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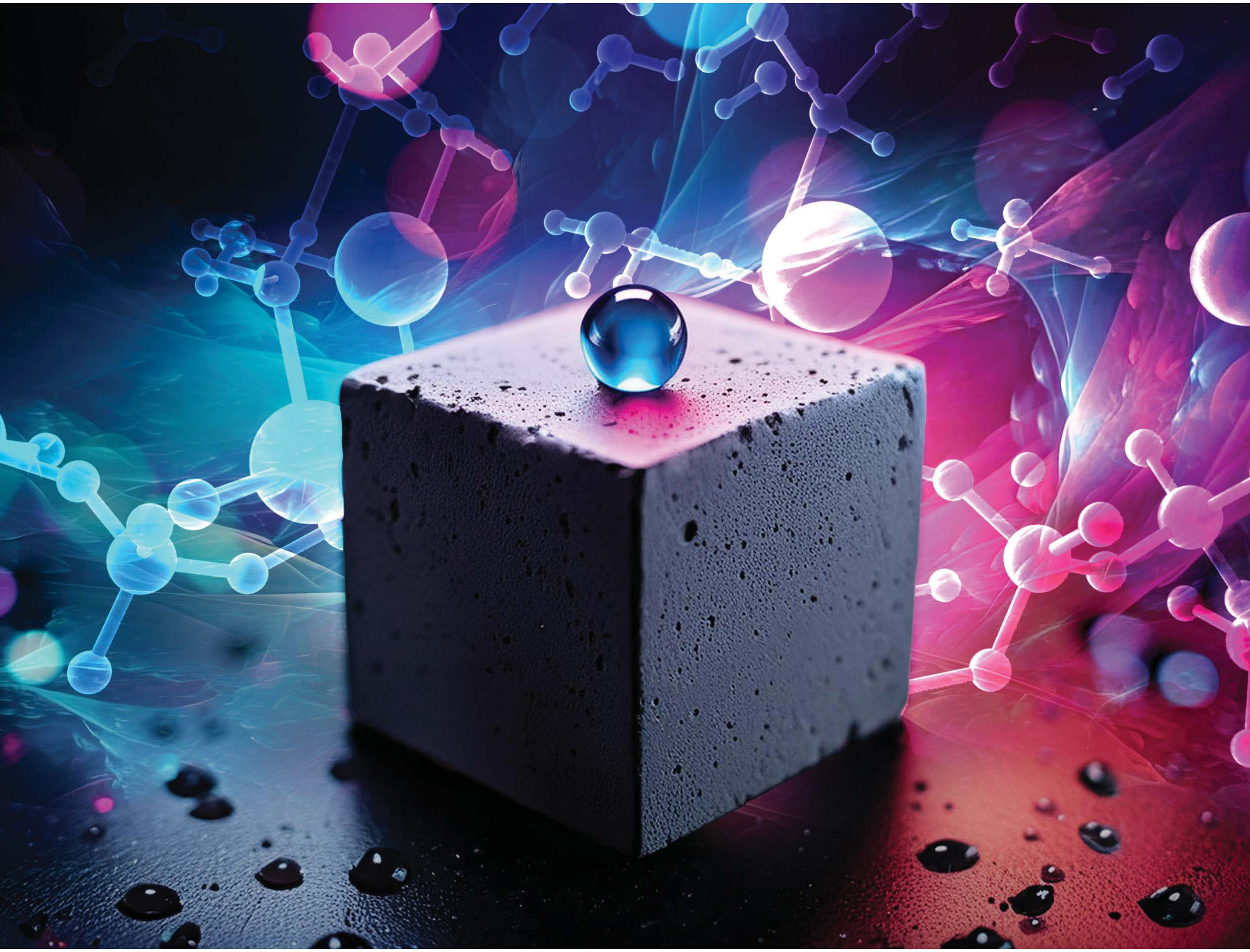

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Surface treatments on concrete: an overview on organic, inorganic and nano-based coatings and an outlook about surface modification by rare-earth oxides

Peter Thissen, * Andreas Bogner and Frank Dehn

Cementitious construction materials like concrete stand as pivotal constituents in the respective industry owing to their wide-ranging benefits in terms of abundant raw material sources, ease of processing, versatile usability, exceptional material properties, durability, and cost-effectiveness. Nonetheless, the production of cement is associated with substantial carbon dioxide (CO_2) emissions, thereby contributing significantly to global greenhouse gas levels. This conundrum underscores the pressing need for innovative solutions that can mitigate the environmental impact while preserving the indispensable attributes of cementitious construction materials. This review article delves into the realm of surface treatments as a promising avenue to augment the service life and sustainability of concrete structures. The primary objective of using coating technologies is to curtail the overconsumption of cement and natural resources – such as water, sand, and gravel – by extending the longevity of cementitious construction materials, which contributes to an alleviation in the environmental footprint of cement production and, subsequently, to a reduction in global anthropogenic CO_2 emissions. In this comprehensive study, we discuss three distinct types of established surface coating: (1) organic coatings, (2) coatings based on nanomaterials like graphene, and (3) inorganic coatings. Through a systematic examination of these approaches, we elucidate their mechanisms of protection, highlighting their potential to enhance the durability, resistance to environmental stressors, and overall performance of cementitious construction materials. Based on a comprehensive literature review, we compare the performance of these surface treatments in terms of protecting different cementitious surfaces against different degradation scenarios. Finally, we give an outlook on new innovative approaches for the protection of cementitious surfaces, including the presentation of the concept of incorporating rare earth metal ions into the surface of cementitious construction materials. This could potentially combine the advantages of organic and inorganic surface treatments as well as integral waterproofing.

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Sustainability spotlight

The application of sustainable surface coatings on mortar and concrete is pivotal in addressing environmental concerns associated with traditional construction practices. The indiscriminate use of conventional coatings contributes to carbon emissions, resource depletion, and environmental degradation. Our article focuses on giving an overview of typical coatings, showing their drawbacks, and introducing a way to eco-friendly coatings that not only enhance durability and performance but also align with the UN's Sustainable Development Goals (SDGs). By reducing the carbon footprint and minimizing resource consumption in construction, advancements contribute to SDG 9 (Industry, Innovation, and Infrastructure) and SDG 13 (Climate Action). This article underscores the urgency of transitioning to sustainable practices in the construction sector, promoting a holistic approach to environmental stewardship, and meeting the challenges posed by climate change and resource scarcity.

1 Introduction

Concrete is a composite material made from cement, aggregate (such as sand and gravel), and water. It is one of the most widely used construction materials due to its strength, durability, and versatility.[1,2] However, buildings and infrastructure constructions are exposed to mechanical and chemical effects, causing changes in the material itself.[3,4] Consequently, these effects provoke technologically, ecologically, and economically complex repairs.[5] One approach to bridge the problems caused by corrosion is the passivation of concrete surfaces because the cost of the restoration and protection of concrete structures

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through surface treatments is much lower than the cost of rebuilding. Such passivation can be, for instance, the functionalization with water-repelling films. For example, the cost of sealing the decks and piers of a 61 m-long bridge is less than 1% of the cost of replacing the structure. Although the surface treatment must be renewed about every 5 years, the cost is still less than that of the replacement.[6] In this article, we want to guide the reader through different fields of application of surface coatings on concrete structures as depicted in Fig. 1.

Concrete is inherently porous and has numerous microcracks in the matrix even when unloaded, making it vulnerable to the ingress of water and other aggressive fluids as well as ions soluble in these fluids. A reduced service life over time is expected for concrete infrastructure exposed to an aggressive environment because of physical and chemical degradation.[7] Likewise, concrete infrastructure located near the groundwater table or in a highly humid environment is also susceptible to deterioration due to the ingress of water.[8] This is also the case for concrete in marine environments. Without intervention, significant maintenance for critical infrastructure is required with high associated repair costs. Therefore, to increase the durability of concrete, either integral waterproofing admixtures or surface treatments are used to mitigate this problem. However, the incorporation of integral waterproofing admixtures (such as densifiers, water repellents, and crystalline admixtures) in concrete may harm some concrete properties such as workability and strength.[9]

Peter Thissen

Peter Thissen studied chemistry in Essen, Germany. Then he went to the Max-Planck Institut für Eisenforschung in Düsseldorf. After receiving his PhD in 2009, he was awarded his first DFG grant and then was a postdoctoral researcher in Dallas, Texas. In 2013, he returned to Germany and became head of the model development of mineral interfaces group at the Karlsruhe Institute of Technology. He was awarded a Heisenberg Grant in 2018 for research on the combined mechanical and chemical interactions on cement-bound materials. His research interests include mainly mineral interfaces such as silicates and carbonates, and he is a hybrid in combining both theoretical and experimental work.

This article centers on chemical surface treatments to improve the durability of cementitious construction materials by limiting/preventing the ingress of water and other substances. Depending on the chemical composition of the surface treatment agents, they can be classified into three categories: (1) organic treatments, (2) treatments utilizing nanomaterials, and (3) inorganic treatments. According to their function, coatings can be classified into standard categories: (A) surface coatings form a continuous film on the surface and create a physical barrier to suppress the ingress of aggressive substances. (B) Hydrophobic impregnations make the surface-near zone water-repellent while leaving the pores open. (C) Pore-blocking treatments reduce the porosity of the surface layer by partially filling the capillary pores. (D) Multifunctional surface treatments combine at least two functions. In this article, all types of surface treatment are collectively referred to as coatings, regardless of the different mechanisms of action.

1.1 Chemical composition and microstructure of concrete

The process of making concrete involves mixing the cement with the aggregate and water and – if necessary – additives and additions. By adding water, the hydration of the cement takes place, during which chemical reactions occur between the cement and the water. This hydration reaction leads to the formation of calcium silicate hydrate (C–S–H), which forms

Andreas Bogner

Andreas Bogner studied chemistry in Stuttgart, Germany, where he also did his doctoral thesis in the field of physical chemistry. After receiving his PhD in 2015, he became a postdoc at the Karlsruhe Institute of Technology, where he is now a research group leader for microstructure analysis at the Institute of Concrete Structures and Building Materials. His main research interests are the further development of methods for microstructure analysis of cementitious materials and the investigation of durability-related damage mechanisms of these materials. He also conducts material testing of surface coatings and inspections of producers of coatings.

