with dense and packed formations with amorphous and smooth surfaces, which contribute directly to increasing the material's hydrophobicity. Fluoropolymer was found to present in fine, smooth and 'needle-shaped' polymers with sizes less than 200 nm, which helps it to attach strongly in the pores. Silicone resin was noticed to form an attached sheet of resins that eases its connection to the pores. Moreover, silane was found to have a gel structure with multiple groves that increase the material's surface area. This gives the material the ability to extend its presence inside the pores and block them.

The suggested materials would have a high impact in protecting concrete structures that exists saline environments, especially in the presence of high humidity, since they were proven to work well in the presence of moisture.

Conflict of interest

None.

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Appendix A. Supplementary data

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References

- [1] L. Bertolini, B. Elsener, P. Pedferri, E. Redaelli, R.B. Polder, *Corrosion of Steel in Concrete: Prevention, Diagnosis, Repair*, John Wiley & Sons, 2013.
- [2] J.G. Dai, Y. Akira, F.H. Wittmann, H. Yokota, P. Zhang, Water repellent surface impregnation for extension of service life of reinforced concrete structures in marine environments: the role of cracks, *Cem. Concr. Compos.* 32 (2) (2010) 101–109.
- [3] J. Liu, Q. Qiu, X. Chen, F. Xing, N. Han, Y. He, Y. Ma, Understanding the interacted mechanism between carbonation and chloride aerosol attack in ordinary Portland cement concrete, *Cem. Concr. Res.* 95 (2017) 217–225.
- [4] A. Suwito, Y. Xi, Service life of reinforced concrete structures with corrosion damage due to chloride attack, in: *Life-Cycle Performance of Deteriorating Structures: Assessment, Design and Management*, 2004, pp. 207–218.
- [5] K.D. Baldie, P.L. Pratt, Crack growth in hardened cement paste, *MRS Online Proc. Lib. Arch.* 64 (1985).
- [6] A.G. Constantinou, K.L. Scrivener, The corrosion of steel reinforcement in carbonated concrete under different humidity regimes, *MRS Online Proc. Lib. Arch.* 370 (1994).
- [7] British Standards Institution, BS EN 206:2013: Concrete. Specification, Performance, Production and Conformity, British Standards Institution, London, 2013.
- [8] C. Ma, G. De Vera, J. López, C. García, C. Andrade, Transport of chlorides through non-saturated concrete after an initial limited chloride supply, in: *PRO 19: 2nd International RILEM Workshop on Testing and Modelling the Chloride Ingress into Concrete*, RILEM Publications, 2001, p. 173.
- [9] G. de Vera, M.A. Climent, E. Viqueira, C. Antón, C. Andrade, A test method for measuring chloride diffusion coefficients through partially saturated concrete. Part II: the instantaneous plane source diffusion case with chloride binding consideration, *Cem. Concr. Res.* 37 (5) (2007) 714–724.
- [10] E.P. Nielsen, M.R. Geiker, Chloride diffusion in partially saturated cementitious material, *Cem. Concr. Res.* 33 (1) (2003) 133–138.
- [11] D. Conciatori, H. Sadouki, E. Brühwiler, Capillary suction and diffusion model for chloride ingress into concrete, *Cem. Concr. Res.* 38 (12) (2008) 1401–1408.
- [12] E. Franzoni, B. Pigino, C. Pistolesi, Ethyl silicate for surface protection of concrete: performance in comparison with other inorganic surface treatments, *Cem. Concr. Compos.* 44 (2013) 69–76.
- [13] A. Brenna, F. Bolzoni, S. Beretta, M. Ormellesse, Long-term chloride-induced corrosion monitoring of reinforced concrete coated with commercial polymer-modified mortar and polymeric coatings, *Constr. Build. Mater.* 48 (2013) 734–744.
- [14] M. Ibrahim, A.S. Al-Gahtani, M. Maslehuddin, A.A. Almusallam, Effectiveness of concrete surface treatment materials in reducing chloride-induced reinforcement corrosion, *Constr. Build. Mater.* 11 (7–8) (1997) 443–451.
