Resistance of hydrophobic concrete with different moisture contents to advanced freeze–thaw cycles

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Abstract
This article is aimed at investigating the long-term performance of three original hydrophobic materials, namely, sodium acetate, fluoropolymer, and silicone resin. Their performance was compared with traditional silane when applied to fully dry concrete, fully saturated concrete, and concrete with 2 and 4% moisture content. A recently developed freeze–thaw process, which is based on temperature and humidity variations, was employed in this study to assess the durability of applied materials. The outcomes of the adopted freeze–thaw system were compared with the results obtained from running a conventional freeze–thaw test. Mass change, water absorption, and micro-cracks development of treated concrete were investigated and compared with untreated concrete after completing 6 months of freeze–thaw cycles. Results confirmed the high affinity of the proposed materials to moisture at application time compared with silane. Additionally, it was demonstrated that moisture content has a critical impact on the bonding between applied materials and concrete, hence their efficacy in enhancing the durability of concrete.

KEYWORDS
adhesion, concrete, freeze–thaw, hydrophobic treatment, moisture content

1 INTRODUCTION
Extending the service life of concrete structures has been a great concern for researchers and industry administrators in the whole world.1–3 In recent years, many research attempts were made to enhance the durability of concrete by either altering its composition or by using different types of additives and admixtures.4–9 Accordingly, hydrophobic materials were used as surface impregnates to control the deterioration of concrete caused by the ingress of water and aggressive chemicals.3,10–17 Silane and siloxane were the most commonly employed hydrophobic materials in this respect owing to their strong tolerance to various environmental effects and chemical attacks.18–24 The effectiveness of these types of materials depends primarily on the extent of penetration that they can achieve.23 More penetration depth inside the pores will result in better protection.13,24 However, some uncertainties regarding their performance, durability, and impact on the environment were raised by some recent research.22,25,26 The failure of such materials to protect wet concrete surfaces and the inclusion of some certain organic solvents in their chemical structure, which adversely affects the environment, prompted researchers to aim into some alternative water-tolerant and environmentally sustainable products.14,16,27,28

Discussion on this paper must be submitted within two months of the print publication. The discussion will then be published in print, along with the authors’ closure, if any, approximately nine months after the print publication.
Researchers, therefore, have expanded their research to include some new materials that are environmentally sustainable and have the ability to function well in the presence of water. Sodium acetate, fluoropolymer, and silicone resin were among these materials that offered an environmentally friendly alternatives to silane and siloxane with optimum protection when applied to wet surfaces.22,26

The performance of sodium acetate, fluoropolymer, and silicone resin was thoroughly investigated against the impact of chloride diffusion and water absorption through concrete.13,16,22,24,26,29 However, the study of current research and literature suggests that, to the best knowledge of authors, no experimental investigations for the long-term performance of such surface applied materials were conducted. Additionally, the impact of moisture content on the effectiveness of applied materials has not been addressed. Accordingly, it is important to test the performance of these materials under harsh environmental conditions, mechanical stresses, and cyclic freezing and thawing that would expedite the deterioration of concrete.3,30 Repeated freezing and thawing processes may create a high pore pressure correlated with a shift in the water level within the pores, which contributes to cracking inside concrete.5,31 It is therefore necessary to safe-guard concrete from both weathering and chemical attacks in order to maintain its serviceability and increase its durability.32,33

In this study, the long-term performance of four protective materials was evaluated to determine their efficacy when added to concrete with various moisture contents. These materials are fluoropolymer, silicone resin, sodium acetate, and solvent-based silane. Moreover, two freeze–thaw mechanisms were used to assess the performance of these materials under harsh conditions. The first system, concrete was subjected to quick freezing and thawing cycles under water. This technique was commonly used in previous studies; however, with a smaller number of cycles than it is used in this research.30,34–36 A new mechanism is proposed in the second freeze–thaw method, where concrete is only in exposure to air and under the impact of temperature change.—CF3 group that line the concrete’s pores and gives them the ability to repel water.26 A similar function is achieved when using silicone resin, where a hydrophobic effect would result from applying it to concrete. Moreover, the used sodium acetate compound when added to the surface of concrete works on the absorption of water that exists in the pores to form crystals. These crystals will cover the pores and work on repelling any further absorbed water.26 The solvent based silane was also applied to the surface of concrete and it was used as a reference to compare its performance with the other used protective materials. The used concrete mix (given in Table 1) was produced following the British standard BS 1881–125.37