Frank Dehn

Frank Dehn studied civil engineering in Karlsruhe, Germany, and received his doctoral degree from the University of Leipzig. After receiving his Dr-Ing. he served for almost 20 years as a managing director and shareholder of a large material research and testing laboratory. Since 2018 he is a university professor for building materials and concrete construction at the Karlsruhe Institute of Technology and head of the Institute of Concrete Structures and Building Materials and director of the materials testing and research facility. He is involved in several national and international standardization committees and expert bodies in the field of concrete technology.

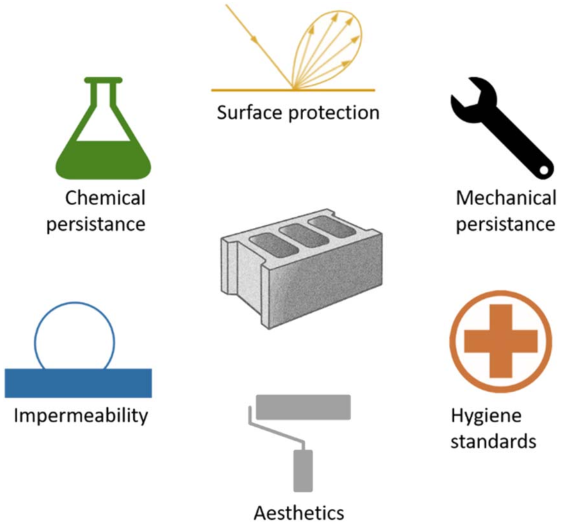


Fig. 1 Important areas of application for coatings on concrete are: Surface protection: a coating can protect concrete from external influences such as UV radiation, weathering, chemical weathering, and wear. Chemical resistance: concrete can be exposed to chemical attacks, especially when used in industrial and agricultural environments, wastewater facilities, or areas with aggressive chemicals. Mechanical resistance: in high-traffic areas such as parking decks, roads, or industrial areas, concrete can be worn down by repetitive loading, traffic, or the use of heavy equipment. Aesthetics: coatings can be used to beautify the surface of concrete or give it a specific texture or color. Impermeability: concrete is naturally porous and can absorb water, which can lead to the ingress of deteriorating substances, or leaching. Hygiene standards: in certain areas such as food processing, hospitals, or laboratories, special hygienic requirements are necessary.

a colloidal gel structure and is responsible for the strength of the concrete.[10,11] Other products of hydration are calcium hydroxide (CH) and various by-products. The aggregates in the concrete serve as fillers around the reaction products – the hardened cement paste – and give the concrete strength and volume. The sand provides an increase of packing density of the concrete, while larger aggregates are leading to mechanical stability and volume filling. The hardened concrete forms a strong, rock-hard structure capable of supporting large compressive but small tensile forces. Typical parameters for characterizing Portland cement-based concretes include the water-to-cement (w/c) ratio, strength after 28 days, and the ratio of calcium silicate hydrate (C–S–H) to aggregates.[12,13] The w/c ratio influences material strength and durability, with lower values typically leading to higher strength. Strength after 28 days provides insights into the development of material strength evolution over time. A higher C–S–H-to-aggregate ratio indicates better bonding, enhancing material strength and durability. These parameters are crucial for material development and optimizing concrete mixtures for various applications.

In addition to Portland cement, the simplest cement, which only consists of the products formed when calcium carbonate is burned with clay, there are several other types of cement. In these, part of the Portland cement is replaced by one or more other components with different reactivity, such as industrial by-products (*e.g.* granulated blast furnace slag, coal fly ash) or natural raw materials such as limestone and quartz powder. This allows the properties to be adapted and the CO_2 footprint to be reduced. Furthermore, concrete can be modified by adding additives such as chemical additives, pigments, or fibers to achieve specific properties such as increased mechanical characteristics (strength, deformation *etc.*), improved resistance to cracking, or better workability. This allows the concrete to be tailored to meet the needs of different construction projects and environments.

Concrete is a porous material with a characteristic pore structure (see Fig. 2),[14,15] whereby the pores can have different sizes and shapes and affect the properties of the material.[16] The pore structure in concrete can be roughly divided into two types: capillary pores and gel pores. Capillary pores are small, interconnected cavities that transport liquids and gases in the

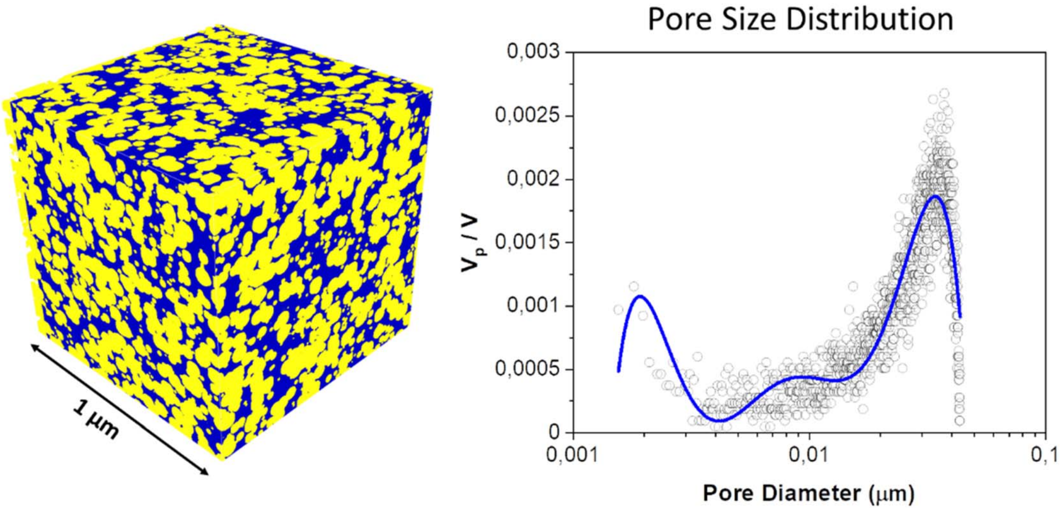


Fig. 2 Left hand: 1 μm^3 cube of simulated C–S–H phases. The yellow color represents the C–S–H phases and the blue color represents the pores. Right hand: typical pore size distribution of C–S–H phases.

concrete. They form during the setting and hardening of the concrete and are typically less than 50 microns in diameter. These pores affect the permeability of the concrete and affect its frost resistance and chemical resistance. The gel pores, also known as hydrated pores, are formed by the hydration reaction of cement with water. They are filled by the hydration products of the hardened cement paste, such as the calcium silicate hydrate gel. The size of the gel pores varies between a few nanometers and a few micrometers[17] and their number and distribution influence the mechanical properties of the concrete, such as its strength and elasticity. The pore structure in concrete affects various properties of the material: a small number of pores and a high share of small pores result in higher strength and density, while a high pore count and larger pores can increase water permeability. A dense pore structure can improve frost-thaw resistance and chemical resistance.

The pore solution in hardened cement paste contains a complex mixture of ions resulting from cement's reaction with water during hydration and interaction with the surrounding environment.[18–20] Typical ions in the pore solution are calcium ions (Ca^{2+}), hydroxide ions (OH^-), sodium ions (Na^+), potassium ions (K^+), sulfate ions ($SO_4{}^{2-}$), and hydrogen carbonate ions ($HCO_3{}^-$).[18] These ions mainly originate from the dissolution of hardened cement paste phases such as calcium silicate hydrate (C–S–H), calcium hydroxide ($Ca(OH)_2$), and other components.[21]

The pore solution in hardened cement paste is highly reactive due to the presence of hydroxide ions, which have a strongly alkaline pH value (~13.6). This alkaline pH value affects the reactivity of the pore solution and allows various chemical reactions with various compounds and has important effects on the properties and behavior of the hardened cement paste. For example, the high pH value of the pore solution affects the solubility of CO_2 and leads to the formation of calcium carbonate ($CaCO_3$). The carbonation reaction as well as the reaction with water from the environment have an important impact on the highly reactive surface of concrete (see Fig. 3).[22,23] The humidity of the air (>30%) combined with earlier thermodynamic studies now allows one to conclude that the mechanism of CO_2 reacting with wollastonite (001) covered by more than one monolayer of H_2O is the correct one to describe these highly interesting phenomena. It is the only way to explain (1) the heterogeneous distribution of carbonates on the surface and (2) a coverage partially higher/lower than one monolayer. This has to be kept in mind for discussing the interactions of coatings with concrete.

2 Surface treatment to improve the properties of concrete

The rapid reaction of cement with CO_2 can be explained based on the specific pore structure and the chemical composition of the pore solution. The pore structure of the cementitious construction material provides a large surface area for gas exchange, while the pore solution contains reactive ions involved in CO_2 uptake.[24–26] The capillaries and voids allow rapid diffusion of CO_2 into the hardened cement paste matrix where the pores provide a large surface area for CO_2 to adsorb and react. Second, the pore solution in the cement contains reactive ions, especially calcium ions (Ca^{2+}). These ions react with CO_2 to form various carbonate-containing compounds. The most important reaction, known as carbonation, is the one between calcium ions and CO_2 which results in the formation of the solid mineral calcium carbonate ($CaCO_3$). Carbonation results in the conversion of calcium silicate hydrate (C–S–H), a main component of hardened cement paste, into calcium carbonate. This process can result in volume reduction (so-called carbonation shrinkage), changes in pore size and distribution, and an increase in strength at least of the carbonation affected concrete surface.[27–29]

Seawater contains a variety of salts and ions originating from the interaction of water with the minerals of the earth's crust, as well as from atmospheric deposition and geological processes. The most important ions in seawater are sodium ions (Na^+), chloride ions (Cl^-), sulfate ions ($SO_4{}^{2-}$), magnesium ions (Mg^{2+}), calcium ions (Ca^{2+}), potassium ions (K^+), carbonate ($CO_3{}^{2-}$) and bicarbonate ions ($HCO_3{}^-$). The concentrations of these ions can vary, but there are generally accepted average values for seawater salinity based on standard measurements. The salinity, which represents the total amount of dissolved salts in seawater, averages about 35 grams of salt per kilogram of seawater (g kg^{-1}) or 35 parts per thousand (‰). It is important to note that the exact composition of seawater varies in different regions and depths of the ocean, depending on factors such as geographic location, currents, sediments, and other environmental conditions.