- [15] L. Basheer, D.J. Cleland, A.E. Long, Protection provided by surface treatments against chloride induced corrosion, *Mater. Struct.* 31 (7) (1998) 459–464.
- [16] M. Ibrahim, A.S. Al-Gahtani, M. Maslehuddin, F.H. Dakhil, Use of surface treatment materials to improve concrete durability, *J. Mater. Civ. Eng.* 11 (1) (1999) 36–40.
- [17] M.R. Jones, R.K. Dhir, J.P. Gill, Concrete surface treatment: effect of exposure temperature on chloride diffusion resistance, *Cem. Concr. Res.* 25 (1) (1995) 197–208.
- [18] K.H. Wong, R.E. Weyers, P.D. Cady, The retardation of reinforcing steel corrosion by alkyl-alkoxyl silane, *Cem. Concr. Res.* 13 (6) (1983) 778–788.
- [19] M.J. Al-Kheetan, M. Rahman, B.N. Muniswamappa, D. Chamberlain, Performance enhancement of self-compacting concrete in saline environment by hydrophobic surface protection, *Can. J. Civ. Eng.* (2019), <https://doi.org/10.1139/cjce-2018-0546>.
- [20] M.C. Bubalo, K. Radošević, I.R. Redovniković, J. Halambek, V.G. Srček, A brief overview of the potential environmental hazards of ionic liquids, *Ecotoxicol. Environ. Saf.* 99 (2014) 1–12.

- [21] M. Rahman, D. Chamberlain, M. Balakrishna, J. Kipling, Performance of pore-lining impregnants in concrete protection by unidirectional salt-ponding test, *Transp. Res. Rec.* 2342 (2013) 17–25.
- [22] M.J. Al-Kheetan, M.M. Rahman, D.A. Chamberlain, A novel approach of introducing crystalline protection material and curing agent in fresh concrete for enhancing hydrophobicity, *Constr. Build. Mater.* 160 (2018) 644–652.
- [23] M.J. Al-Kheetan, M.M. Rahman, D.A. Chamberlain, Development of hydrophobic concrete by adding dual-crystalline admixture at mixing stage, *Struct. Concr.* 19 (5) (2018) 1504–1511.
- [24] M.M. Rahman, D.A. Chamberlain, Application of crystallising hydrophobic mineral and curing agent to fresh concrete, *Constr. Build. Mater.* 127 (2016) 945–949.
- [25] C. Nunes, Z. Slížková, Hydrophobic lime based mortars with linseed oil: characterization and durability assessment, *Cem. Concr. Res.* 61 (2014) 28–39.
- [26] A.T. Albayrak, M. Yasar, M.A. Gurkaynak, I. Gurgey, Investigation of the effects of fatty acids on the compressive strength of the concrete and the grindability of the cement, *Cem. Concr. Res.* 35 (2) (2005) 400–404.
- [27] J.T. Kevern, Using soybean oil to improve the durability of concrete pavements, *Int. J. Pavement Res. Technol.* 3 (5) (2010) 280–285.
- [28] F.H. Wittmann, R. Jiang, R. Wolfseher, T. Zhao, Application of natural products to make integral water repellent concrete, in: E. Borelli, V. Fassina (Eds.), *Proceedings Hydrophobe VI*, Aedificatio Publishers, 2011, pp. 117–124.
- [29] M.J. Al-Kheetan, M.M. Rahman, D.A. Chamberlain, Remediation and protection of masonry structures with crystallising moisture blocking treatment, *Int. J. Build. Pathol. Adapt.* 36 (1) (2018) 77–92.
- [30] M.J. Al-Kheetan, M.M. Rahman, D.A. Chamberlain, Influence of early water exposure on modified cementitious coating, *Constr. Build. Mater.* 141 (2017) 64–71.
- [31] P. Reiterman, J. Pazderka, Crystalline coating and its influence on the water transport in concrete, *Adv. Civ. Eng.* 2016 (2016) 1–8.