A total of 102 concrete cubes with the size of 100 mm × 100 mm × 100 mm were cast to serve the testing methodology of this research. They were all cured in a water bath for 28 days at a temperature of 21°C. Subsequently, they were all dried in an oven at a temperature of 105°C to drive off all the moisture from the pores.38 A total of 96 cubes out of 102 were preconditioned with different moisture contents before treatment; full drying, full saturation, 2 and 4% moisture contents. After the preconditioning process, concrete was treated with sodium acetate, fluoropolymer, silicone resin and silane. Six cubes out of 102 cubes were used as control/reference for comparison reasons. Moreover, 48 cubes were assigned to serve the purpose of each freeze–thaw test.

### 2.2 Test methods

#### 2.2.1 Exposure to freeze–thaw cycles

Concrete was exposed to two different freeze–thaw methods. In the first method, concrete samples were placed in Weiss–Voetsch Environmental Testing Chamber C340 while they were immersed in water following the instructions of GB/T 50082–2009.39 The temperature was adjusted to vary between −10 and 6°C for 4 hr,

<table>
<thead>
<tr>
<th>TABLE 1 Concrete mix design</th>
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</thead>
<tbody>
<tr>
<td>Component</td>
</tr>
<tr>
<td>Cement (CEM II/32.5 N; sulphates &lt;3.5%, chlorides &lt;0.10%, and initial setting time around 1.25 hr)</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Fine aggregate (sharp silica sand, uniform grain size distribution between 1 mm and 300 μm)</td>
</tr>
<tr>
<td>Coarse aggregate (crushed stones with sharp edges and maximum size of 20 mm)</td>
</tr>
<tr>
<td>Total</td>
</tr>
<tr>
<td>Water/cement ratio</td>
</tr>
</tbody>
</table>
reflecting a fast freeze–thaw process, and to conform with the average temperature in winter seasons of London Boroughs. This test was carried out for a total period of 6 months with 1,080 freeze–thaw cycles. Upon completion of 1,080 cycles, the mass of all samples was examined to determine the change in their masses before and after the exposure to freeze–thaw.

Throughout the newly developed freeze–thaw method, an environmental chamber was built to regulate humidity and temperature. The chamber was designed by utilizing an original commercial freezer as the source for the freezing cycles and by adding heating and ventilation systems within the freezer to support the thawing cycles. In addition, heat and humidity control systems are further designed to satisfy the criteria for software-controlled scheduling of 24-hr cycles between −20 and 20°C temperatures and 60% steady humidity. Samples were put within the chamber that was set to operate for 6 consecutive months with 180 freeze–thaw cycles. Upon completion of the freeze–thaw testing, the difference in mass of concrete samples in respect to their initial mass prior to freeze–thaw cycles was recorded. Figure 1a,b shows the change in temperature throughout the operation of the standard rapid freeze–thaw test (in water) and the recently developed air freeze–thaw method.3

2.2.2 | Crack propagation detection

The formation of cracks and their significance after the completion of the freeze–thaw tests were observed by using the XUE Electronic Optical Microscope.

2.2.3 | Water absorption

The efficacy of the materials to protect concrete from water penetration in severe conditions was tested by operating the ISAT experiment on the damaged samples (after completing the freeze–thaw cycles). Initial surface absorption test (ISAT) was employed to assess the water uptake through concrete by adopting the instructions of BS 1881–208.38

3 | RESULTS AND DISCUSSION

3.1 | Mass change during freeze–thaw

3.1.1 | Fast freeze–thaw cycles

After the end of the 1,080 freeze–thaw cycles in water, the change in the masses of all concrete samples was measured to evaluate the deterioration rate in concrete. Figure 2 shows the percentage of mass reduction in all preconditioned concrete after the 1,080 cycles.