When cementitious construction materials come into contact with seawater, the seawater penetrates the pores of these materials and causes an ion exchange reaction. The reactive ions in the pore solution, such as calcium ions (Ca^{2+}), can react and exchange with the ions in the seawater. Typically, there is an exchange of sodium ions (Na^+) from the seawater with calcium ions in the cement, releasing sodium ions into the pore solution and calcium ions into the seawater. In addition, other ions such as chloride ions (Cl^-) and sulfate ions ($SO_4{}^{2-}$) are also exchanged between the pore solution of the cementitious binder and the seawater. The exact composition of the exchange depends on the concentrations and specific conditions of the seawater and binder. These reactions can lead to changes in the chemical composition of the cementitious construction material, especially in the pore solution, resulting in the formation of mineral phases and alteration of the original microstructure.

Coatings of concrete surfaces serve to protect the concrete from various harmful influences. A crucial factor in this protection lies in the difference in the diffusion coefficients of water between the concrete and the coating material. The diffusion coefficient of water in concrete is typically in the range of 10^{-9} to 10^{-12} m^2 s^{-1}.[30–34] In comparison, many coating materials have significantly lower diffusion coefficients, for example in the range of 10^{-11} to 10^{-14} m^2 s^{-1}.[35–38] By using a coating with a lower diffusion coefficient than the concrete itself, the diffusion of water into the concrete is significantly

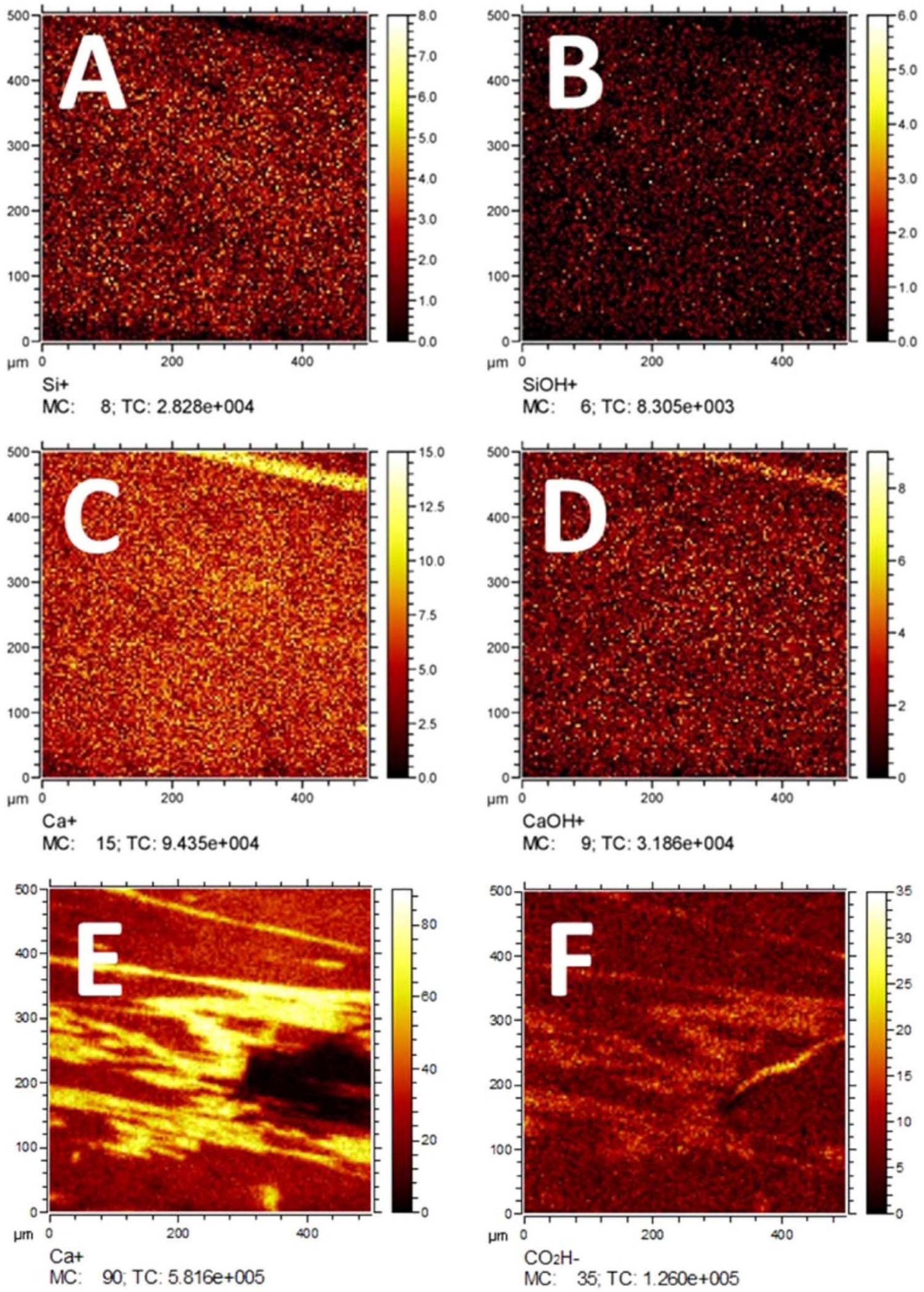


Fig. 3 500 × 500 µm Time-of-Flight Secondary-Ion Mass Spectrometry (ToF-SIMS) mappings of the wollastonite surface are depicted. (A)–(D) show representative results of the wollastonite (001) after sputtering the surface. Sputtering was performed with an argon ion beam energy of 2 keV on a 2 × 2 mm^2 spot. In this state, several considerations are in order. First, Ca and Si are distributed homogeneously over the surface. Second, we can confirm a coexistence of Ca–OH and Si–OH groups which are also homogeneously distributed. After exposure to air for 24 h, the distribution of Ca has changed into an inhomogeneous one, as can be seen in (E), and is directly correlated to the distribution of carbonates, shown in (F). Reprinted with permission from ACS Applied Materials & Interfaces 2015 7 (8), 4706-4712. Copyright 2023 American Chemical Society.

reduced. This results in improved durability and lifespan of the concrete by reducing the penetration of water, chemical substances, and harmful pollutants. A coating with a low diffusion coefficient acts as an additional barrier between the concrete surface and the surrounding environment, effectively protecting the concrete against corrosion and chemical attack, as well as – depending of the type of coating – possibly also against wear and erosion. With a low diffusion coefficient in the coating, the risk of freeze–thaw cycles, which can lead to damage to the concrete surface, is also minimized. By reducing water diffusion, water penetration into the concrete is reduced, minimizing the risk of volume changes due to freezing and thawing. This reduces the likelihood of cracks and spalling in the concrete surface. However, it should be noted that the exact diffusion coefficient values are highly dependent on the specific coating materials and conditions. An accurate determination of the diffusion coefficients usually requires specific laboratory tests and analyzes to evaluate the effectiveness of the coating concerning water diffusion.

Carbonation and chloride ions are known to be the two major factors responsible for the premature corrosion of steel reinforcement in concrete. Surface coatings on concrete can provide effective and efficient protection for both concrete and the steel embedded in it and can enhance the long-term durability of concrete materials and concrete structures exposed to aggressive environments. In practice, concrete is often cracked, and the crack-bridging ability of coatings is an important factor to be considered in evaluating their performance characteristics. Natural exposure tests need therefore be carried out with the coatings stretched over cracks.[39]

In the context of solutions, the Debye-Hückel theory provides a mathematical framework for describing these interactions, particularly in electrolyte solutions. This theory demonstrates that in a dilute electrolyte solution, the logarithm of the ionic activity coefficient is linearly proportional to the square root of the ionic strength, highlighting the significance of the Bjerrum length (see Fig. 4) and, subsequently, the diffusion coefficient.[40–42]

This intricate interplay between diffusion, electrostatics, and molecular interactions has profound implications for a myriad of fields, particularly in the natural world. For instance, in biological systems, the diffusion of ions and molecules across cell membranes is crucial for various cellular processes, and the Debye-Hückel theory aids in understanding these transport phenomena. Moreover, the polarity of molecules plays a decisive role in their diffusion behavior, as polar molecules tend to interact more strongly with the surrounding medium, affecting their diffusion rates.

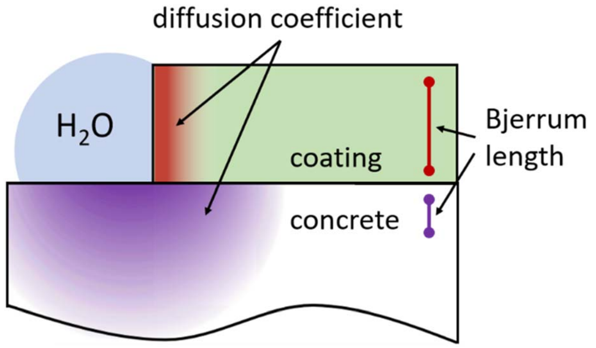


Fig. 4 The diffusion coefficient, often denoted as *D*, plays a pivotal role in understanding various processes in the realm of physical chemistry. It is a measure of how quickly molecules or ions move through a medium. One fundamental relationship that emerges from this is the inverse proportionality between the diffusion coefficient and the Bjerrum constant. The Bjerrum constant, typically symbolized as ξ, is the separation at which the electrostatic interaction between two elementary charges is comparable in magnitude to the thermal energy scale. In coatings the diffusion coefficient of water is smaller and therefore the Bjerrum length is larger than in concrete.

The chemistry of coatings, on the other hand, represents a distinct domain where the diffusion coefficient and its underlying principles find practical application. Surface coatings are often designed to modify the properties of materials, offering protection against environmental factors and enhancing durability. Understanding the diffusion of active components within these coatings is crucial in tailoring their performance. For example, in anti-corrosion coatings, the diffusion of corrosion inhibitors within the coating matrix is essential for providing long-term protection to underlying substrates. The diffusion coefficient not only governs the rate at which these inhibitors migrate to the coating's surface but also influences their interaction with aggressive species.