- [32] L. Ferrara, T. Van Mullem, M.C. Alonso, P. Antonaci, R.P. Borg, E. Cuenca, A. Jefferson, P.L. Ng, A. Peled, M. Roig-Flores, M. Sanchez, Experimental characterization of the self-healing capacity of cement based materials and its effects on the material performance: a state of the art report by COST Action SARCOS WG2, *Constr. Build. Mater.* 167 (2018) 115–142.
- [33] R.P. Borg, E. Cuenca, E.M. Gastaldo Brac, L. Ferrara, Crack sealing capacity in chloride-rich environments of mortars containing different cement substitutes and crystalline admixtures, *J. Sustain. Cem. Based Mater.* 7 (3) (2018) 141–159.
- [34] M. Li, V.C. Li, Cracking and healing of engineered cementitious composites under chloride environment, *ACI Mater. J.* 108 (3) (2011).
- [35] E. Cuenca, L. Ferrara, Self-healing capacity of fiber reinforced cementitious composites. State of the art and perspectives, *KSCCE J. Civ. Eng.* 21 (7) (2017) 2777–2789.
- [36] X. Li, L. Andruzzi, E. Chiellini, G. Galli, C.K. Ober, A. Hexemer, E.J. Kramer, D.A. Fischer, Semifluorinated aromatic side-group polystyrene-based block copolymers: bulk structure and surface orientation studies, *Macromolecules* 35 (21) (2002) 8078–8087.
- [37] R.F. Brady, Clean hulls without poisons: devising and testing nontoxic marine coatings, *J. Coat. Technol.* 72 (900) (2000) 45–56.
- [38] E. Passaglia, M. Aglietto, F. Ciardelli, B. Mendez, 13 C NMR characterization of polymers from 2, 2, 2-trifluoroethyl methacrylate, *Polym. J.* 26 (10) (1994) 1118.
- [39] T. Hayakawa, J. Wang, M. Xiang, X. Li, M. Ueda, C.K. Ober, J. Genzer, E. Sivaniah, E.J. Kramer, D.A. Fischer, Effect of changing molecular end groups on surface properties: Synthesis and characterization of poly (styrene-*b*-semifluorinated isoprene) block copolymers with—CF₂H end groups, *Macromolecules* 33 (21) (2000) 8012–8019.
- [40] A. Zaggia, G. Padoan, L. Conte, A. Morelli, Fluorinated poly (acrylates): influence of fluorinated chain length and hydrocarbon spacer on surface properties, *Chem. Eng. Trans.* 17 (2009) 1753–1758.
- [41] M.J. Al-Kheetan, M.M. Rahman, D.A. Chamberlain, Moisture evaluation of concrete pavement treated with hydrophobic surface impregnants, *Int. J. Pavement Eng.* (2019), <https://doi.org/10.1080/10298436.2019.1567917>.
- [42] C. Christodoulou, C.I. Goodier, S.A. Austin, G.K. Glass, J. Webb, Assessing the long-term durability of silanes on reinforced concrete structures, in: *Proceedings of the 1st International Congress on Durability of Concrete*, 2012, p. 14.
- [43] British Standards Institution, BS 1881-125:2013: Testing Concrete. Methods for Mixing and Sampling Fresh Concrete in the Laboratory, British Standards Institution, London, 2013.
- [44] British Standards Institution, BS 1881-208:1996: Testing Concrete Recommendations for the Determination of the Initial Surface Absorption of Concrete, British Standards Institution, London, 1996.
- [45] American Association of State Highway and Transportation Officials, AASHTO T 259 Resistance of Concrete to Chloride Ion Penetration, AASHTO, Washington, D.C., 2002.
- [46] M.M. Rahman, D.A. Chamberlain, Performance of crystalline hydrophobic in wet concrete protection, *J. Mater. Civ. Eng.* 29 (6) (2017).
- [47] British Standards Institution, BS 14629:2007: Products and systems for the protection and repair of concrete structures – Test methods – Determination of chloride content in hardened concrete, British Standards Institution, London, 2007.
