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Comprehensive review on hydrophobic modification of concrete: Progress and perspectives

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Abstract:
The inherent nature of concrete is porous, hydrophilic, and microcracked, making it susceptible to water penetration into its matrix. This is the primary source of durability concerns. Furthermore, this type of penetration leads to considerable issues for concrete structures, resulting in significant financial burdens due to regular repairs and maintenance and a reduction in the structure's lifespan. In this study, the properties, uses, and advancements of hydrophobic concrete are investigated, focusing on durability, corrosion resistance, and sustainability. The various types and techniques for producing hydrophobic concrete are explored. Additionally, the paper presents the impacts of hydrophobic treatment on concrete properties such as compressive strength, water absorption, and permeability. Potential applications of hydrophobic concrete, including use in bridges, tunnels, and marine structures, are also discussed. The review concludes by examining the benefits, challenges and limitations of hydrophobic concrete technology, including aspects like cost-effectiveness, compatibility with other construction materials, and potential environmental repercussions. In summary, this review highlights the potential of hydrophobic concrete to transform the construction industry by offering enduring and sustainable solutions to water-related issues.

Keywords:
cement; concrete; permeability; durability; waterproof; hydrophobic

1 Introduction

The longevity and functionality of building materials are pivotal for sustainable construction practices, especially to mitigate the environmental and economic consequences of frequent replacements, maintenance, and repairs [1]. Water penetration into the concrete matrix, due to its porous structure and hydrophilic properties [2], underpins major physical and chemical deterioration processes in concrete structures, leading to durability issues. Water ingress allows the entry of corrosive ions into the concrete matrix [3]. For instance, in marine environments, water facilitates salt penetration into the concrete causing significant damage to rebars and leading to a reaction between the ions in the salts and cement paste. This, in turn, further deteriorates the material. De-icing salt used in freezing conditions behaves in a similar manner. Corrosion products, with a higher volume than the original reinforcement, induce stress in the concrete, which results in radiating cracks around rebars, significantly reducing the matrix's durability and strength [4].

Water ingress in cold regions can also trigger freezing and thawing, inducing internal stresses due to ice formation within the concrete pores. This can introduce new cracks and cause existing microcracks in the concrete matrix to expand with each cycle, leading to significant damage [5]. Water permeation also presents the issue of carbonation, involving the absorption of CO2 and other harmful pollutants from the atmosphere. The absorbed CO2 reduces the pH of the pore solution in the matrix, which creates acidic conditions around the steel rebars, leading to corrosion [6].

Therefore, preventing or reducing water penetration into concrete appears to be the primary strategy for addressing durability issues in concrete structures, resulting in more robust concrete with an extended service life [7]. Various methods are available for this waterproofing, with hydrophobically modified concrete gaining increasing popularity [8].

This study aims to review the hydrophobic modification of mortar and concrete, addressing two types of treatments to render concrete waterproof and hydrophobic. It reviews different methodologies for inducing hydrophobicity in concrete, the applications of hydrophobic concrete, and the properties of concrete influenced by hydrophobic modification. This encompasses properties in the rheological or fresh state, such as setting times and workability; mechanical attributes like flexural and compressive strength; and durability properties including corrosion resistance, water permeability, sorptivity, freeze-thaw resistance, and carbonation resistance. It also covers microstructural characteristics impacted by hydrophobic modification, all of which will be discussed in the following sections.

2 Overview of hydrophobic modification of concrete

2.1 Durability of concrete and inspiration from biomimetics

In general, a variety of treatments have been employed to address durability issues in concrete. This is done by reducing the concrete's permeability in the following ways:

- reducing the water–cement ratio,
- making use of water-reducing admixtures or plasticizers,
- using pozzolans and other additives that act as fillers,
- crystalline pore-blocking admixtures,
- providing hydrophobic treatment to concrete.

While the initial four methods mentioned contribute to enhanced concrete durability, the issue of water permeation persists due to the hydrophilic nature of the concrete material. Consequently, the concept of hydrophobicity has been explored, which renders the concrete surfaces water-repellent, thereby mitigating effects related to water permeation into the matrix. The idea of hydrophobic surfaces originates in nature [9]. The hydrophobicity and self-cleaning mechanisms observed in various plants, including lotus leaves, aloe vera leaves, rose leaves, and petals, are referred to as the "Lotus Effect" [10, 11], as illustrated in Figure 1. These leaves, besides possessing a wax-like coating, also display micro- and nanoscale roughness, leading to a self-cleaning effect in addition to hydrophobicity [12]. When water falls on such leaves, it forms a round droplet that easily rolls off, taking with it any dirt or dust particles on the leaf surface. Other examples of hydrophobic surfaces in nature include butterfly wings and water strider legs [13, 14]. These natural surfaces have served as inspiration for the design of new, more durable concretes, an approach referred to as “biomimetics”, meaning to mimic biology [15, 16]. Biomimetics holds vast potential for transforming the infrastructure industry by offering solutions previously unattainable with conventional techniques.

Figure 1. Rose leaves and aloe vera leaves exhibiting hydrophobicity [17]

2.2 Fabrication of hydrophobic concrete

Concrete can be rendered hydrophobic using two primary methods: surface treatment and integral/bulk/volume hydrophobic modification (Figure 2).

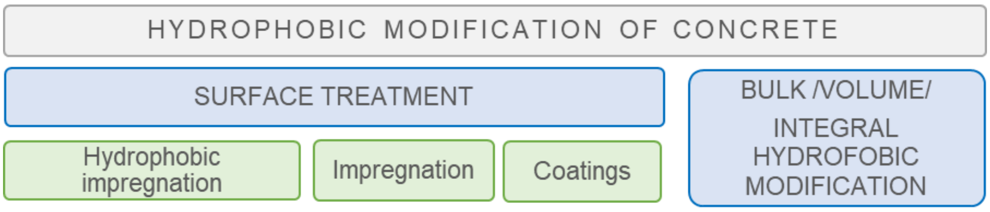


Figure 2. Methods to induce hydrophobicity in concrete

In surface treatment, the hydrophobic characteristic is primarily present on or near the concrete surface, while the bulk of the concrete remains hydrophilic. This approach has little to no impact on the mechanical properties of the concrete. However, a significant drawback of coatings is that they create an impervious barrier on the concrete surface, trapping moisture inside. This can lead to continuous degradation of the protective surface layer due to vapor formation, causing internal vapor pressure. Furthermore, the water-repellent property might be susceptible to the sun's UV rays, and if the sample's surface is damaged or wears off, the newly exposed internal concrete surface remains hydrophilic. Therefore, protection is ensured as long as the specimen's surface remains undamaged and the coating stays intact [18].

The surface treatment methods can be further classified into three sub-categories (as shown in Figure 3) as follows:

a) Hydrophobic impregnation: The pores near the concrete surface are lined with a thin layer of hydrophobic agents, making the near-surface pores hydrophobic. Silanes and siloxanes are the most commonly used surface impregnating agents.
b) Impregnation: The impregnation product is deposited in the pores near the surface, which partially or totally fills the pores in an attempt to make them less permeable.

c) Coatings: This involves the development of a continuous layer over the surface that acts as a sealant. Silanes/siloxanes or a combination of both are generally used for coating concrete surfaces [19].

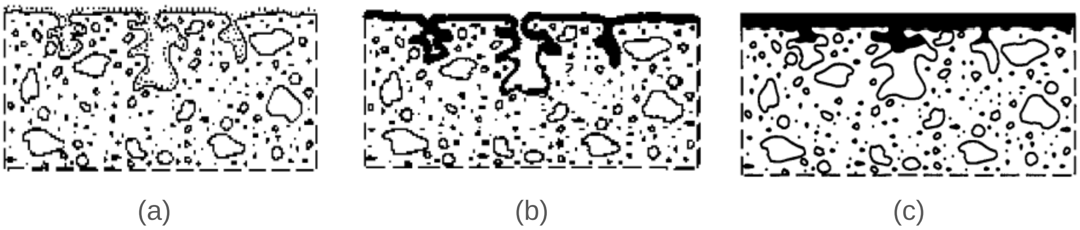

(a) (b) (c)

Figure 3. Illustration of the three types of hydrophobic surface treatments: (a) hydrophobic impregnation; (b) impregnation; (c) coating [20]

In integral hydrophobic treatment, a hydrophobic admixture is introduced to the concrete while it is still fresh during the mixing process. This results in the entire concrete matrix exhibiting bulk hydrophobicity. The advantage of this method is its resistance to peeling or surface damage. Specifically, it does not require regular maintenance, and even after fractures, cracks, or surface damage occur, the exposed internal surface remains hydrophobic. The downside to this technique is that, in most instances of integral hydrophobation, a noticeable reduction in mechanical strength occurs. This limitation may restrict the use of this type of concrete for non-structural applications [21-23].

2.3 Surface classification according to Water Contact Angle (WCA) values

Based on the values of Water Contact Angle (WCA), Sliding Angle (SA), and Contact Angle Hysteresis (CAH), surfaces are classified into superhydrophilic, hydrophilic, hydrophobic, overhydrophobic, and superhydrophobic, as listed in Table 1.