The major objective of hydrophobic treatment is increasing the contact angle of water and reducing the surface free energy of the cementitious construction material like concrete or mortar.[43] According to the equation of Young-Dupre

$$\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} = \cos\theta \tag{1}$$

where γ_{SV} is the surface free energy of the solid in contact with vapor, γ_{SL} is the solid–liquid interfacial free energy and θ is the contact angle, a less wetting surface will occur with the increase of the contact angle, since $\cos\theta$ is decreasing as θ increases. The surface becomes hydrophobic when the contact angle is greater than 90°.[44,45] An ideal hydrophobic product will prevent the penetration of water and water-soluble ions, but will permit the water vapor exchange.[46] In addition to this, the most suitable coating for the protection of cementitious construction materials should also have a combination of the following properties: gaseous and liquid resistance, good adhesion and crack-bridging ability, and alkali resistance.[47] Some surface treatments can even protect cementitious materials when applied after there are already alterations due to weathering.[48,49]

3 Comparison of surface treatment performances

This chapter gives an overview of important parameters to assess the performance of surface treatments of cementitious construction materials for different areas of application. It is discussed, which type of surface treatment offers the best performance for different applications. In addition, the methods to determine the quality of protection are briefly discussed. There are two general types of methods to investigate the durability of the surface treatments: (I) direct methods (like Infrared Spectroscopy (IR), Scanning Electron microscopy with Energy Dispersive X-ray Analysis (SEM/EDX) and MALDI-TOF) give information about the presence and the degradation of the surface treatment and (II) indirect methods, which characterize the performance of the surface treatments over time (under natural or accelerated weathering).[50]

Many different types of surface treatment are used to improve the durability of cementitious construction materials. It is difficult to compare the effect of these surface treatments, firstly due to the diversity of cementitious materials used in different studies (concrete or mortar, different w/c, different types of cement, different age of the specimen) and secondly due to differences in the application of the surface treatments (*e.g.* applied mass per surface, type of application, type and duration of curing, age of testing). In addition, there are different parameters used to assess the performance of surface treatments even concerning one degradation mechanism of the cementitious construction materials. The conditions for similar tests can also vary (different duration, different concentrations of ions or gases, different temperature, and different humidity).

Thus, the comparison of the performance of the surface treatments in this review focuses for each topic mainly on one parameter and this parameter is for each study normalized on the value for the untreated reference material. Other good overviews of the assessment of performance can be found in the given reviews.[51–53]

3.1 Water permeability

Since water and water-borne ions are essential for many forms of deterioration mechanisms on and in concrete, high resistance to water penetration is an important criterion for surface treatments. Parameters to determine the water permeability are water absorption, capillary water suction as the relative capillary index, water permeability index, and contact angle.[54] Values for water absorption are calculated based on the difference in mass of specimens in the wet state and after oven drying at 105 °C until constant mass. To determine the capillary water suction, the specimens are standing in a small layer of water and the change in mass relative to an untreated reference is determined. The Autoclam method is often used to obtain the water permeability.[55]

Fig. 5 gives an overview of exemplary results of the relative water absorptions of concretes and mortars with different surface treatments. The lower the value, the higher the reduction in water absorption became by the surface treatment in comparison to the untreated substrate.

Pigino *et al.* reported a strong reduction of water absorption after the application of tetraethylorthosilicate (TEOS) on concrete almost independent of the water-to-cement ratio.[56] They found that capillary suction leads to deposition of the reaction products mainly in small pores. However, Hou *et al.* found for mortar at 50 °C only a small reduction of water absorption, which could be improved by the addition of colloidal nano-SiO_2.[57] A higher w/c resulted in a more pronounced reduction of water absorption. In another study, they found that colloidal nano-SiO_2 decreases the transport properties of hardened cement pastes mainly due to its blocking of pores of about 0.1 μm, while TEOS can decrease both the pore volume content and the sizes of the threshold pores smaller than 0.1 μm. The linear reduction of the transport properties was explained with the reduction of the capillary pores smaller than 0.1 μm.[58] Application of TEOS by brushing resulted in an experiment conducted by Franzoni *et al.* in a similar performance as reported by Hou *et al.*, although, the former found a significantly better performance if TEOS was applied by immersion.[58,59]

For a variety of different inorganic coatings, Jia *et al.* found a similar reduction of water absorption, mainly due to blockage of pores larger than 100 nm.[60] Nevertheless, there was only a small decrease in the water transport properties. Mirza *et al.* conducted one of the few studies comparing several treatment agents of the same type.[61] Given in Fig. 5 are the mean values, but they found for each type one or two outliers, which showed worse performance than the untreated reference. In their experiments, silicate had the best performance, and acrylic coatings were the worst. Zhu *et al.* determined the coefficient of capillary suction instead of water absorption and therefore this normalized parameter is shown in Fig. 5.[62] They reported a good performance of a silane paste. They also compared the effect of silane treatment of concrete made with recycled aggregate concrete for which they observed a larger impregnation depth than in natural aggregate concrete. The higher porosity of the recycled aggregate concrete resulted in a more pronounced improvement of the protection against water absorption. Experiments conducted by Levi *et al.* lead to the conclusion, that a fluorinated polyurethane showed a better performance than a commercial silane, which was more effective than a commercial siloxane.[63] All three types of surface treatment offered a stronger reduction in normalized water absorption for older concrete than for younger concrete.

Medeiros *et al.* reported a strong reduction in water transport for surface treatments based on silane/siloxane, acrylic, and especially polyurethane.[64,65] They found, that dispersing the silane/siloxane in organic solvent resulted in a higher efficiency in decreasing the water penetration compared to dispersing in water and explained this with the deeper penetration in concrete due to the lower viscosity of the solvent. The results of two different surface treatments for each type are shown for the study of Almusallam *et al.*, which give an impression of the scattering in performance.[66] From this it can be only derived, that the polymer emulsions offered the least protection of the mortar.

Summarizing the results in Fig. 5, it can be concluded, that surface treatments show the strongest reduction of water absorption in older concrete and cementitious materials with a higher water-to-cement ratio. These materials have a higher water absorption in their untreated state and therefore a comparable absolute reduction by coating results in a higher relative reduction of water absorption.

In the following, we will report on findings from other sources, which aren't depicted in Fig. 5, since no value for the untreated reference material was available. Nolan *et al.* found that silane surface treatment can reduce water absorption in combination with controlled permeability formwork – a concept, that allows excess air and bleedwater from the setting concrete to drain out of the formwork and therefore leading to a more dense near-surface concrete.[67] In this combination, the special formwork is mostly responsible for the reduction in air permeability and the silane is mainly responsible for the reduction in sorptivity.

Ma *et al.* observed, that the amount of silane coupling agent used increases the penetration depth of this silane coupling

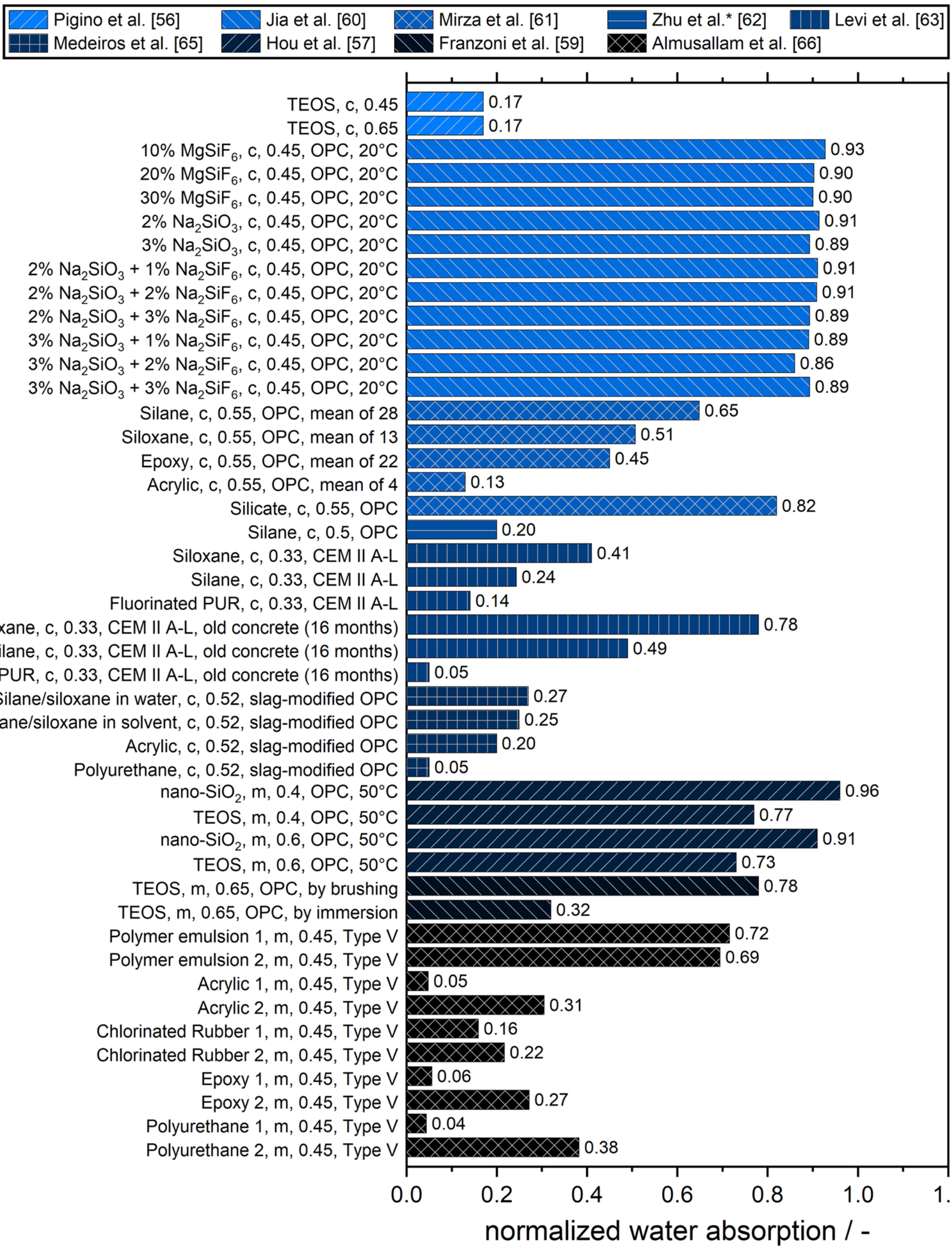


Fig. 5 Comparison of normalized water absorption of cementitious material with surface treatment. For each literature source, the values are normalized on the untreated cementitious material. Given is the type of binder (c = concrete or m = mortar), then w/c-ratio, then the type of cement and additional information where applicable. (* = Normalized coefficient of capillary suction).