The impact of the water freeze–thaw cycles was severe on all treated and untreated concrete samples regardless of their moisture content before treatment. However, the mass loss in control samples was the highest during the whole 6 months. When applying silane to the surface of dry concrete (Figure 2a), minimum damage was exhibited compared to other treatments with a maximum loss in mass of 4%. Referring to previous results published by the authors of this study,26 the rejection rate of dry concrete to silane was noticed to be minimal at the time of application, which allows silane to penetrate deeper in the pores and strengthen the pore structure. The formation of the silane’s active content, silanol group, needs a very low moisture content or no moisture to be activated and then create a strong link with the pores. This might explain the high
resistance of silane to deterioration when applied to dry concrete.

Increasing the moisture content of concrete before the application of silane is noticed to decrease the efficacy of silane in protecting concrete against deterioration through the freeze–thaw cycles (Figure 2a-d). When silane was applied to fully saturated concrete, the mass loss in concrete was maximum and close to control, which refers to the absence of the active content in the pores. The presence of alkoxy groups in silane, which provide it with its hydrophobic nature, are expected to react with the silicates in the pores 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.40

Sodium acetate has managed to provide a high level of protection when applied to concrete with high moisture contents. The loss in the concrete’s mass was less than 4% when the material was applied to concrete with 2 and 4% moisture contents and when it was applied to fully saturated concrete. However, the mass loss reached more than 5% when sodium acetate was applied to fully dry concrete. This might refer to the need of its main component, sodium acetate, to a certain amount of water to form its active crystals.3,26

Both fluoropolymer and silicone resin materials have followed similar trend at all saturation levels with an average performance between sodium acetate and silane. However, deterioration in concrete treated with fluoropolymer was less in case of applying the material to dry concrete. This refers to the low surface energy of the fluorinated side chain of fluoropolymer, which reduces its adhesion to applied surfaces in the presence of water.26,41–44 On the other hand, silicone resin when applied to fully saturated concrete showed better

**FIGURE 2** The influence of 1,080 freeze–thaw cycles in water on the mass reduction of preconditioned concrete: (a) Fully dry, (b) 2% moisture content, (c) 4% moisture content, and (d) fully saturated
performance than fluoropolymer due to its interaction mechanism with concrete that depends on the presence of moisture to adhere strongly to the pores.26

### 3.1.2 Air freeze–thaw cycles

The deterioration rate of concrete after its exposure to cyclic air freeze–thaw was less than that when exposed to water freeze–thaw. Figure 3 shows the mass increase in concrete after 180 cycles of air freeze–thaw.

It is witnessed that the increase in the mass of all treated samples was minimal when compared to control with a maximum weight gain of 0.5% in the case of fully saturated concrete treated with silane. Other materials have shown similar performance to each other with very slight difference, even with changing the preapplication moisture content. The impact of the air freeze–thaw test on samples is much less than the water freeze–thaw test, which is reflected on the deterioration rate of concrete. The slow temperature variation of surrounding air, during the whole testing period, would have less impact on concrete than the fast temperature variation of surrounding water and water that already exists in the pores. Comparing treated concrete with control shows that the temperature alteration was much severe on control than treated concrete, which reflects the efficacy of protection during the freeze–thaw action. Even when the rejection rate of concrete to protective materials is very high, the remaining amount of material has managed to resist the impact of this type of freeze–thaw cycles.26 For instance, despite the waste of more than 40% of silane when applied to saturated concrete, the material has succeeded to reduce the damage that was induced by temperature alteration.

**FIGURE 3** The impact of air freeze–thaw on the mass change of concrete preconditioned with: (a) Full drying, (b) 2% moisture content, (c) 4% moisture content, and (d) full saturation
<table>
<thead>
<tr>
<th>Protective material</th>
<th>Saturation level prior to application</th>
<th>2%</th>
<th>4%</th>
<th>Fully saturated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium acetate</td>
<td>Fully dry</td>
<td>0.04 mm</td>
<td>0.01 mm</td>
<td>0.02 mm</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>1 mm</td>
<td>1 mm</td>
<td>1 mm</td>
</tr>
<tr>
<td>Fluoropolymer</td>
<td>2%</td>
<td>0.01 mm</td>
<td>0.01 mm</td>
<td>0.05 mm</td>
</tr>
<tr>
<td></td>
<td>4%</td>
<td>1 mm</td>
<td>1 mm</td>
<td>1 mm</td>
</tr>
<tr>
<td>Silicone resin</td>
<td>4%</td>
<td>0.02 mm</td>
<td>0.02 mm</td>
<td>0.01 mm</td>
</tr>
<tr>
<td></td>
<td>Fully saturated</td>
<td>1 mm</td>
<td>1 mm</td>
<td>1 mm</td>
</tr>
<tr>
<td>Silane</td>
<td>Fully saturated</td>
<td>0.01 mm</td>
<td>0.01 mm</td>
<td>0.10 mm</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>1 mm</td>
<td>1 mm</td>
<td>1 mm</td>
</tr>
</tbody>
</table>
3.2 Crack propagation