Table 1. Classification of surfaces based on water contact angles [12, 24, 25]

S.No.	Type of surface	Water Contact Angle (WCA)	Sliding Angle (SA)
1.	Superhydrophilic	WCA < 10˚	-
2.	Hydrophilic	10˚< WCA <90˚	-
3.	Hydrophobic	90˚< WCA <120˚	-
4.	Overhydrophobic	120˚< WCA <150˚	-
5.	Superhydrophobic	WCA > 150˚	SA < 10˚

Superhydrophobic surfaces are characterised by hierarchical roughness over their surfaces, and these surfaces mimic the lotus leaf which is known for its self-cleaning properties and hydrophobicity [14, 26, 27]. This type of surface exhibits a very high water contact angle, a very low roll-off angle, low contact angle hysteresis, and low surface energy [14, 28]. To synthesise hydrophobic surfaces, two essential conditions are required:

a) To cause a reduction in the surface energy of the surface by using compounds, such as silanes, siloxanes, and polymers, which aid in lowering the surface energy [12].
b) To induce hierarchical roughness on the surface, i.e., nanoscale irregularities are imposed onto the microscale pillars, leading to a composite interface with air trapped in the pillar pockets (Figure 4), clearly indicating maximum wetting on a flat surface and minimum wetting on the hierarchical structured surface.

The CAH was found to be the lowest for hierarchical structures, a necessary condition for rendering a surface superhydrophobic [29]. Nanomaterials employed to construct these hierarchical structures are predominantly filler materials, including nanosilica, nano-sized silica fume, rice husk ash particles, fibres, and metakaolin [30]. These materials can be applied either directly to the surface or integrated into the concrete during the mixing process.

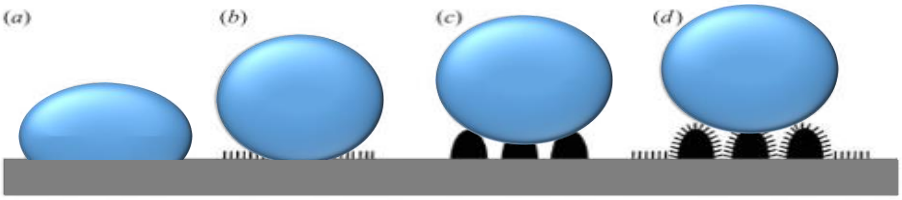


Figure 4. Schematic of wetting for different types of surfaces: a) flat surface, b) nano-structured surface, c) micro-structured surface, d) hierarchical-structured surface [29]

2.4 Wettability theories and Young's equation

2.4.1 Young's equation

Thomas Young is recognised for developing the concept of surface tension and contact angles as a measure of a surface's wetting capacity [31]. According to Young's theory, when a liquid droplet rests on a solid surface, three interfaces are created due to interfacial tension forces. These interfaces correspond to liquid-vapor (γ_{lv}), solid-liquid (γ_{sl}), and solid-vapor (γ_{sv}) interfaces, as depicted in Figure 5. When in equilibrium, all three interfacial tension forces balance out at a line known as the three-phase contact line. This equilibrium can be expressed using the following equation:

$$\gamma_{\mathrm{sl}} + \gamma_{\mathrm{lv}} cos\theta_y = \gamma_{sv} \tag{1}$$

where θ_y denotes the apparent contact angle.

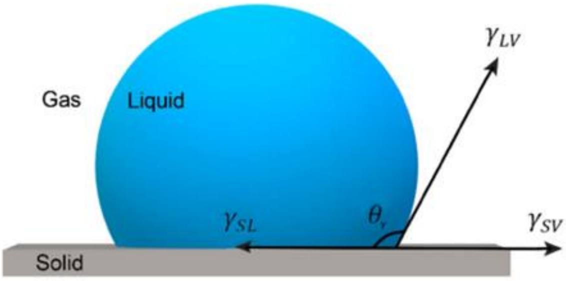


Figure 5. Contact angle and interfacial tension forces for a liquid droplet resting on a solid surface [32]

According to Young's equation, if the surface tension at the solid–liquid interface exceeds that at the solid–vapor interface, a hydrophobic state (>90°) will emerge. This necessitates lower solid surface energy, resulting in weaker liquid adhesion to the solid surface. The intrinsic contact angle, a property inherent to the material, can be calculated using Young's equation. However, this does not consider the influence of CAH or surface roughness on the contact angle.

2.4.2 Wenzel model

Wenzel [33] introduced a wetting theory that incorporates the surface roughness parameter in contact angle measurements. Surface roughness is a crucial factor in achieving superhydrophobic states on substrates. Wenzel theorised that for a substrate to reach a Wenzel wetting state, also known as "the homogeneous wetting state" (as depicted in Figure

6 (a)), a liquid droplet must penetrate surface protrusions and contact the entire rough surface. Consequently, the Wenzel equation is expressed as follows:

$$\gamma_{sl} \cdot r + \gamma_{lv} cos\theta_{w} = \gamma_{sv} \cdot r \tag{2}$$

where θ_w denotes the apparent Wenzel contact angle and r denotes the roughness factor which represents the effect of surface roughness on the wetting parameters.

The Wenzel Equation implies that surface roughness increases the hydrophobicity of a material by increasing its contact angle.

2.4.3 Cassie–Baxter model

The Cassie–Baxter model posits that a water droplet is not in complete contact with the surface and has air trapped beneath it in pockets of the pillars where the droplet rests [34] (as depicted in Fig. 6 (b)). This model draws inspiration from superhydrophobic surfaces found in nature, such as the self-cleaning effect observed on lotus leaves, where water droplets easily slide off the surface [35]. To exhibit the Cassie–Baxter state, the interfacial surface tension force balance equation can be expressed as follows:

$$\gamma_{sl} \cdot \varphi_s + (1 - \varphi_s) \cdot \gamma_{lv} + \gamma_{lv} cos\theta_{cb} = \gamma_{sv} \cdot \varphi_s \tag{3}$$

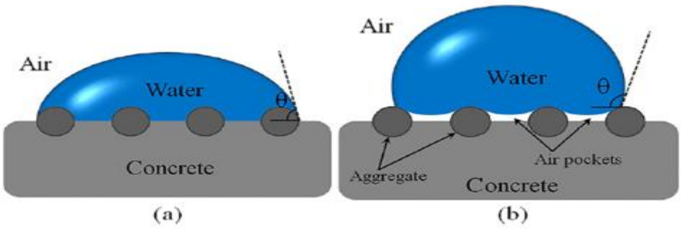


Figure 6. Water droplets on rough surfaces: a) Wenzel model, and b) Cassie Baxter model [36]

2.5 Applications of hydrophobic concrete

Hydrophobic and superhydrophobic cementitious composites have various applications:

- The anti-icing properties of hydrophobic concrete contribute to preventing hazardous conditions on roads and runways due to ice formation.
- It also aids in preventing the concrete from cracking and spalling due to freeze–thaw cycles.
- The self-cleaning property of these surfaces leads to reduced maintenance costs for structures [37].
- It can improve the service life and durability of key infrastructure elements, such as dams, bridges, reservoirs, water and effluent treatment plants, tunnels, and foundations, which are subjected to aggressive environments, and thereby shielded from premature deterioration.
- Hydrophobic mortars and cement pastes have applications in architectural heritage restoration and provide higher durability to such structures.
- In marine areas, reinforced concrete is at risk from corrosion induced by chloride carried into concrete pores by water. Hydrophobic modification has proven an effective method for protecting new and existing structures exposed to such conditions [38].

3 Literature review: hydrophobic concrete/mortar

3.1 Surface Treatment Approach

Surface treatment for the hydrophobic modification of concrete can be accomplished through coatings or impregnations, as previously discussed. These coatings consist of surface-energy-reducing admixtures that can be applied with or without the inclusion of nanoparticles to further enhance hydrophobicity.

Evaluations of hydrophobic coatings applied to concrete specimens revealed that a sealer composed of silane/siloxane produced the most effective results, notably slowing the rate of reinforcement corrosion when compared to sodium silicate and silicon resin solutions [39].

In another study, a water repellent based on a silane/siloxane copolymer, specifically designed for high-performance concrete (HPC), was tested. Both untreated and weathered concrete surfaces showed signs of water penetration, whereas the treated concrete surface clearly demonstrated the effect of water repellency.

The weathered sample surface exhibited a contact angle of only 71°, while the contact angle of the treated concrete surface increased from 30° to 93° (as depicted in Figure 7) [40].