- [48] A. Al-Otoom, A. Al-Khlaifa, A. Shawaqfeh, Crystallization technology for reducing water permeability into concrete, *Ind. Eng. Chem. Res.* 46 (16) (2007) 5463–5467.
- [49] S. Pawlenko, *Organosilicon Chemistry*, Walter de Gruyter Inc, Berlin, 2011.
- [50] E.W. Abel, F.G. Stone, G. Wilkinson, *Comprehensive Organometallic Chemistry II: A Review of the Literature 1982–1994*, Elsevier, 1995.
- [51] V.G. Cappellesso, N. dos Santos Petry, D.C.C. Dal Molin, A.B. Masuero, Use of crystalline waterproofing to reduce capillary porosity in concrete, *J. Build. Pathol. Rehabil.* 1 (9) (2016).
- [52] X. Xiao, Q.S. Zhang, X.Y. Liang, X.N. Zhang, Research on chloride ion diffusion of concrete water-based capillary crystalline water proofer and its penetration depth by using electron microscope, *Adv. Mater. Res.* 857 (2014) 27–34.
- [53] F. Qin, F. Yang, H. Liu, Waterproof measures for swimming pools: use of cement based permeable crystalline waterproof composite coatings, *Chem. Eng. Trans.* 59 (2017) 535–540.
- [54] M. Kumar, N.P. Singh, N.B. Singh, Effect of water proofing admixture on the hydration of Portland cement, *Indian J. Chem. Technol.* 16 (2009) 499–506.
- [55] R.N. Wenzel, Resistance of solid surfaces to wetting by water, *Ind. Eng. Chem.* 28 (8) (1936) 988–994.
- [56] W. Barthlott, C. Neinhuis, Purity of the sacred lotus, or escape from contamination in biological surfaces, *Planta* 202 (1) (1997) 1–8.
- [57] Y. Inoue, Y. Yoshimura, Y. Ikeda, A. Kohno, Ultra-hydrophobic fluorine polymer by Ar-ion bombardment, *Colloids Surf. B* 19 (3) (2000) 257–261.
- [58] L.W. Teng, R. Huang, J. Chen, A. Cheng, H.M. Hsu, A study of crystalline mechanism of penetration sealer materials, *Materials* 7 (1) (2014) 399–412.
- [59] F. Sandrolini, E. Franzoni, B. Pigino, Ethyl silicate for surface treatment of concrete—Part I: Pozzolanic effect of ethyl silicate, *Cem. Concr. Compos.* 34 (3) (2012) 306–312.
- [60] X. Pan, Z. Shi, C. Shi, T.C. Ling, N. Li, A review on concrete surface treatment Part I: types and mechanisms, *Constr. Build. Mater.* 132 (2017) 578–590.
- [61] S.H. Ghaffar, M. Fan, Structural analysis for lignin characteristics in biomass straw, *Biomass Bioenergy* 57 (2013) 264–279.
- [62] B. Hortling, T. Tamminen, E. Kenttä, Determination of carboxyl and non-conjugated carbonyl groups in dissolved and residual lignins by IR spectroscopy, *Holzforchung-Int. J. Biol. Chem. Phys. Technol. Wood* 51 (5) (1997) 405–410.
- [63] G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, John Wiley & Sons, 2004.
- [64] M. Gademann, D. Vollmar, R. Signorell, Infrared spectroscopy of acetic acid and formic acid aerosols: pure and compound acid/ice particles, *Phys. Chem. Chem. Phys.* 9 (32) (2007) 4535–4544.
- [65] C. Rey, V. Renugopalakrishnan, B. Collins, M.J. Glimcher, Fourier transform infrared spectroscopic study of the carbonate ions in bone mineral during aging, *Calcif. Tissue Int.* 49 (4) (1991) 251–258.
- [66] C. Iacovita, R. Stiuflu, T. Radu, A. Florea, G. Stiuflu, A. Dutu, S. Mican, R. Tetean, C.M. Lucaci, Polyethylene glycol-mediated synthesis of cubic iron oxide nanoparticles with high heating power, *Nanoscale Res. Lett.* 10 (1) (2015) 391.