Some microcracks have developed at the end of the air freeze–thaw test, without showing any scaling on the surface of concrete. Table 2 shows the effect of the air freeze–thaw cycles on all concrete samples.

It was evident from the results in Table 2 that some microcracks have developed on the surface of deteriorated concrete (after finishing the freeze–thaw test). All the developed cracks in treated concrete appear to have small sizes when compared to their control, as the surface applied materials have contributed in protecting concrete from severe cracking. However, a difference in crack propagation is noticed with different materials and different preapplication conditions. For instance, applying silane to fully saturated concrete allowed the propagation of large cracks (0.10 mm), in contrast to other protective materials with different preapplication conditions. This refers to the deficiency of silane to work effectively when applied to wet surfaces due to the high refusal rate of wet surfaces to silane.26 On the other hand, some fine cracks (0.04 mm) have developed when the sodium acetate was applied to fully dry surfaces. This could be caused by the absence of water that is necessary for the development of the active crystals.26

3.3 Water absorption

After the completion of 1,080 water freeze–thaw cycles, concrete cubes were tested for water absorption by using ISAT to assess the ability of surface applied treatments on protecting deteriorated concrete from water ingress under harsh environments. Figure 4 shows the water absorption rate of preconditioned concrete after the impact of water freeze–thaw cycles.

A clear increase in the water absorption rate is noticed after the exposure to water freeze–thaw cycles. Applying the materials to fully dry surfaces has shown different levels of protection depending on the properties of the applied material. Silane has managed to present the highest protection rate for concrete against water absorption after the impact of freeze–thaw, when applied to dry concrete. When silane applied to dry surfaces, alkoxy groups that are bonded with silicone atoms in silane will react with the silicate, which already exists in concrete, and adhere strongly in the pores.26 Despite the scaling effect of this freeze–thaw test, silane managed to provide a good protection to concrete, as treatment increased the protection by more than 88% when compared to untreated concrete. This proves the high penetration depth of silane when applied to dry surfaces. On the other hand, increasing the moisture content of...
concrete over 2% before the application of silane, has shown a high deficiency in the protection level, where water absorption has increased significantly. When silane was applied to fully saturated concrete, the protection level was noticed to reach its minimum since the bonding between silane and concrete will be difficult to be achieved in the presence of water. Adding to that, the penetration depth of silane will be less if it was applied on saturated concrete; after scaling takes place, silane will be less effective in protecting concrete since it only presents near the surface.

Due to the high affinity of sodium acetate to water, its application on saturated concrete or even partially saturated concrete (2 and 4% moisture content), has managed to significantly decrease the water absorption of deteriorated concrete, and provide high level of protection when compared with the other materials and control. The formed crystals of sodium acetate work on absorbing the already existing moisture to form hydrogen bonds with concrete and link properly in the pores. However, the absence of moisture from the fully dry concrete will cease the formation of such bonds and works on reducing the efficacy of sodium acetate when applied to fully dry surfaces.

Silicone resin needs some moisture inside the pores to adhere properly to concrete. This could be noticed in Figure 4 as silicone resin has achieved better performance than silane and untreated concrete with increasing the moisture content above 2%. The presence of silicone resin inside the pores worked on enhancing the strength of the pores and decreased crack formation due to the expansion of water inside the pores.

Concrete treated with fluoropolymer has shown a convergent performance to silicone resin when applied to different saturation levels, but with a slight better performance when applied to dry surfaces. The low surface energy of the fluorinated side chain of fluoropolymer works on reducing the adhesion of the material to concrete in the presence of moisture.