agent and decreases the amount of absorbed water as well as the chloride penetration depth.[68]

The surface water content during the application has a strong influence on the silane impregnation depth of cement-based materials, as Bao *et al.* demonstrated. The mortars with higher water-to-cement ratio have deeper penetration of silane impregnation. As the initial moisture content at the surface of mortars increases, the depth of surface silane impregnation gradually decreases. Therefore, the initial water content (determined by water-to-cement ratio at environmental conditions) affects the water repellency of surface impregnation of cementitious materials. The dosage during application affects the performance: the amount of absorbed water and the coefficient of capillary absorption were averagely reduced by approximately 0.7 times when the dosages of the surface impregnation silane gel were increased from 200 to 600 g m^{-2}.[69]

Baltazar *et al.* studied the influence of surface preparation of the cementitious substrate before silicate surface treatment on the performance. In terms of water permeability, the best performance among the treated specimens was obtained for specimens not subjected to any type of surface preparation. This means that there is no advantage in increasing the roughness of the substrate before the application of silicate-based impregnation products for water-ingress protection purposes. The highest moisture content improved the performance of the impregnation – especially for the more porous concrete – most likely because the increased moisture content of the substrate promoted the stagnation of the impregnation product at the specimens' surface, resulting in a more impermeable surface.[70]

Courard *et al.* reported for silanes and siloxanes, that this hydrophobic treatment can significantly increase the contact angle of water. After accelerated carbonation aging for one month, the contact angle of water slightly decreased, but the hydrophobic performance was still within the requirement described in the European standard EN 1504-2.[43]

A comparison between film formers and penetrants as water-repellent treatment was conducted by Bader *et al.* They observed, that both types of treatment led to hydrophobic properties by reducing the surface free energy with the extent depending on the chemical functionalities of the used water-repellent agents. The film former successfully hindered water from extracting the soluble calcium-bearing constituents from the hardened cement paste and, therefore, prevented the deposition of efflorescence onto the surfaces of high-performance concrete. The smaller penetration depths of the penetrants due to the low permeability of the investigated high-performance concrete most likely allowed for the formation of transport pathways into the bulk material, thus allowing water to extract the soluble calcium-bearing constituents.[71]

Liu *et al.* investigated the effect of adding nano-materials like $CaCO_3$, SiO_2, and TiO_2 to a silicon emulsion surface treatment. The found a significant improvement in the protection of the concrete impregnated with nano-modified silicone emulsion: the water absorption of concrete decreased to 19.39% of the control group with the addition of nano-SiO_2 modified silicone emulsion.[72]

Tian *et al.* compared the performance of ISR (integral water-repellent treatment) and SSR (surface water-repellent treatment), concluded, that both methods can improve the durability of concrete, and provided the following explanation. In contact with hydrostatic water, capillary suction is effectively suppressed both by ISR and SSR. SSR achieves a higher efficiency by sealing the pores on the concrete surface and repelling water from the surface of the test specimen. For concrete with ISR with 4% silicone resin emulsion, a reduction of the water absorption speed by approx. 50% compared to untreated concrete is stated. Applying 600 g m^{-2} silicone resin on the surface resulted in a decrease in the water absorption rate of the concrete specimen by 91.7%.[73]

3.2 Chloride permeability

There are several mechanisms by which chloride transports into cementitious construction materials, including diffusion under the influence of a concentration gradient, absorption due to capillary action, and migration in an electrical field. Diffusion is the primary mechanism of chloride transport in concrete if there is no electrical field present and if the water saturation in the concrete pore structure is stable at 60–70%.

The diffusion coefficient is often used as a parameter to measure the permeability of an ion. However, the diffusion coefficients of ions are dependent on other ions and subsequently, there are different values for the diffusion coefficients of an ion, depending on the counter ion. Therefore, it should always be stated, in relation to which other ions a diffusion coefficient was measured. However, in cementitious materials, there is always a variety of ions present. Also, the concentration of ions can influence this coefficient.[74–77]

The diffusion coefficient of chloride ions in water is about $2.03 \times 10^{-9}\ m^2\ s^{-1}$ and in seawater $1.72 \times 10^{-9}\ m^2\ s^{-1}$.[78,79] For diffusion of chloride ions in mature OPC pastes, the activation energy was shown to be substantially higher than that for diffusion of the ions in normal aqueous solutions. Investigations with various types of cement confirmed that diffusion of chloride ions is strongly influenced by cement composition. Blended cement pastes containing pulverized fuel ash or granulated blast furnace slag showed lower diffusion rates at 25 °C than OPC pastes of the same w/c and these differences could not be explained by variations between the pore structure of these materials.[80] The w/c ratio also has a strong influence on the diffusion coefficients, since the pore structure depends on it.[81,82] There are several publications dedicated to the testing and determination of chloride diffusion coefficients in concrete.[83–91]

Fig. 6 gives an overview of the diffusion coefficients of chloride determined under different conditions with different methods for different cementitious construction materials. The results of Geng *et al.*, Aguiar *et al.*, Hassani *et al.*, Zhang *et al.*, and Coppola *et al.* clearly show that the diffusion coefficient increases with increasing water-to-cement ratio, which is related to an increase in porosity.[92–96] On the contrary, no significant differences are observed in chloride penetration changing the cement dosage at the same w/c ratio. The type of cement considerably affects the chloride diffusion in concrete; in particular, it has been confirmed that Portland (composite) limestone cement (CEM II) should be avoided in environments rich in chlorides, but instead pozzolanic (CEM IV) or blast furnace (CEM III) cement should be preferred.[96] Chindaprasirt *et al.* have drawn a similar conclusion for mortar, that under normal circumstances the incorporation of pozzolans such as fly ash (FA), palm oil fuel ash (POA), and rice husk ash (RHA) is very beneficial to the performance in term of chloride resistance. However, the resistance changes when the cementitious construction material is carbonated. Then the resistance to chloride penetration of mortar containing pozzolans is lowered depending on the type and level of replacement. Without pozzolan, OPC mortar contains a high amount of calcium hydroxide and when subjected to carbon dioxide, the effect of carbonation is thus small. However, the incorporation of pozzolan reduces the amount of calcium hydroxide and thus decreases the pH value of mortar. When such a mortar is exposed to carbon dioxide, the pH value decreases further and renders the mortar susceptible to chloride attack.[97]

Coppola *et al.* also observed a strong influence of the migration mechanism on the diffusion coefficient. Accelerated tests lead to much higher diffusion coefficients and even to a different order of values between different cement types.[96] The influence of different conditions for the measurements was investigated by Qu *et al.*, who found small variations between

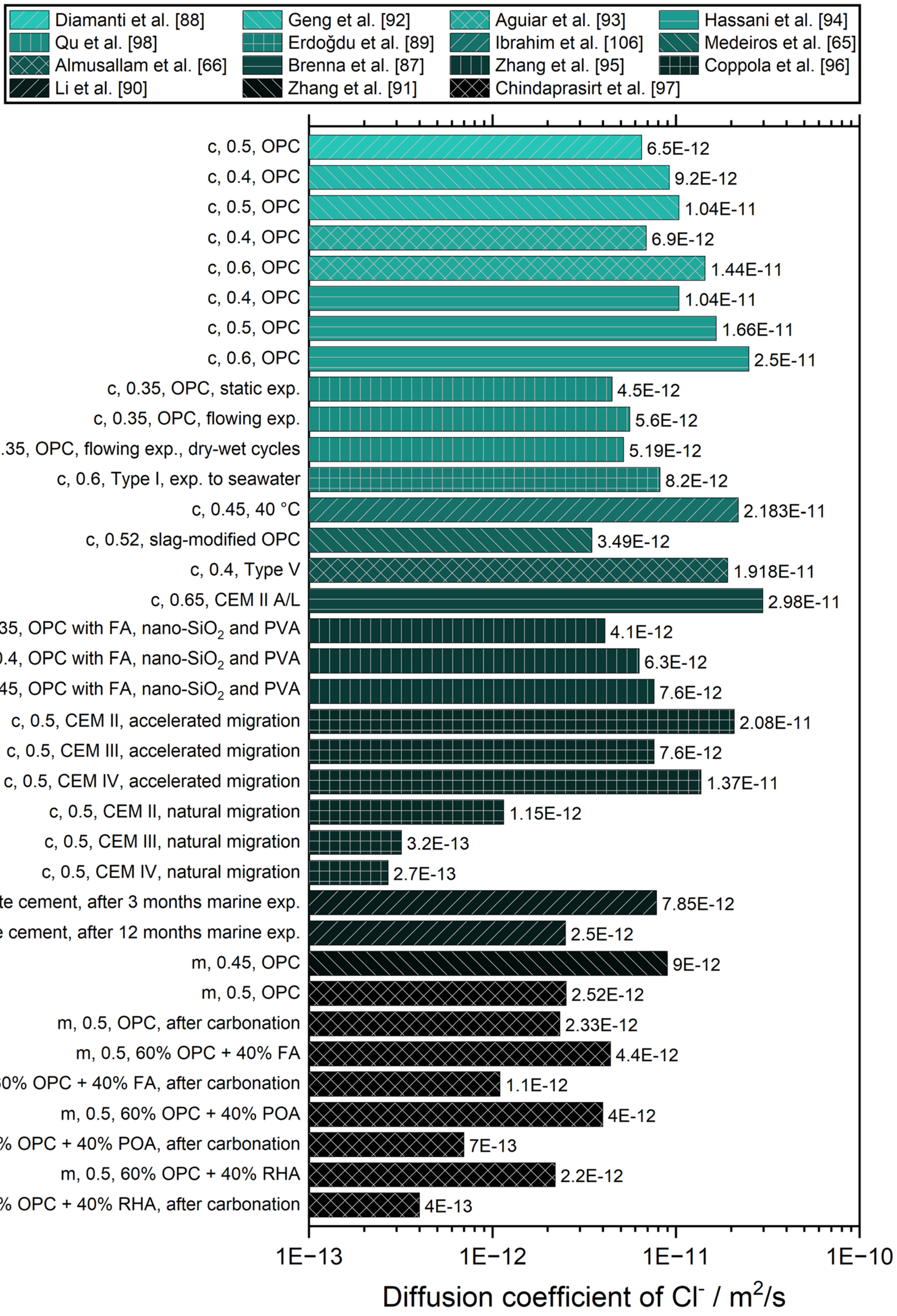


Fig. 6 Chloride diffusion coefficients in cementitious construction materials under different conditions. Given is the type of binder (c = concrete or m = mortar), the w/c-ratio, the type of cement, and additional information where applicable.