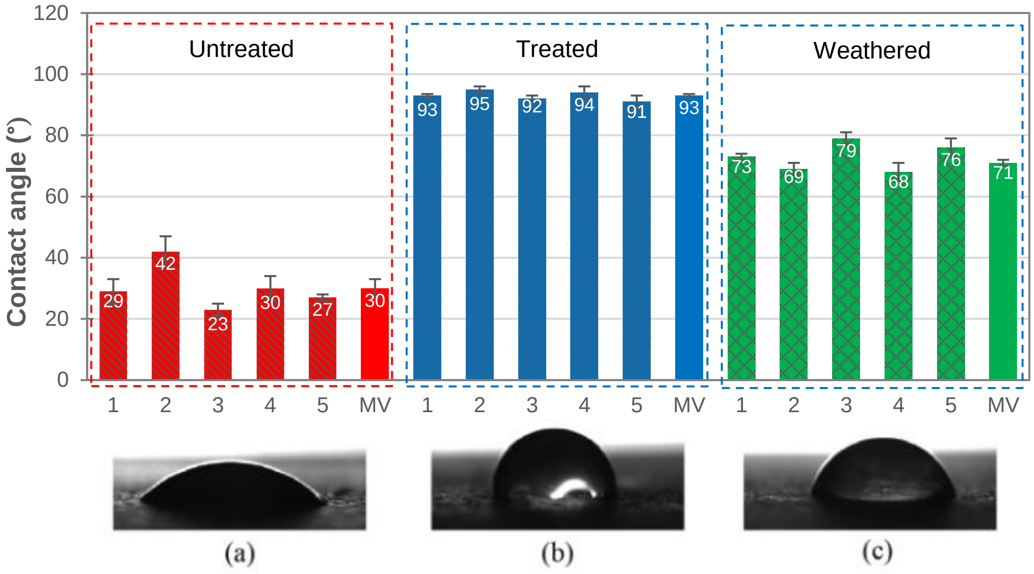


Figure 7. Water contact angle values for: (a) untreated, (b) treated, and (c) weathered samples (MV showing the mean value of the water contact angle) [40]

In a separate study for lightweight mortars, various solutions were used including methyl silicone resin solutions, aqueous emulsions of methyl silicone resin in potassium hydroxide, and alkyl-alkoxy-silane in organic solvents. These mortars were designated as C2L-mortars, which contain 20 % cork aggregate and hydrated lime, and C2S-mortars, which contain 20 % cork aggregate, quartz sand, and no hydrated lime. The water absorption decreased by roughly 71 % and 84 % for C2L and C2S mortars, respectively, when treated with an alkyl-alkoxy-siloxane hydrophobizing agent, compared to that for the reference mortar samples. The smallest contact angle was observed for the mortar containing 20 % cork and lime.

The highest contact angle among all samples, a WCA of 133,7°, was reported for C2S mortars with alkyl-alkoxy-silane modification. Hydrophobation enhanced the corrosion resistance of the samples. C2L mortars suffered the most damage, including peeling and a mass loss of approximately 14,63 % after 50 freeze–thaw cycles. Samples with sand demonstrated superior frost resistance when compared to mortars with lime (Figure 8) [41].

In a study exploring the surface impregnation technique, six different surface impregnation agents were employed, four of which were hydrophobic silane-based agents, and the remaining two were sodium silicate pore blockers.

Upon application to concrete, it was revealed that the pore blockers had no significant impact on preventing chloride ions from penetrating the RCC composite under marine conditions.

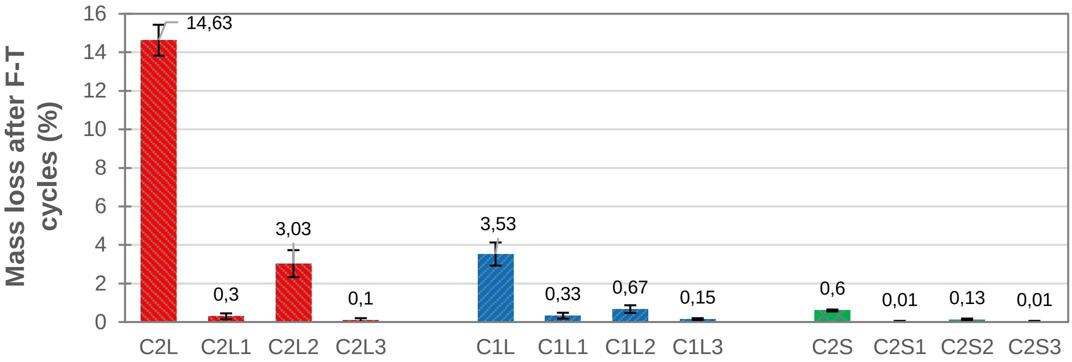


Figure 8. Mass loss after freeze–thaw cycles of hydrophobized samples with cork [41]

Sodium silicate-impregnated samples absorbed only 30 % less water than untreated specimens, whereas silane-impregnated samples absorbed a considerably lower amount of water [42]. The properties of concrete treated with octyltriethoxysilane, a waterborne-silane-based hydrophobic agent, as an impregnant were also evaluated. The investigation reported improved density, compactness, chloride resistance, and hydrophobicity in the impregnated concrete. Treated samples exhibited low capillary water absorption, which was only 5,4 % of the value for the reference samples [43]. In another study, two silane-based impregnation agents—one solvent-based (SB) and the other water-based (WB) were used to modify concrete surfaces to achieve hydrophobic properties. The solvent-based impregnating agent was found to be more effective in reducing water ingress than its water-based counterpart [44]. A hydrophobic material commercially known as KLD-1 was used to enhance the hydrophobic properties of concrete. The material was sprayed onto the samples prior to the application of curing agents, which resulted in a decrease in concrete permeability and water absorption rate. The compressive strength of the treated cubes suffered a strength loss of 32 % and 17 % under favourable and unfavourable curing regimes, respectively. However, when the KLD-1 treatment was followed by a wax-based curing compound, concrete strength increased by approximately 36 % when compared to that of the untreated mix [45].

A superhydrophobic cement mortar coating for application on concrete surfaces was produced using Portland cement, sand, Infrared Reflective pigment, TiO2 nanoparticles, carbon black, and 1H, 1H, 2H, 2H-Perfluorodecyltriethoxysilane. All the coated surfaces exhibited superhydrophobic properties with a WCA greater than 150° and SAs lower than 10° (Figure 9). It was found that no frozen water droplets appeared on the surface at temperatures up to -12 °C, suggesting that such resistance to ice formation can protect the surface from freeze–thaw damage [46].

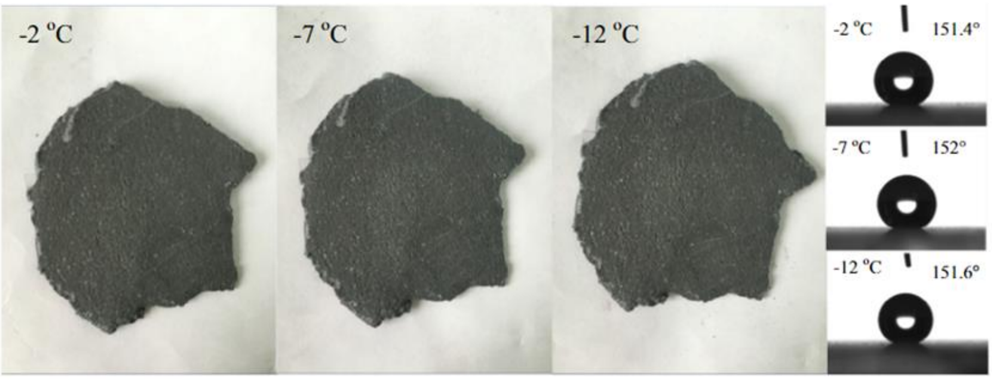


Figure 9. Anti ice–rain performance of concrete and corresponding WCA's after one-hour trial at different temperatures [46]

In another study, vacuum impregnation was performed on cement mortar blocks using iso-octyltriethoxysilane and anhydrous ethanol. After 15 days of immersion of surface modified mortar samples in water, the cumulative water uptake was reduced by 90 %, and the WCA of the surface modified mortar specimens was 140°, whereas that of the reference sample was 14°, thereby showing the conversion of a hydrophilic surface into a hydrophobic one using surface modification of the mortar specimens. [47]. In a study by Gao et al., trimethoxymethylsilane, dimethoxydimethylsilane, nano SiO2, and isopropanol were used on cement concrete specimens. The compressive strength loss rate of the superhydrophobic pavement cement concrete (SPCC) specimens was approximately 40 % when compared to that of the ordinary pavement cement concrete (OPCC) specimens. However, SPCC demonstrated a significant improvement in salt frost resistance. The application of superhydrophobic materials on the cement concrete pavement surface provides robust salt-frost resistance and effectively prevents surface erosion due to de-icing salt solutions. It also prevents stress accumulation within the material due to freeze–thaw cycles [48].

Facio and Mosquera used a blend of organic and inorganic silica oligomers containing silica nanoparticles on building substrates such as sandstone. The addition of silica nanoparticles reportedly led to the formation of superhydrophobic surfaces with a high WCA of approximately 150° and contact angle hysteresis of approximately 7° [49]. A study that employed Poly Methyl Hydrogen Siloxane (PMHS) oil emulsion and metakaolin or silica fume as particulates to create coatings on cement mortar tiles revealed that the inclusion of hierarchical surfaces using metakaolin or silica fume increased the contact angle. A concentration of 0.5% silica fume or metakaolin resulted in an overhydrophobic surface, while a 5 % concentration produced a superhydrophobic surface. A maximum contact angle of 156° was achieved for a concrete specimen with a PVA fibre surface treated with a metakaolin-based emulsion [50].