- [67] M. Ibrahim, A. Nada, D.E. Kamal, Density functional theory and FTIR spectroscopic study of carboxyl group, *Indian J. Pure Appl. Phys.* 43 (2005) 911–917.
- [68] R. Chang, *Physical chemistry for the biosciences*, University Science Books, Sausalito, USA, 2005.
- [69] B.K. Sharma, *Objective Question Bank in Chemistry*, Krishna Prakashan Media, 1997.
- [70] F. Woodard, *Industrial Waste Treatment Handbook*, Elsevier, 2001.
- [71] J.G. Ferry, Methane from acetate, *J. Bacteriol.* 174 (17) (1992) 5489–5495.
- [72] L.E.M. Palomino, Z. Pászti, I.V. Aoki, H.G.D. Melo, Comparative investigation of the adhesion of Ce conversion layers and silane layers to a AA 2024–T3 substrate through mechanical and electrochemical tests, *Mater. Res.* 10 (4) (2007) 399–406.
- [73] P.B. Wagh, S.V. Ingale, S.C. Gupta, Comparison of hydrophobicity studies of silica aerogels using contact angle measurements with water drop method and adsorbed water content measurements made by Karl Fischer's titration method, *J. Sol-Gel Sci. Technol.* 55 (1) (2010) 73–78.
- [74] P.B. Wagh, R. Kumar, R.P. Patel, I.K. Singh, S.V. Ingale, S.C. Gupta, D.B. Mahadik, A.V. Rao, Hydrophobicity measurement studies of silica aerogels using FTIR spectroscopy, weight difference method, contact angle method and KF Titration Method, *J. Chem. Biol. Phys. Sci.* 5 (3) (2015) 2350.
- [75] A. Krishnan, R. Gettu, R. Dhamodharan, P.S. Nair, Exploratory use of a fluoropolymer to modify cement mortar for waterproofing, *Int. J. 3 R's* 4 (3) (2013) 595–601.
- [76] M. Pianca, E. Barchiesi, G. Esposto, S. Radice, End groups in fluoropolymers, *J. Fluorine Chem.* 95 (1–2) (1999) 71–84.
- [77] Y. Huang, W. Liu, X. Zhou, Silicone/silica nanocomposites as culture-stone protective materials, *J. Appl. Polym. Sci.* 125 (S1) (2012) E282–E291.
- [78] B. Pang, Y. Zhang, G. Liu, W. She, Interface properties of nanosilica-modified waterborne epoxy cement repairing system, *ACS Appl. Mater. Interfaces* 10 (2018) 21696–21711.
- [79] R.S. Woo, H. Zhu, M.M. Chow, C.K. Leung, J.K. Kim, Barrier performance of silane-clay nanocomposite coatings on concrete structure, *Compos. Sci. Technol.* 68 (14) (2008) 2828–2836.

- [80] L. Schueremans, D. Van Gemert, S. Giessler, Chloride penetration in RC-structures in marine environment—long term assessment of a preventive hydrophobic treatment, *Constr. Build. Mater.* 21 (6) (2007) 1238–1249.
- [81] R.D. Chambers, *Fluorine in Organic Chemistry*, CRC Press, 2004.
- [82] A. Costa, J. Appleton, Chloride penetration into concrete in marine environment—Part I: main parameters affecting chloride penetration, *Mater. Struct.* 32 (4) (1999) 252–259.
- [83] J.P. Broomfield, *Corrosion of Steel in Concrete: Understanding, Investigation and Repair*, CRC Press, 2006.
- [84] M.K. Moradillo, B. Sudbrink, M.T. Ley, Determining the effective service life of silane treatments in concrete bridge decks, *Constr. Build. Mater.* 116 (2016) 121–127.
- [85] H. Hilsdorf, J. Kropp, *Performance Criteria for Concrete Durability*, CRC Press, 2014.