static exposure to chlorine solution, flowing exposure, and flowing exposure combined with dry–wet cycles.[98]

A comparison of the performance of different surface treatments in preventing chloride diffusion is summarized in Fig. 7. For the sake of comparison, besides organic and inorganic surface treatments also polymer modified concrete (PMC) coatings are shown. Interestingly, the studies by Aguiar *et al.* included an epoxy coating which, in their experiment, completely prevented the diffusion of chloride.[93,99]

In addition to the data plotted in Fig. 7, further findings from other sources are presented in the following. It was shown for concrete, that sodium silicate-based impregnates are ineffective at preventing the ingress of water and chloride ions in humid subtropical marine environments while surface impregnation

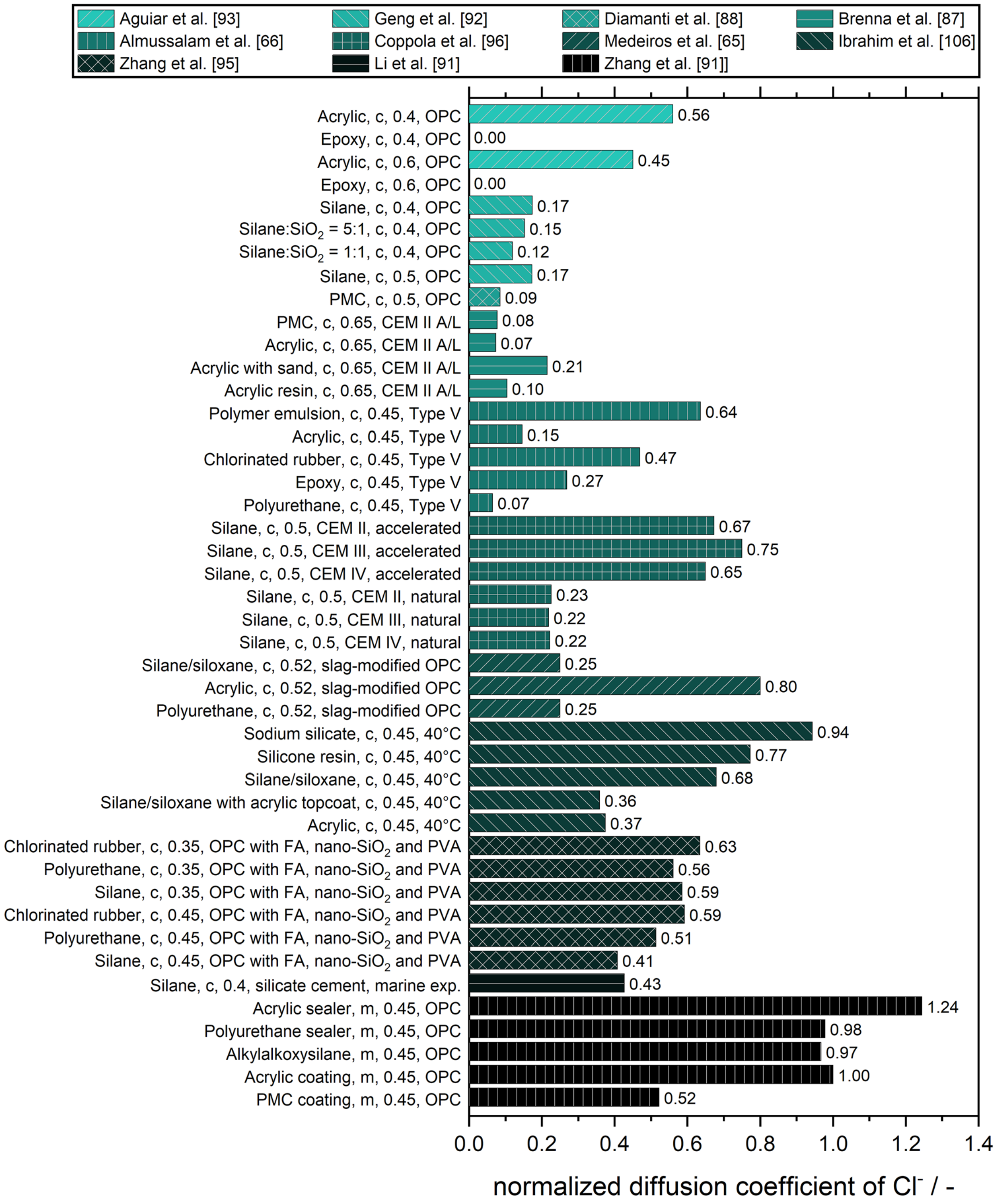


Fig. 7 Comparison of normalized diffusion coefficients of chloride of cementitious construction materials with surface treatment. For each literature source, the values are normalized on the diffusion coefficient of Cl^- given for the untreated material by the authors. Given is the type of binder (c = concrete or m = mortar), the w/c-ratio, the type of cement, and additional information where applicable.

of concrete with silane has proved to be a highly efficient measure to reduce water absorption and to build a chloride barrier which prevents chloride penetration into the pore structure during accelerated dry–wet exposure to salt water.[48]

The mechanism of action of the silane-based surface-applied corrosion inhibitor in slowing down the chloride penetration inside the matrix of hardened cement paste is basically due to the water-repellent effect as confirmed by data of concrete electrical resistivity and accelerated chloride migration test results.[96] The concrete specimens where the surface treatments include the application of a coating procedure perform better in reducing the chloride ingress and air permeability than the specimens with the penetrant treatments. The long-term performance of these surface treatments with coating on the top of the concrete surface is also better than that of the penetrant treatments.[100]

Medeiros *et al.* found, that the application of a hydrophobic agent results in a minor reduction of the chloride diffusion coefficient (11% and 17% for the silane/siloxane dispersed in water and solvent, respectively).[64] They concluded, that the main effect of hydrophobic treatment is the reduction of the sorptivity of the concrete (reduced by 2.12 and 7.0 times for the silane/siloxane dispersed in water and solvent, respectively) and pointed out, that although the hydrophobic agent does not markedly influence the chloride diffusion coefficient (in saturated concrete), these materials effectively inhibit water penetration (which can be contaminated with chloride ions) by capillary suction. Since according to Kropp, the capillary suction mechanism is one of the main factors responsible for the chloride contamination of the reinforced concrete in non-saturated conditions, it can be concluded that the hydrophobic agents are efficient only if the cementitious material is not saturated with water. In the latter case, the main transport mechanism would be capillary suction.[101] Therefore, in saturated conditions and water under pressure conditions, hydrophobic surface treatments do not provide satisfactory effectiveness.[64]

In another study, they reported a reduction of the chloride diffusion coefficient after treatment of a concrete surface using sodium silicate, indicating only a small reduction of the immersion water absorption of the concrete. However, the capillary water absorption of such treated concrete was highly reduced. The treatment with sodium silicate could increase the service life in the same way as silane/siloxane pore liner and an acrylic coating. However, using a polyurethane coating offered the best protection.[102]

Liu *et al.* found that the addition of nano-materials ($CaCO_3$, SiO_2, and TiO_2) to a silicone emulsion increased the chloride ion resistance rate by 76.13%.[72,103] A similar study showed that adding Submicron/nano-carbon to an epoxy coating increased the resistance to chloride diffusion by 66%.[104]

3.3 Carbonation

The carbonation depth is determined after a chosen time of exposure of the specimen to CO_2: either the natural concentration in air or a higher concentration (usually between 3% and 20%) in accelerated lab experiments. Therefore, the specimen is split in two halves and the acid-base indicator phenolphthalein is applied on the new surfaces to be able to detect the depth until the carbonation reaction has reduced the pH value of the cementitious material.

It was shown that a change in CO_2 concentration will not change the carbonation process. Since carbonation occurs instantly, at the carbonation front a CO_2 concentration of zero is maintained. The only effect of a high CO_2 concentration is a faster transport of the CO_2 molecules to the interface between air and pore solution in the pores and thus a faster reaction process. Therefore, despite the fact that the carbonation process itself does not change, higher CO_2 concentrations still may involuntarily give rise to other effects, ultimately under- or overestimating the service life of concrete structures.[105]

Fig. 8 gives an overview of the carbonation depths of cementitious materials with different surface treatments normalized on the values obtained for the untreated materials as a reference.

Pigino *et al.* found that applying TEOS to concrete made with ordinary Portland cement (CEM I) with w/c = 0.45 completely prevented carbonation.[56] A similar observation was made by Ibrahim *et al.* for a silane/siloxane as well as for an acrylic coating.[106,107] Beushausen *et al.* reported a low normalized carbonation depth for an acrylic dispersion.[108] They also studied the influence of weathering on the performance of the surface treatments. Surprisingly, prolonged weathering increased the carbonation resistance of the samples coated with acrylic dispersion and acrylic resin. They attributed this to the increasing maturity of the concrete and the coating over time, resulting from temperature and moisture exposure in the weathering chamber, in combination with good resistance against UV exposure. However, they restrict their findings to the fact that cracks could occur in larger samples and real structures when exposed to temperature cycles in real environments, which probably would lead to the expected reduction in protection over time.