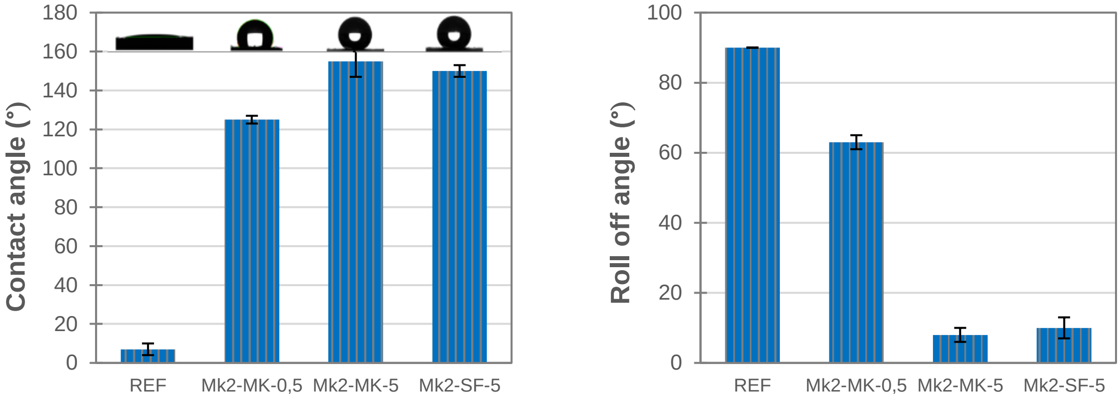


Figure 10. Water contact angle and sliding angle values with single and double coatings [51]

In a particular study, silica fume and polyvinyl alcohol-based fibres were utilised in an oligomeric siloxane product to produce coatings. A replica of micropillared moulds, composed of polydimethylsiloxane (PDMS), was also created. For samples coated with a low surface energy material, such as a siloxane-based film, and using a PDMS mould on ultra-high performance concrete (UHPC), the WCA measurements reached as high as 164°, while the CAH was reduced to 2,5°. These results showcased all the properties of a superhydrophobic surface (as illustrated in Figure 10). Notably, even in the absence of siloxane-based surface treatment, hydrophobic surfaces with a significantly high WCA were directly produced after demoulding from a silicone-based (PDMS) microtextured mould [51].

In a different study, a hydrophobic admixture derived from ethoxylated polyols and carboxylic acid was used to produce shotcrete as a repair material. This shotcrete was wet-sprayed onto the samples. For a water to cement ratio (w/c) of 0,55; the inclusion of the hydrophobic admixture reduced water absorption by over 85 % when compared to that of the reference sample. In the case of surface impregnation, there was a remarkable 94 % reduction in water absorption [52]. In yet another study, a superhydrophobic coating for concrete was prepared using rice husk ash dispersed in an ethanolic solution of fluoroalkyl silane and 1H,1H,2H,2H-perfluorodecyl triethoxy silane. The uncoated concrete cube specimens exhibited a WCA of 72,9 ± 6,8°. However, the concrete specimens coated with the hydrophobic coating showcased a significantly higher WCA of 152,3±0,5°, rendering the specimens superhydrophobic. Additionally, it was observed that the total water uptake was reduced by 40,38 %, and the sorptivity was diminished by 44,44 % when the coated concrete specimens were compared to the uncoated reference concrete cubes (as depicted in Figure 11). It is worth noting that despite the increase in WCA, the concrete carbonation rate was not lowered as the coating did not reduce the permeability of water vapour and CO_2 into the concrete [53].

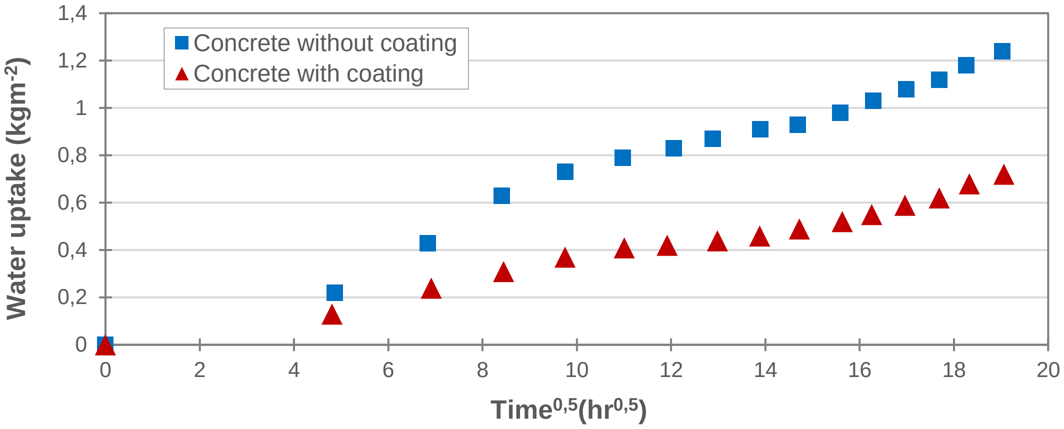


Figure 11. Cumulative water uptake by concrete cube for 15 days; with and without coating [53]

A study delved into the nanocasting technique to imprint a negative template of a lotus leaf-like microstructure onto cement paste using a flexible polydimethylsiloxane (PDMS) material. The PDMS mould, serving as a negative replica of the lotus leaf microstructure, allowed for the creation of a superhydrophobic cement paste by imprinting the complementary structure of the negative replica onto the cement paste. This structure was realised when the viscosity of the cement paste was reduced to 0,09 Pa. SA and contact angles as high as 140° were obtained with a low roll-off angle of less than 5°, characteristics that align with a superhydrophobic surface [54].

Another study investigated the application of room-temperature vulcanised silicone rubber (RTV) and TiO_2 on cement mortar blocks to enhance self-cleaning properties and durability. The prepared coating exhibited a WCA of 153,1° and an SA of 7,8°, indicating superhydrophobicity. This coating proved to be highly robust, resisting mechanical damage and abrasion tests and remaining stable through 10 freeze–thaw cycles with temperatures ranging from -40 °C to 100 °C [55]. An additional study utilised N-propyltrimethoxysilane (NP) and polymethyl-hydrogen siloxane oil (PMHS) as low-surface-energy surfactants, with acidic ludox colloidal silica serving as nanoparticles on cement mortar specimens. The cumulative water uptake was reduced by 85,7 % and the water sorptivity decreased by 95,2 % when compared to those of the reference concrete sample. The water contact angle was 20° ± 5° in the unmodified mortar, while the addition of NP or PMHS resulted in a hydrophobic surface with contact angles of 130° ± 4° and 123° ± 6°, respectively, and sliding angles of 27° ± 3° and 23° ± 2°, respectively. However, when the silica solution was added to the mix in conjunction with NP and PMHS, the surface demonstrated superhydrophobicity with a WCA of 162° ± 3° (as illustrated in Figure 12) [56].

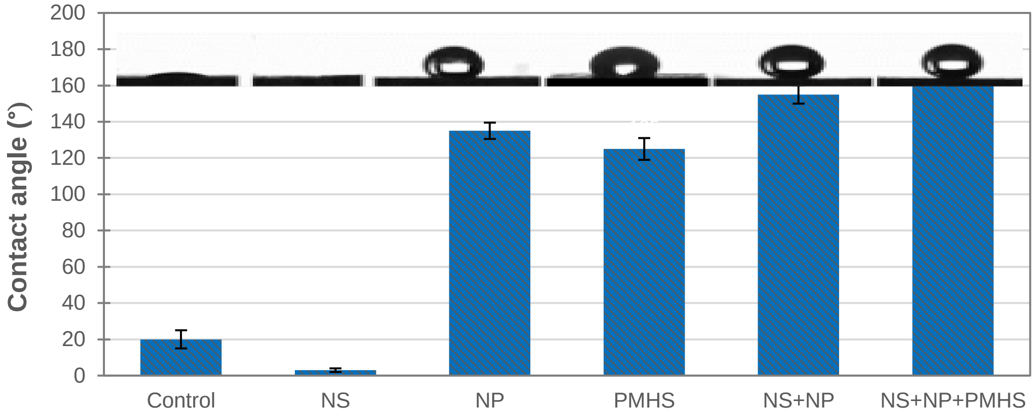


Figure 12. Water Contact Angles on concrete surface with varying coating constitutes [56]

Table 2 summarises the highest WCA's and SA's measured for the surface hydrophobic treatments.

Table 2. Water contact angles and sliding angles for surface hydrophobic treatments [49, 57, 50, 51, 25, 54, 53, 41, 58, 46, 47, 59, 56]

S.No.	Research paper	Highest WCA obtained	SA/ CAH	State of hydrophobicity achieved by surface treatments
1.	[49]	150°	7°	superhydrophobic
2.	[57]	151°	-	superhydrophobic
3.	[50]	120-140°	-	overhydrophobic
4.	[51]	164°	2,5°	superhydrophobic
5.	[25]	> 120°	-	overhydrophobic
6.	[54]	140°	< 5°	overhydrophobic
7.	[53]	152,3°± 0,05°	-	superhydrophobic
8.	[41]	133,7°	-	overhydrophobic
9.	[58]	130°± 4°	27° ± 3°	overhydrophobic
10.	[46]	150,4°± 0,3°	8,9° ± 2,2°	superhydrophobic
11.	[47]	140°	-	overhydrophobic
12.	[59]	> 150°	< 10°	superhydrophobic
13.	[56]	162°	5°	superhydrophobic

3.2 Integral hydrophobic modification

Integral hydrophobic modification, which has been practiced since ancient times using natural additives such as black gram and oxblood, has evolved over time to incorporate more effective hydrophobic agents such as silanes, siloxanes, industrial waste products, and crystalline admixtures. This section reviews the literature on integral hydrophobic agents and examines the effects of their incorporation on the properties of mortar and concrete.