![Figure 4](image-url)
The impact of 180 air freeze–thaw cycles on the efficacy of surface applied materials in reducing water absorption is shown in Figure 5. Water absorption rates of concrete exposed to this test are showing similar trend to those under the impact of water freeze–thaw test. However, the amount of water absorbed after the exposure to this test is less than that in the water freeze–thaw test.

The results clearly demonstrate that the alteration in the air temperature has accelerated the water absorption rate in concrete. The formation of some microcracks in treated and untreated concrete, as shown in Table 2, has participated in increasing the water absorption rate despite the presence of protection within the concrete texture. However, the application of the protective materials has managed to reduce the deterioration rate of concrete. This is seen in Figure 5 when comparing the water absorption of treated concrete with control (untreated concrete).

The highest water absorption rate was recognized in concrete preconditioned with full saturation prior to the application of protective materials. This could be linked with the rejection rate of the applied materials proved by Al-Kheetan et al. 2019,26 where less active content of the materials will be available in concrete after their application to fully saturated concrete. Additionally, the long-term temperature alteration has contributed in weakening the adhesion of the protective materials to concrete, causing the applied materials to break down especially on the surface. However, sodium acetate has demonstrated the highest resistance to deterioration, when applied to fully saturated concrete, with the least water absorption rate among all other treated concrete. Sodium acetate has the least rejection rate between all applied materials,26 which increases the presence of its active content compared to other materials. On the other hand, concrete treated with silane absorbed the highest amount of water since its interaction mechanism with concrete

**FIGURE 5** The effect of air freeze–thaw cycles on the water absorption of concrete treated and preconditioned with: (a) Full drying, (b) 2% moisture content, (c) 4% moisture content, and (d) full saturation
depends mainly on the absence of water at the time of application or the presence of very small amount of water.

Concrete treated with silicone resin showed a modest protection against water absorption when applied to fully saturated surfaces but better than fluoropolymer and silane. The presence of more than 70% of the active content of silicone resin in concrete, as demonstrated by Al-Kheetan et al. 2019, contributed in increasing the de

Fluoropolymer has provided good protection to concrete during the freeze–thaw impact. However, this protection decreased with increasing the moisture content prior to its application to concrete. Still, fluoropolymer has offered better protection than silane when applied to surfaces with moisture contents higher than 2%.

4 CONCLUSIONS

The durability of four surface applied materials when applied to concrete with different moisture contents was evaluated by exposing concrete to harsh environmental impacts. Two sources of harsh conditions were utilized in this research; freeze–thaw under the effect of air temperature alteration and freeze–thaw under the effect of water temperature alteration. Both conditions showed different impact on concrete with different severity. The impact of the water freeze–thaw cycles was more severe on concrete than the air freeze–thaw cycles.

Sodium acetate, fluoropolymer, silicone resin, and silane were applied to concrete with four different moisture contents: Fully dry concrete, 2% moisture content, 4% moisture content, and fully saturated concrete. The damage induced by the two freeze–thaw tests on concrete was assessed by measuring the change in the concrete masses, and the change that appears on the surface of concrete. In the case of water freeze–thaw test, scaling was observed in all treated and untreated concrete. However, in the case of air freeze–thaw test, scaling was absent and some microcracks have been developed on the surface of concrete but with different sizes depending on the used protective material and the moisture content prior to treatment. Moreover, water absorption of deteriorated concrete was assessed as well to determine the level of protection provided by the applied materials.

Sodium acetate has provided concrete with the highest level of protection when applied to saturated concrete. However, its performance when applied to dry concrete was less than other applied materials like silane. This refers to its interaction mechanism with concrete that depends on the presence of moisture at the time of application. On the other hand, silane showed the best performance when applied to dry surfaces, and the level of its protection started to degrade with increasing the moisture content of concrete prior to application.

Due to the need of silicone resin for moisture to form its linkage with concrete, it has shown good performance when applied to concrete with moisture content equal or higher to 2%. In contrast to silicone resin, fluoropolymer has shown the highest efficacy when applied to dry surfaces. However, it had higher affinity to water than silane.

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DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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