Regarding the influence of water-to-cement ratio on the performance of surface treatments, Courard *et al.* concluded, that the impact of hydrophobic impregnation on carbonation is directly related to w/c ratio and active product concentration: for lower w/c ratio (0.5 and 0.6) the carbonation depth decreases when the hydrophobic impregnation concentration increases and/or when the hydrophobic impregnation penetration depth increases. For w/c = 0.5, the hydrophobic treated specimens showed lower carbonation depth than untreated concrete and the protection increased with increasing active concentration, which led to the conclusion, that the repulsive force on water seems to be effective for reducing the carbonation process. To give some values, the carbonation depth of untreated concrete was 9.7 mm after 168 days of carbonation with 3% of CO_2 whereas the surface treatment with silane 99% reduced the carbonation depth to 5 mm. Such a treatment didn't seem to have a positive effect on higher w/c ratios like 0.7. For the concrete with w/c = 0.7, the hydrophobic treated specimens have slightly higher carbonation depth than untreated concrete. This was independent of the concentration of the active product, which they attributed to the interaction between the hydrophobic treatment and the porosity as well as pore structure and moisture content of concrete: hydrophobic treatment on the surface of larger pores has less influence on flow as the ratio (volume of fluid/surface of the pore) is higher.[43]

Since the carbonation starts with the diffusion of dissolved CO_2 molecules in pore water of concrete and then the formation of calcium carbonate with calcium hydroxide (portlandite) *via* carbonic acid, this process strongly depends on the CO_2 concentration, porosity and pore structure, and moisture content of concrete.[109–111] In cementitious materials with higher w/c more large pores are present, causing CO_2 gas to penetrate the concrete smoothly (the CO_2 gas permeability is not influenced after the hydrophobic treatment). However, the drying rate of concrete is fast and not influenced by the hydrophobic treatment for w/c = 0.7. Thus, the content of water in the pores favors the carbonation process after the hydrophobic treatment. Therefore, the carbonation depth in surface-treated concrete is slightly increased in comparison with the untreated concrete at w/c = 0.7.[43]

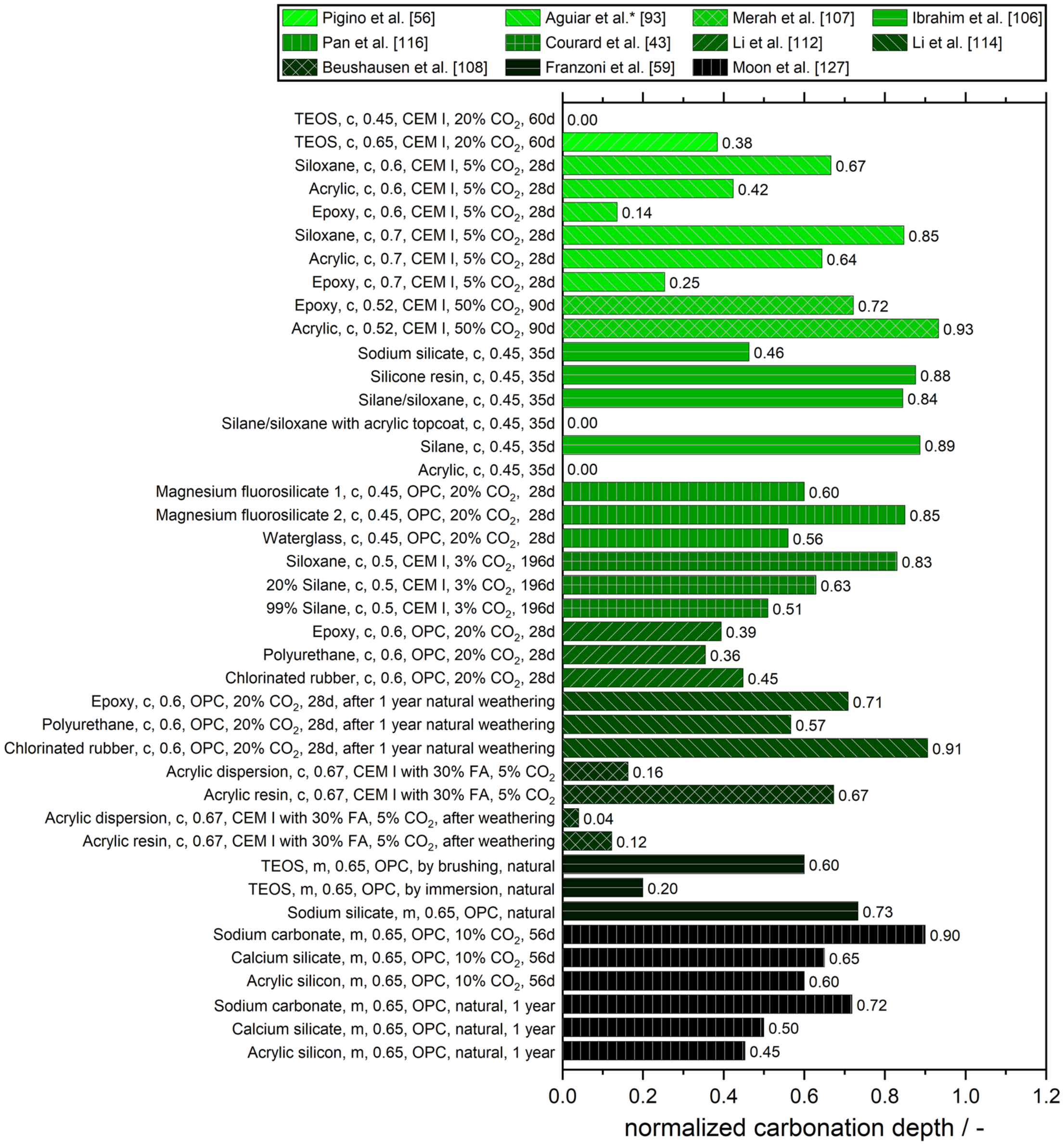


Fig. 8 Comparison of normalized carbonation depth of cementitious construction material with surface treatment. For each literature source, the values are normalized on untreated cementitious material. Given is the type of binder (c = concrete or m = mortar), then w/c-ratio, the type of cement, and additional information where applicable. (* = Normalized coefficient of carbonation coefficient).

Li *et al.* compared the performance of three types of organic film coatings: polyurethane (PO), epoxy resin (EP), and chlorinated rubber (CR), and concluded, that such organic film coatings can significantly improve concrete carbonation resistance and that a thicker film coating can result in better protection.[112] The ranking of the performance was as follows: PO > CR > EP. The CO_2 diffusion coefficients of the organic coatings before aging range between 10^{-12} and 10^{-10} m^2 s^{-1}, whereas that of ordinary concrete is approximately 10^{-8} m^2 s^{-1}.[113] Organic film coatings have higher densities than normal concrete; thus, the former can restrain the diffusion of CO_2 into concrete and enhance concrete carbonation resistance. Regarding the aging of these materials, they found that carbonation resistance gradually decreases and exhibits an S-shaped curve. This degradation of coating carbonation resistance is explained by defects in organic coatings caused by aging, such as granulation, porosity, and cracking. They observed service lives of the coatings under ultraviolet aging, coupled aging, and natural aging within the ranges of 19.4–29.2 days, 13.0–19.6 days, and 1.5–3.0 years, respectively. The ranking order of the weathering resistances of the coatings was as follows: PO > EP > CR, with polyurethane being the surface treatment with the strongest protection and the best resistance against weathering.[43]

The same group reported in another study values for service lives of concrete regarding carbonation resistance, which are 46.5 years for uncoated concrete and 51.3, 51.8, and 53.7 years for concrete with CR, EP, and PU coatings, respectively, using 20 mm of concrete carbonation depth as a criterion. The critical carbonation depth depends on the depth in which steel reinforcement is located, which can corrode if the carbonation has lowered the pH value to such an extent that the passivation layer around the steel from being surrounded by the highly alkaline concrete is lost. After the end of the service life of the coatings, they no longer have any influence on the development of concrete carbonation. However, the carbonation resistance of concrete can be improved again through effective repainting of coating, which will prolong the service life of concrete against carbonation.[114]

Park *et al.* measured the diffusion coefficient of carbon dioxide with a permeation-measuring apparatus using a differential pressure method to assess the performance of coating materials and obtained the following order: acrylic, epoxy, polyurethane, and polyvinyl chloride (not shown in Fig. 8).[113] However, anti-carbonation coatings must not only prevent the penetration of gas and water, but at the same time, they must be permeable to water vapor to allow the support to breathe.[115]

Epoxy resin showed better protection than acrylic and siloxane resins in the study conducted by Aguiar *et al.*[99] They also did a service life analysis and concluded, that desired service lives of concretes of 50 or 100 years were only obtained with the use of surface protection treatments. For example, with the partial safety factor method for the strongest exposure to carbonation (exposure class XC4) for concrete with $w/c = 0.6$ without surface protection treatment in humid regions a service life of 40 years was estimated while this could be increased to 99 years, 284 years and >500 years for siloxane, acrylic and epoxy respectively. However, this estimation doesn't take degradation of the surface protection into account, which would result in much lower realistic values.[99]

A comparison of inorganic surface treatments was conducted by Pan *et al.* Their results indicated that magnesium fluorosilicate and waterglass decreased the carbonation depth and increased surface hardness of concrete, while their effects were limited on compressive strength. A greater reduction in carbonation was found when sodium fluorosilicate pretreatment was used because it could not only accelerate the hardness of waterglass but also react with cement.[116] All three treatments showed an obvious increase in the carbonation resistance of concrete. The carbonation depth of concrete was reduced by about 15–40% by magnesium fluorosilicate surface treatment and the effect increased with higher concentration. Waterglass showed a more significant effect in improving the carbonation resistance of concrete than the other treatment methods (reduction of 44%).[116]

Tian *et al.* reported a gradual decrease of the carbonization depth with an increasing addition of silicone resin. However, when the SR (silicon resin) emulsion content was increased (2%, 3%, or 4%), the carbonization coefficient of the tested coefficient didn't change much, showing that the anti-carbonation ability of the silicon resin emulsion is limited.[73]

3.4 Sulfate attack

Sulfate attack in the narrower sense means the reaction of the aluminum-containing hydration products in cementitious materials with sulfate ions from the environment to ettringite which is correlated with an expansion and therefore the forming of cracks as well as flaking, spalling, and finally disintegration. This is also sometimes observed for aluminum-free binders, where this is ascribed to the formation of gypsum. In addition, at low temperatures and in the presence of carbonates, thaumasite can form, which leads to a softening of the matrix.[117] These attacks can be summarized as physical sulfate attacks. Then, there are also the chemical and microbiological attacks, which are both a combination of sulfate attack and acid attack.[118,119]

All these types of sulfate attacks can be quantified by weight loss, by loss in strength, or by visual evaluation of cracking, flaking, spalling, and blistering. To quantify the performance of surface treatments, sometimes the loss of adhesion is determined. Fig. 9 gives an overview of studies that quantified the physical sulfate attack. Here, the weight loss of the treated specimen normalized on the values of the untreated reference are given. Since the incorporation of sulfate can in the short term result in a gain in weight, the normalized values of the weight loss can be negative – meaning a weight gain of the treated specimen.