Aavik and Chandra conducted integral hydrophobic modification using natural additives, such as black gram paste and gram oil emulsion, derived from edible oil, in samples of cement mortar, lightweight aggregate concrete and standard concrete. The addition of black gram paste resulted in air entrainment comparable to that obtained with traditional air entraining agents. However, the use of gram oil emulsion led to a decrease in air entrainment in the matrix, resulting in an increase in the density of both mortar and concrete. In the study, it was determined that the inclusion of black gram led to excellent adhesion, resulting in a strength increase of approximately 8-10 % when compared to normal specimens. This also resulted in reduced water absorption relative to specimens without it. The specimens with gram oil emulsion absorbed the least amount of water [60].

Another natural additive that was investigated is oxblood, which was used to produce integral water-repellent concrete. There was a strength reduction observed in the integral water-repellent concrete made using oxblood as an additive. This reduction is attributed to two main causes: firstly, the high water content in oxblood, which increases the net water–cement ratio of concrete; and secondly, oxblood's aerating function, which leads to a reduction in strength. It was found that the addition of oxblood to the concrete mix decreased capillary water absorption, which in turn enhanced the concrete's durability. This is evident in terms of reduced chloride ion penetration and improved frost resistance of the concrete (Figure 13) [61].

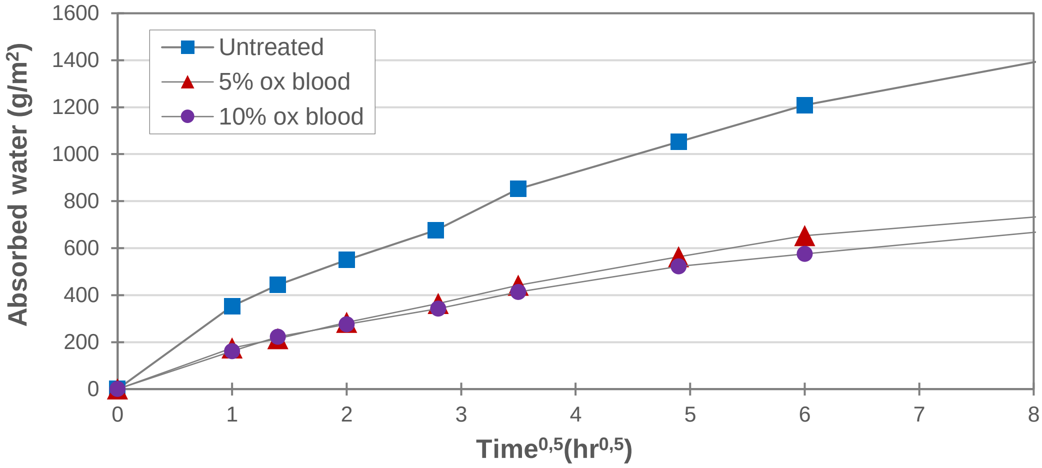


Figure 13. Water absorption as a function of the square root of time of neat concrete and concrete made integral water repellent by addition of oxblood [61]

Another investigation using natural additives involved the use of linseed oil for hydrophobic modification in lime mortars and lime metakaolin mortars. Due to linseed oil's non-polar nature, it can transition capillary surfaces from hydrophilic to hydrophobic, thereby reducing the amount of water and salt that can infiltrate the mortars. Linseed oil diminishes the flexural and compressive strengths of lime mortar, but this loss in strength is restored by metakaolin. The inclusion of linseed oil in lime mortar and lime metakaolin mortar reduced capillary water absorption by approximately 98 % and 83 %, respectively, also decreasing salt intrusion [62].

Metal soaps, composed of calcium stearates and zinc stearates, were also investigated for use in concrete samples. The addition of metal soaps to concrete significantly reduces its strength due to decreased hydration reactions. Even a minor addition of 1 % soap led to an approximately 50 % reduction in compressive strength when compared to those of the reference concrete samples. However, the addition of metal soaps to fresh concrete resulted in decreased chloride ion penetration, leading to increased durability [63]. The potential of hydrophobic modifiers, such as vegetable oil soap stocks and synthetic fatty acid stillage residues, to impart hydrophobicity to concrete was also examined. The concrete strengths for cube and prism samples with hydrophobic modifiers were found to be 15-20 % higher than those without additives. These complex hydrophobic modifiers were reported to reduce water absorption and capillarity by 3 to 3,5 times [64]. A comparative study was conducted involving rapeseed oil and alkyl alkoxysilane as hydrophobic admixtures, along with Silica Fume (SF). The different samples were designated as follows: 1 - Reference series; 2 - Silane series; and 3 - Oil series. The compressive strength was substantially lower in the specimens with internal hydrophobic agents compared to the reference samples. Conversely, the incorporation of silica fume in concrete led to a higher compressive strength than the reference material (Figure 14).

Interestingly, the oil samples exhibited a more ductile fracture, while the silane samples showed a brittle fracture [65].

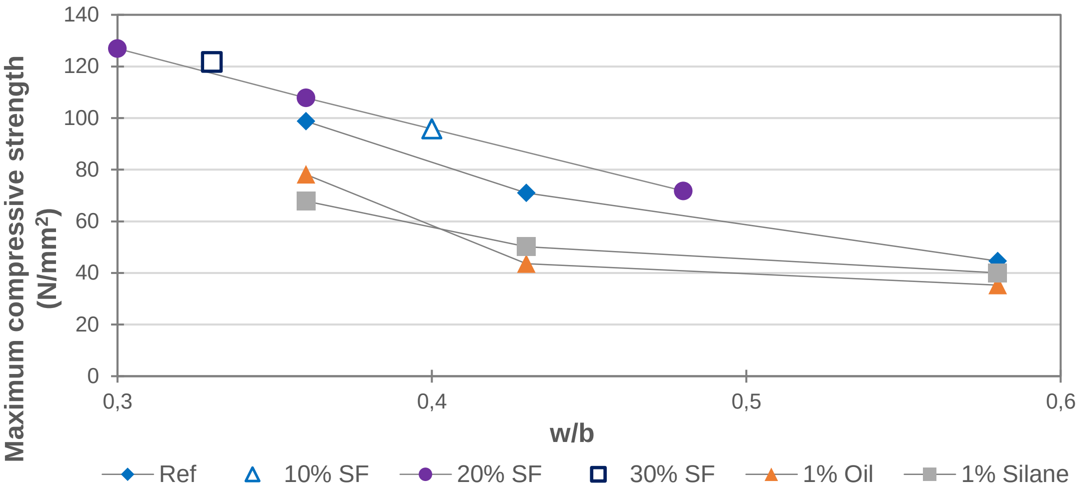


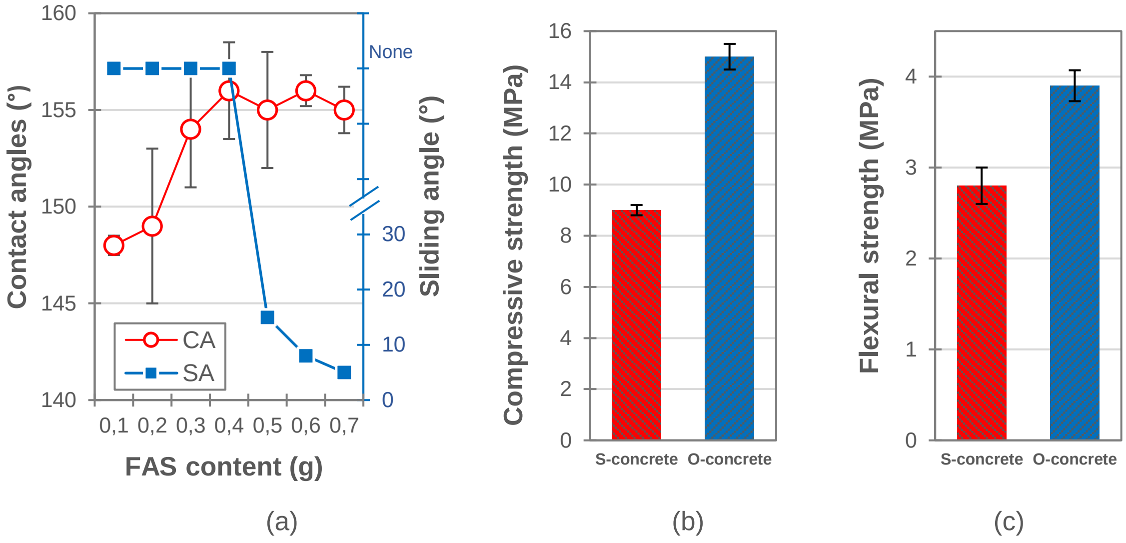
Figure 14. Maximum compressive strength of reference samples when compared to those of samples with different admixtures [65]

Another comparative study involved the use of stearic acid, DryCit (a commercial hydrophobic agent), and rapeseed oil on cement concrete specimens to assess the induced hydrophobicity. All the selected admixtures were observed to reduce the compressive strength of the material, with reductions ranging from 10 % to 18 %. However, the introduction of internal hydrophobic agents improved the water resistance of the materials. Among the three selected agents, rapeseed oil proved to be the most effective admixture, followed by stearic acid. Furthermore, increasing the dosage of these agents resulted in enhanced water resistance for all mixes [66]. In another study, rapeseed oil was compared with extra virgin olive oil and two commercial hydrophobic agents: one organofunctional silane-based (Commercial Hydrophobic Agent 1) and the other octyltriethoxysilane-based (Commercial Hydrophobic Agent 2) in cement concrete. The compressive strength of the reference samples was at least 50 % greater than that of the concrete with bulk hydrophobic agents. Rapeseed oil, at 3 % of the cement weight, provided a higher resistance to scaling than olive oil at the same concentration [67].

Silanes and siloxanes are the most commonly used hydrophobic agents in surface and integral hydrophobic concretes. A study used a silane emulsion on concrete samples and found that although integral hydrophobic concrete using silane emulsion does not entirely prevent chloride penetration, it can significantly reduce it. The addition of 1% silane had minimal effect on chloride penetration, but 2 % silane demonstrated noteworthy results when compared to the reference concrete [68]. In another study, polyethyl hydrosiloxane (PEHSO) and superplasticiser (SP) were used to create a modified multi-component binder (MMCB) concrete with Silica Fume (SF), finely ground ponded ash (FGPA), and finely ground granulated blast furnace slag (FGGBFS) as additives. The addition of the PEHSO admixture resulted in a slight decrease in the strength of the MMCB concrete mixes. All concretes exhibited very low capillary porosity, with the lowest value of 2,6 % capillary porosity being displayed by concrete containing 15 % SF and 45 % FGGBFS. The application of SP and SP-PEHSO admixtures proved beneficial in providing protection against corrosion in steel by facilitating its passivation in concrete. Moreover, the use of the SP-PEHSO admixture helped to develop concrete with very high resistance to freezing and thawing. This resistance exceeded approximately 700 cycles for MMCB concrete with a 15 % FGPA mix, 45 % FGGBFS, and 15 % SF sample [21].

In another study, a silane-based hydrophobic admixture was used to investigate its impact on the corrosion of steel reinforcement bars in concrete. The results showed that the compressive strength of concrete with the silane admixture decreased by approximately 10 % to 20 % when compared to that of reference concrete samples. In uncracked concrete specimens, the silane hydrophobic admixture prevented the corrosion of reinforcement when exposed to a chloride solution. This can be attributed to the reduced water permeability through the pores, which in turn decreases the ingress of chloride ions. However, the opposite was observed in the case of cracked specimens. Interestingly, the reference concrete provided better corrosion protection than the one with the silane admixture in the case of cracked specimens. This can be explained by the fact that oxygen diffusion occurs more rapidly in the gaseous phase of hydrophobic concrete when compared to the slower diffusion through water-filled pores in the case of reference concrete [69].

A study utilised a silane-based hydrophobic admixture, specifically butyl-ethoxy silane, on concrete specimens (both uncracked and intentionally cracked) reinforced with a hot-dip galvanised steel plate. This was done to investigate the impact of the hydrophobic admixture on the corrosion of galvanised reinforcing steel embedded in concrete. The polarization resistance of galvanised steel plates embedded in the modified concrete was found to increase, when compared to that in unmodified concrete, by adding 1 % butyl-ethoxy silane solution to cement. When subjected to wet-dry cycles in a chloride-aqueous solution, the concrete specimens with the hydrophobic admixture showed enhanced corrosion resistance of the galvanised steel reinforcement. Furthermore, chloride penetration decreased by approximately 60 % in sound and cracked concrete specimens [70]. Concrete samples with silane-based compounds demonstrated that the addition of silane to concrete significantly reduces its strength, with the decrease being approximately one-third when compared to the reference samples. A probable explanation for this reduction is that the hydration reaction slows down due to the addition of silane. In silane-based integral hydrophobic concrete, a decrease in capillary water absorption was observed, as well as a decrease in chloride ion ingress. This led to improved durability and an extended service life. It was found that using integral water-repellent concrete is more effective in aggressive environments, such as marine settings, when compared to simply lowering the water–cement ratio. The capillary water absorption in concrete decreased with the addition of silane, with the optimum amount of silane for this effect found to be 4 % [71].



(a) (b) (c)

Figure 15. (a) Influence of FAS content on the wettability of concrete, (b) compressive strength of S-concrete and O-concrete, (c) flexural strength of S-concrete and O-concrete [72]

In a study by Song et al., superhydrophobic concrete (S-concrete) was prepared via the addition of Fluoro Alkyl Silane (FAS) and a Cu mesh. Ordinary concrete was designated as O-concrete. They observed that the addition of FAS to concrete reduced its strength, with S-concrete having only 60 % of the strength when compared to O-concrete (Figure 15 (b), (c)). S-concrete exhibited superhydrophobicity with high contact angles reaching up to 158° ± 0.8° and sliding angles of 6,1° ± 1,2°. It also demonstrated high surface robustness and retained its superhydrophobicity even under sandpaper abrasion (Figure 15(a)). S-concrete displayed better corrosion resistance than O-concrete. The mass loss increased with the number of freeze–thaw cycles, reaching 6,7 % at the end of 110 cycles in the case of O-concrete. However, for S-concrete, no mass loss was observed even after 130 freeze-thaw cycles. After 190 cycles, only a 0,26 % mass loss was observed, illustrating the improved freeze–thaw durability of the concrete [72].

In a previous study, Poly Methyl Hydrogen Siloxane (PMHS) fluid was used to produce a hydrophobic fibre-reinforced cementitious composite. A single dose of hydrophobic emulsion reduces the 1-day and 7-day compressive strengths. However, the 28-day strengths show almost the same value with only a small decrease. Strain hardening behaviour was observed in the matrices, and the composites were observed to exhibit several microcracks. Higher ultimate flexural stress and strain were recorded upon the addition of hydrophobic emulsions. The hydrophobic emulsion samples showed little to no effects from freezing and thawing through at least 350 cycles. Conversely, the reference samples started showing some degradation at the beginning of 150 cycles [50].

In another study, an aqueous emulsion of alkyl-triethoxy-silane was employed as an admixture in no-fines concrete with recycled aggregates, aiming to enhance its hydrophobic properties. The inclusion of hydrophobic admixtures resulted in a decrease in the strength of no-fines concrete. Additionally, the complete substitution of natural aggregates with recycled aggregates led to a strength reduction of approximately 30 %. The capillary water absorption was reduced by approximately 70 % due to the use of hydrophobic admixtures in no-fines concrete. However, the total replacement of natural aggregates by recycled aggregates increased capillary water absorption by 50 %. It was noted that all no-fines concrete mixes were highly susceptible to carbonation due to the material's macrovoid structure. This structure facilitated the easy penetration of carbon dioxide and water into the concrete matrix [73].

In another study, Poly Methyl Hydrogen Siloxane (PMHS) and Polyvinyl Alcohol Surfactant (PVAS) were utilised to create Engineered Cementitious Composites (ECC) and Superhydrophobic Engineered Cementitious Composites (SECC). It was discovered that the early-stage compressive strengths decreased significantly (approximately 50 %) when the PVAS and PMHS admixture was employed, although the 28-day strength was comparable to the reference samples, with only a minor reduction observed. Both flexural stress and strain were enhanced by the addition of hydrophobic admixtures to the concrete, resulting in a 25% increase in flexural stress and 40 % increase in flexural strain at maximum stress when compared to the reference samples. Hydrophobicity was evaluated through contact angle measurements on coated tile specimens, and it was found to have increased by more than 120 % when compared to the reference samples. When microparticles were added, the tiles displayed an overhydrophobic state with contact angles exceeding 120° [25].

The inclusion of a silane emulsion in concrete samples led to a decrease in the compressive strength of these samples. This reduction became more pronounced as the proportion of silane emulsion in the mix increased. The likely reason for this is that the silane emulsion slows down the hydration rate of Portland cement, leading to a weakening of the cementitious matrix's microstructure. Furthermore, the addition of the silane emulsion to concrete samples lowered capillary absorption, which consequently led to a decrease in chloride penetration into the concrete matrix [74].

In a study involving cement mortar samples, Polydimethylsiloxane (PDMS) was used. It was observed that any fractured surface, as well as the powder of Superhydrophobic Calcium Aluminate Cement (SCAC), exhibited superhydrophobic properties, with WCAs exceeding 150° and rolling angles below 10°. Remarkably, SCAC retained its superhydrophobicity even after severe and repeated mechanical damages such as sandpaper abrasion, sand impact, electric cutting, and knife scratches. The study reported that SCAC showed enhanced corrosion resistance for reinforcement bars compared to unmodified CAC [75]. In another study, the use of Polydimethylsiloxane (PDMS) was explored in calcium aluminate cement concrete. With an increase in the oil-to-water volume ratio from 1:1 to 4:1, porosity increased by approximately 38 %, density decreased by about 60%, while compressive strength dropped by 84 %. The concrete demonstrated bulk superhydrophobicity with a WCA of 166° [76].

A study employed Stearic Acid Emulsion (SAE) to induce hydrophobicity in cement mortar. The findings revealed that as the SAE content increased in the sample, the fluidity, and thus the workability, of the cement paste decreased. When comparing modified mortar with the unmodified version of the same age, the compressive strength reduced by 16,2 %, and the flexural strength dropped by 20 %. A WCA of 131.5° and Sliding Angle (SA) of 81,7° were reported when cement mortar was modified using SAE, indicating the surface's hydrophobicity (Figure 16). An examination using scanning electron microscopy (SEM) revealed a substantial number of voids appearing when SAE was introduced into the cement mortar. This suggests that the structure of the hardened cement paste had become less dense [77].

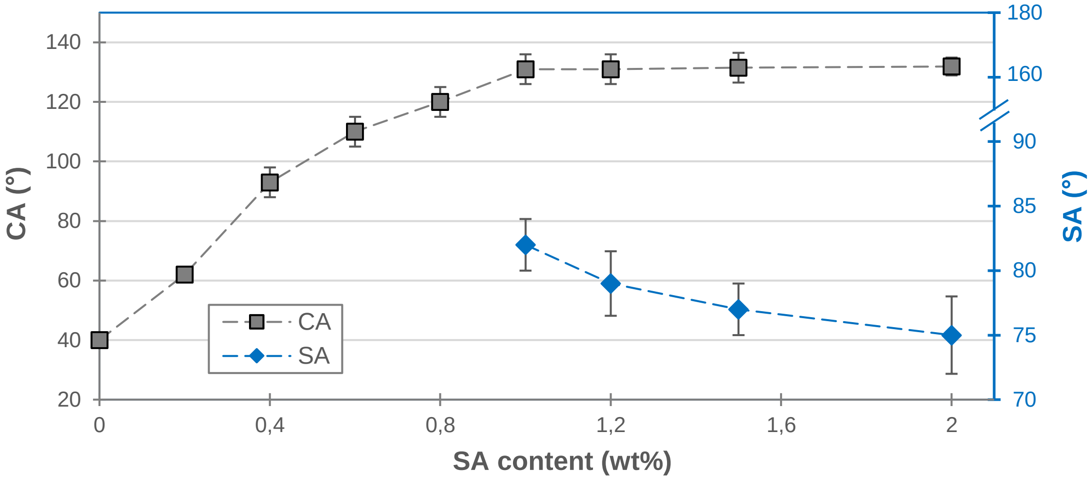


Figure 16. Influence of stearic acid content on the surface WCA of the SAE modified samples [77]

Concrete samples were treated with silicones such as sodium methyl siliconates, alkyl silane esters, and silicon resin emulsions. It has been noted that when silicones are used as admixtures in concrete, they delay the setting times of the concrete. In some instances, this delay is unacceptable for construction purposes. Sodium methylsiliconate solutions reportedly increased the compressive strength and durability of concrete when used in moderation. However, alkyl silane esters and silicone resin emulsions showed no discernible effect on the concrete's compressive strength or durability, and in some cases, they even proved detrimental [78]. Silicone Hydrophobic Powder-50 (SHP-50) and Silica Fume (SF) were incorporated into concrete that consisted of 20 % fly ash (FA). The lowest values for water permeability and percent air content were observed in the mix containing Ordinary Portland Cement (OPC) + 20 % FA + 5 % SF + 0,3 % SHP-50, sand, and aggregate. These findings corroborated the results of compressive strength measurements. A similar trend was observed for chloride ion penetrability, with the mix demonstrating the lowest water penetration also showing the lowest chloride ion penetration [79].

A waterproofing agent known by the brand name Krystol Internal Membrane (KIM) was tested on cement mortars and concrete. As the percentage of KIM used increased, the amount of water percolation correspondingly decreased. This blockage of pores resulted in an increase in the compressive strength and durability of both the mortar and concrete specimens. Moreover, the corrosive impact of H_2SO_4 lessened with the addition of KIM. This suggests a reduction in the pore size of the cement paste, preventing the acid from infiltrating the pores [80].

A dual-crystalline material, commercially known as LYN-1, was incorporated into the concrete mix during preparation. As the percentage of this admixture increased from 0 %, 1 %, and 2 % to 8 %, there was a corresponding and continuous increase in the slump values (workability) from 40 mm, 60 mm, and 190 mm to 210 mm, respectively. Despite such high slump values, the concrete exhibited no segregation. With a 2 % content of LYN-1, the concrete strength reached 81 % on the 28th day, suggesting this level to be most beneficial in terms of strength. Water absorption declined in all concrete specimens when compared to those in reference samples without any admixture [81]. Permeability-reducing admixtures (PRAs), such as hydrophobic pore blockers and admixtures inducing crystallisation effects, were employed in concrete samples to examine their impact on the samples' hydrophobicity. It was noted that the apparent volume of permeable voids in hardened concrete diminished by approximately 3,4 % to 5,3 % due to the introduction of crystallising self-sealers, and the coefficient of permeability decreased by approximately 25 %. The hydrophobic pore sealer led to a roughly 4 % reduction in the apparent volume of permeable voids, while there was a 17 % decrease in permeability due to its addition. Furthermore, PRAs reduce the rate of absorption. For hydrophobic pore blockers, sorptivity decreased by roughly 10 % [82].

In a separate study involving calcium stearate as a hydrophobic additive in cement concrete specimens, it was noted that the admixture did not significantly affect the concrete's compressive strength. However, with a 0,4 % addition of calcium stearate to the concrete, water absorption decreased significantly by approximately 53 %. The penetration of chloride ions was curbed by approximately 15 % due to the inclusion of 0,4 % calcium stearate in the concrete, which subsequently reduced the corrosion attack from chloride ions by 28,5 %. The introduction of calcium stearate reduced the rate of corrosion in reinforced concrete, and as the quantity of calcium stearate in the concrete increased, the corrosion level decreased. Additionally, the corrosion rate declined with the use of higher grade concrete [83].

In a study by Grumbein et al., LB plus-agar enriched with 1 % glycerol and 0,1 mM $MnSO_4$ was used for biofilm growth and as an admixture in cement mortar samples. The Hybrid Mortar (HM) sample, containing 2 % biofilm, exhibited an increased contact angle of approximately 90°. For an HM sample with 10 % lyophilised biofilm, contact angles as high as approximately 110° were observed. The rise in contact angle was attributed to the alteration of the mortar's nano- and micro-topology, as the addition of bacterial biofilm to the samples stimulated the growth of spike-like crystal structures on the material's inner and outer surfaces [84].

Furthermore, integral hydrophobicity was also tested in concrete and mortar samples using industrial by-products such as fly ash, amorphous carbon powder, and GGBS. These materials showed significant promise in enhancing hydrophobicity. Wong et al. used superhydrophobic paper sludge ash (PSA) to create samples of cement pastes with hydrophobic PSA admixed in cement pastes with hydrophobic PSA surface-coated on, and concretes with hydrophobic PSA admixed in. This superhydrophobic PSA was produced according to a previous study by Spathi et al. (2015), which involved dry milling paper sludge ash with 4 % stearic acid for eight hours to achieve a maximum WCA exceeding 150° [85]. It was observed that the workability of the cement paste and concrete mix decreased as the proportion of PSA increased. The lowest water absorption was observed in samples coated with superhydrophobic PSA. Sorptivity also decreased as the percentage of hydrophobic PSA in the concrete increased. Incorporation of 2 %, 4 %, 8 %, and 16 % PSA in concrete led to a reduction in sorptivity of 62 %, 72 %, 83 %, and 92 %, respectively, when compared to the control samples. When ink droplets were placed on the surface of samples containing superhydrophobic PSA, they formed beads and did not stain the sample surface. Conversely, in the control samples, the ink droplets were quickly absorbed, staining the surface [86].

Hydrophobic concrete was synthesised by incorporating superhydrophobic ground granulated blast-furnace slag (H-GGBS), which was produced using stearic acid via a ball milling process. This was used in lightweight aggregate concrete to enhance its hydrophobic properties. As the percentage of superhydrophobic GGBS in concrete increased, so did the flowability when compared to the reference mix. All the H-GGBS mixes exhibited excellent workability, which further increased with a higher percentage of H-GGBS in the concrete. However, the addition of superhydrophobic GGBS led to a reduction in concrete strength, more noticeable at 1 and 7 days but less so at later stages. The compressive strength was approximately 98 % and 83 % of the reference sample's compressive strength for 15 % and 20 % replacements, respectively. A similar trend was observed for flexural strength. The use of superhydrophobic GGBS resulted in improved durability. With a 15 % addition of ultra-hydrophobic GGBS, the lightweight concrete demonstrated superior hydrophobic performance with a water contact angle of 92° [87].

In one study, tire rubber grains with particle sizes in the range of 0-2 mm were utilised. Cement mortar specimens were prepared by partially or totally replacing sand, the fine aggregate, with tire rubber. This substitution was found to be highly effective in guarding against the penetration of small water droplets. The finest grain size of tire rubber was the most effective, leading to an approximately 95 % reduction in water absorption. All tire rubber mortars resulted in at least an 80 % reduction in water absorption. WCAs for all the samples were found to be greater than 100°, and in some cases even increased to 125°, indicating the hydrophobicity of the mortar specimens [88].

In another study, oleic acid-modified fly ash was incorporated into cement paste samples. The inclusion of this modified fly ash affected the compressive and bending strengths of the samples, with these strengths decreasing as the proportion of modified fly ash in the sample increased. When balancing mechanical and water-repellent properties, the cement containing 12 % modified fly ash performed optimally. While there was significant water ingress initially, it gradually reached a plateau. WCA measurements revealed that the inclusion of modified fly ash increased the cement's hydrophobicity. The WCAs of samples with 4 %, 12 %, and 20 % modified fly ash were 39°, 65°, and 87°, respectively, indicating a gradual increase in hydrophobicity with an increasing content of modified fly ash in the cement [89]. The water absorption for the reference and modified samples is depicted in Figure 17.

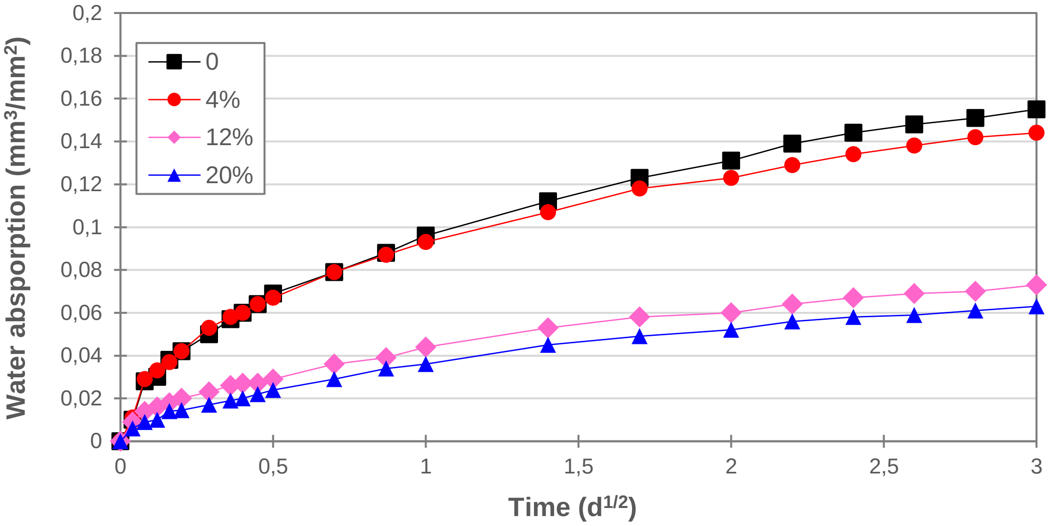


Figure 17. Cumulative water absorption of cement paste samples prepared with modified fly ash [89]

An integral hydrophobic concrete and cement paste were developed using waste amorphous carbon powder (ACP). Specifically, ACP is a hydrophobic by-product of paraffin production, and it was utilised to induce integral hydrophobicity. A noticeable decrease in the workability of paste and concrete samples containing ACP was observed. The ACP-modified paste samples exhibited higher compressive strength and lower porosity when compared to the control samples. The water absorption in ACP-modified cement paste was found to be reduced by up to approximately 23 %. The electrical resistivity of cement paste and concrete increased by up to 187 % and 43 %, respectively, when the ACP content was 15 % and 2 0% [90]. Table 3 provides a summary of the highest WCAs achieved along with their corresponding SA values, as well as the level of hydrophobicity achieved by integral hydrophobic treatments.

Table 3. Water contact angles and sliding angles for integral hydrophobic treatments [85, 84, 72, 87, 89, 88, 75, 76, 77]

S.No.	Research paper	Highest WCA obtained	SA/ CAH	State of hydrophobicity achieved by integral treatments
1.	[85]	> 150°	-	superhydrophobic
2.	[84]	~ 90° - 110°	-	hydrophobic
3.	[72]	158° ± 0,8°	6,1° ± 1,2°	superhydrophobic
4.	[87]	92°	-	hydrophobic
5.	[89]	87°	-	hydrophobic
6.	[88]	> 100°	-	overhydrophobic
7.	[75]	> 150°	< 10°	superhydrophobic
8.	[76]	~ 166°	-	superhydrophobic
9.	[77]	131,5°	81,7°	overhydrophobic

4 Characterization of hydrophobic concrete using microstructure analysis

Various techniques, such as X-ray diffraction (XRD), SEM, X-ray fluorescence (XRF), and thermogravimetric analysis (TGA) can be used to analyse the microstructure of cementitious materials. The alterations induced by hydrophobic coatings and admixtures within the concrete matrix are discussed below.

The minimum crystal size observed was 95 nm and the maximum was 200 nm. For LYN-1 particles, they were smaller than macropores, air voids, and microcracks, suggesting their easy integration within any concrete without causing the formation of new voids [81]. SEM analysis revealed the appearance of a large number of voids when SAE was incorporated into the cement mortar, implying that the structure of the hardened cement paste had become less dense. The inclusion of SAE led to an increase in total pore volume, pore size, and pore connectivity in the cement mortar [77]. The X-ray diffraction patterns for PC and PCKIM were nearly identical, but PCKIM displayed lines due to SiO_2. The diffraction patterns of hydrated samples were similar, showing intense lime presence due to $Ca(OH)_2$ resulting from hydration and C3S/C2S phase depletion. The C3S/C2S phase depletion was slightly less pronounced with KIM, suggesting that KIM had a retarding effect [80].

XRF data showed that paper sludge ash primarily consists of calcium aluminosilicate with minimal impurities. XRD analysis revealed gehlenite, calcite, lime, and mayenite as the present crystalline phases [85]. The presence of bacterial biofilms in mortar samples was found to alter their nano- and micro-topology, encouraging the formation of spike-like crystals on their inner and outer surfaces [84]. Furthermore, TGA showed that the addition of silicon resin (SR) did not result in any new crystal formation up to an amount of 4 % [90]. Superhydrophobic pavement cement concrete (SPCC) and ordinary pavement cement concrete (OPCC) displayed the same surface crystal structure. The formation of nano/microstructures on the specimen surface due to the use of superhydrophobic materials was found to be crucial in imparting superhydrophobic properties to the surface and enhancing the frost resistance of SPCC [48]. Microstructure analysis of superhydrophobic surfaces indicated that nearly all such surfaces possess micro/nano hierarchical structures, which contribute to the transformation of hydrophobic surfaces into superhydrophobic surfaces. In addition to surface-energy-lowering compounds, such as silanes, the presence of such indentations/microstructures significantly enhances the WCA, making the surfaces superhydrophobic.

5 Conclusions

The advancement of hydrophobic concrete is a significant stride in the domain of building materials. By incorporating hydrophobic agents into concrete mixtures or applying them as a surface treatment, the water resistance of the material is enhanced, reducing water penetration and subsequent damage from freeze–thaw cycles and chemical attacks. Hydrophobic concrete also offers potential benefits, such as increased durability, reduced maintenance costs, and improved sustainability, by minimizing the frequency of repair and replacement. This study evaluates the efficacy of hydrophobic treatments for concrete and mortar in deterring water penetration into their matrices. Upon examining the rheological, mechanical, and durability attributes affected by these modifications, the following conclusions are reached:

- Surface treatment of concrete has proven to be a more effective hydrophobic method than bulk treatment. However, its efficacy heavily relies on the depth to which hydrophobic agents can penetrate the surface. Moreover, surface treatment necessitates an additional step of application to the concrete surface beyond the casting process.
- Hydrophobic surface treatments may inhibit concrete's ability to "breathe," leading to moisture accumulation within the material. This can trigger issues such as efflorescence, characterised by the formation of white, powdery deposits on the concrete surface. Many hydrophobic treatments also contain chemicals that are potentially harmful to the environment if not properly discarded.
- Although surface treatment is more effective in repelling water, the life of coatings is highly dependent on their adhesiveness to the surface and their mechanical robustness against abrasion and other mechanical damage. Once damaged, the coating exposes the internal hydrophilic surface of the concrete to the external environment, thereby defeating the purpose of the treatment. Additionally, hydrophobic treatments can be costly, especially if they must be reapplied on a regular basis to remain effective.
- Integral modification offers advantages over surface treatment as it does not require constant maintenance and is not susceptible to deterioration from peeling or surface damage. Another benefit of bulk treatment is that, unlike surface treatments, the internal exposed surface of concrete or mortar remains hydrophobic and continues to repel water even after damage or breakage. Integral hydrophobic concrete provides consistent performance throughout the entire structure, unlike surface hydrophobic treatments, which can be affected by cracks or other surface damage.
- A significant concern associated with bulk hydrophobation is that, despite most internal hydrophobic admixtures successfully mitigating water penetration into the concrete, they substantially reduce the compressive strength due to interference with the concrete's hydration reactions. Hence, studies recommend their use in non-structural elements.
- Incorporating nanoparticles into hydrophobic admixtures or coatings enhances hydrophobicity and, consequently, the durability of concrete and mortars. This is because the nanoparticles facilitate the formation of micro- and nano-hierarchical structures. This holds true for both surface and bulk modifications.
- Modified industrial waste products have been utilised as hydrophobic agents to create waterproof concrete. This not only mitigates water ingress but also addresses waste disposal issues. Examples include modified fly ash, rice husk ash, granulated glass blast furnace slag, wastepaper sludge ash, and amorphous carbon powder from the paraffin wax industry. It was also observed that these products had a minimal effect on compressive strength, broadening their potential use as hydrophobic agents.

Despite the numerous benefits of hydrophobic concrete, several challenges persist, such as ensuring proper mixing and distribution of hydrophobic agents, potential impacts on concrete strength and workability, and a limited understanding of the long-term effectiveness and economics of the treatment. However, these issues are addressable through ongoing research and development, leading to the enhancement and refinement of hydrophobic concrete. In conclusion, hydrophobic concrete presents a promising solution to improve the durability and longevity of concrete structures across a diverse range of applications, including bridges, roads, buildings, and infrastructure. Consequently, this field is poised to attract increasing attention from researchers and industry professionals in the years ahead.

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