As also for the other attacks, Aguiar *et al.* reported stronger protection for concretes with a higher water-to-cement ratio. However, they found that uncoated concretes with higher water-to-cement ratios withstood the sulfate attack better due to the high porosity which not only has the negative consequence of a higher ingress of sulfate ions but also has the positive effect of providing room to accommodate expansions caused by reactions that occur during this attack. At $w/c = 0.6$, there was almost no difference between acrylic and epoxy coating whereas at $w/c = 0.4$, the epoxy coating performed better.[93]

Sakr *et al.* observed that mixing silane or methylmethacrylate (MMA) with 5% nano-clay or nano-silica mitigated the physical salt attack by Na_2SO_4. However, an improvement due to the addition of the nanomaterials was only significant for the higher w/c. Surprisingly, the investigated surface treatments performed relatively worse for higher w/c.[120]

Ibrahim *et al.* concluded from their study, that a combined surface treatment consisting of a silane/siloxane treatment and an acrylic topcoat was the most effective in minimizing the damage due to sulfate attack. No signs of cracking of the coating or softening of the cement paste were noted for these specimens. This good performance could be attributed to the fact that the topcoat forms a layer over the concrete, providing an effective barrier against the diffusion of sulfate ions, in addition to the protection provided by silane/siloxane.[106]

Investigating the change in compressive strength of specimens exposed to $MgSO_4$ solution to evaluate the resistance against sulfate attack of surface treatments is tricky. Basha *et al.* reported an increase in compressive strength until 6 months both for untreated mortar specimens and specimens coated with epoxy and composite epoxy coating. Since the increase for the untreated sample was higher, the relative change in compressive strength would lead to the conclusion, that the resistance against sulfate attack gets worse with an epoxy coating applied. However, there were no visible signs of degradation for the coatings.[104]

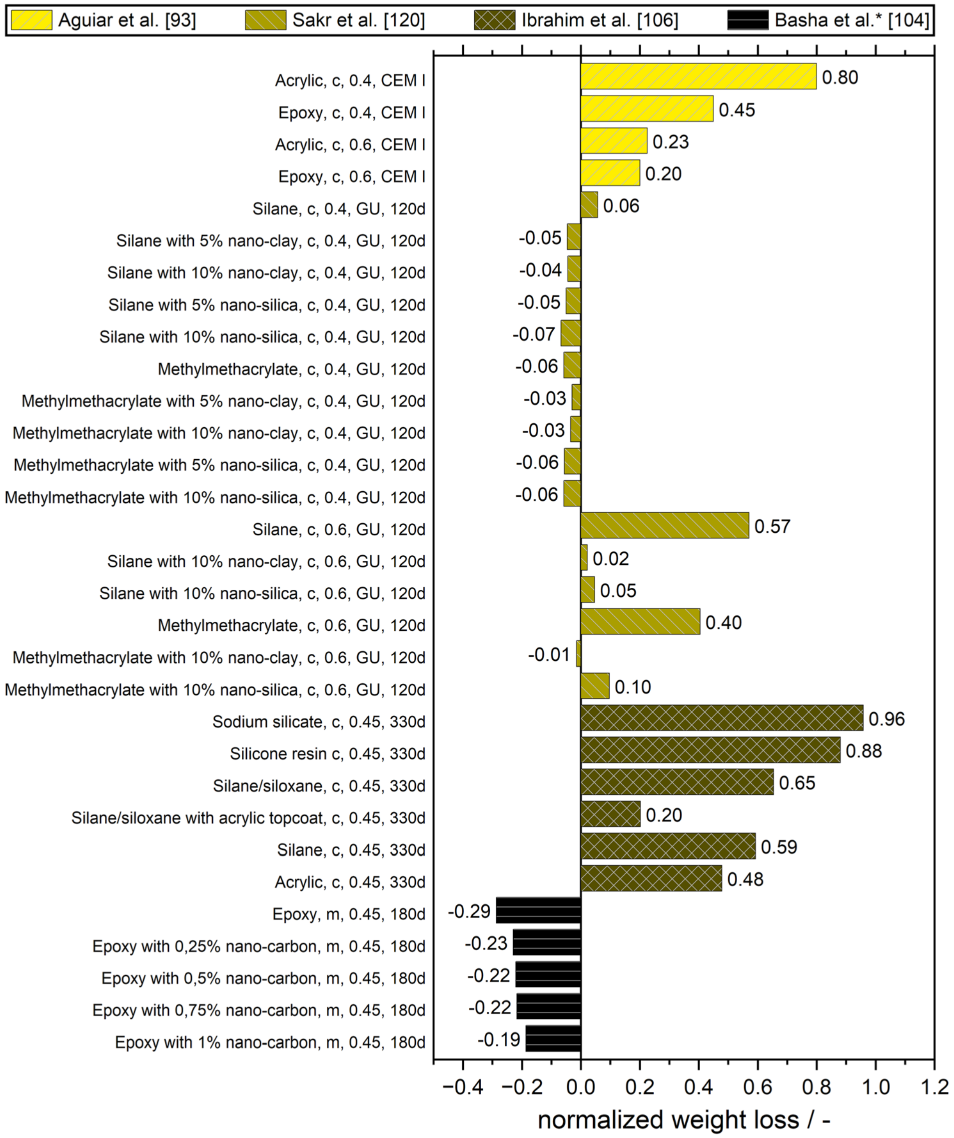


Fig. 9 Comparison of normalized weight loss of cementitious construction material with surface treatment after exposure to sulfate. Positive values mean weight loss and negative values stand for gains in weight. For each literature source, the values are normalized on untreated cementitious material. Given is the type of binder (c = concrete or m = mortar), then w/c-ratio, the type of cement, and additional information where applicable. (* = Normalized coefficient of loss of compressive strength).

Not shown in Fig. 9 are the observations of Suleiman *et al.* and Chen *et al.* Epoxy- and silane-based surface treatment materials were found to be adequate for protecting both cured and non-cured concrete exposed to physical sulfate attack, although they work in different ways. Epoxy provides a thick protective membrane on the concrete surface, which can hardly be penetrated by sulfates, thus mitigating capillary rise on the concrete. Whereas, silane penetrates the concrete surface and chemically reacts within the concrete pores, providing molecules that perform as a water repellent. The application of a water-based solid acrylic polymer resin did not provide adequate protection of concrete against physical sulfate attack.[121] Chen *et al.* introduced a novel method to prevent water and ions from penetrating cement-based material. They impregnated concrete and mortar with a 0.15 mol L^{-1} octadecane carboxylic acid (OCA) solution resulting in a significant reduction in capillary absorption as well as in a reduction of the penetration depth and the mass of absorbed sulfate solution to around one-quarter of that in the non-impregnated mortar. This waterproofing effect increased with the amount of impregnation.[122]

The following are some examples of chemical sulfate attacks. Vipulanandan *et al.* found an extension of the lifetime of concrete coated with glass-fiber mat-reinforced epoxy coating by over 70 times when immersed in 3% sulfuric acid.[123] Basha *et al.* compared neat epoxy coatings with composite coatings where submicron/nano-carbon has been added. Composite coatings with a share of 1% of these particles gave the best performance. They increased the resistance against weight loss when exposed to sulfuric acid by 32% compared to the neat epoxy. The adhesion/bond strength of specimens coated with the composite coating increased by 4% to 67% compared to that coated with neat epoxy. They attributed the improved performance of the composite epoxy coatings to the capability of the carbon particles to densify the epoxy matrix and therefore to decrease the diffusion of the aggressive agents to the concrete substrate as indicated by the mineralogical composition and by results of the durability evaluation.[104] The degradation caused by bases and acids was quantified by visual inspection and by adhesion tests by Aguiar *et al.* for different coatings on concrete specimens.[93] They found a strong degradation after sulfuric acid attack for all coated concretes. Ammonium hydroxide solution was investigated as an example of a base that leads to dissolution. This caused only insignificant degradation on the coated concrete specimen.

3.5 Freeze–thaw attack

Freeze–thaw damage is linked with water permeability and – depending on the location of the building component – with chloride permeability. Therefore, freeze–thaw resistance should be proportional to water (and chloride) permeability. However, freeze–thaw damage itself also increases water (and chloride) permeability.

Similar to sulfate attack, freeze–thaw attack is quantified by weight loss, loss in compressive strength, or by visual evaluation of cracking, flaking, spalling, and blistering. In addition, sometimes the loss of modulus of elasticity is measured. Different freeze–thaw tests not only differ in the number of freeze–thaw cycles but also the type of cycles and whether they are carried out in water or salt solutions. A comparison of the normalized weight loss of different surface treatments for concrete and mortar due to freeze–thaw attack can be found in Fig. 10.

Liu *et al.* found a substantial reduction of surface scaling by silane treatment. However, this could not prevent bulk moisture uptake or the occurrence of internal frost damage when concrete is insufficiently air-entrained. Salt scaling was dominated by the capillary suction process in the thin surface region

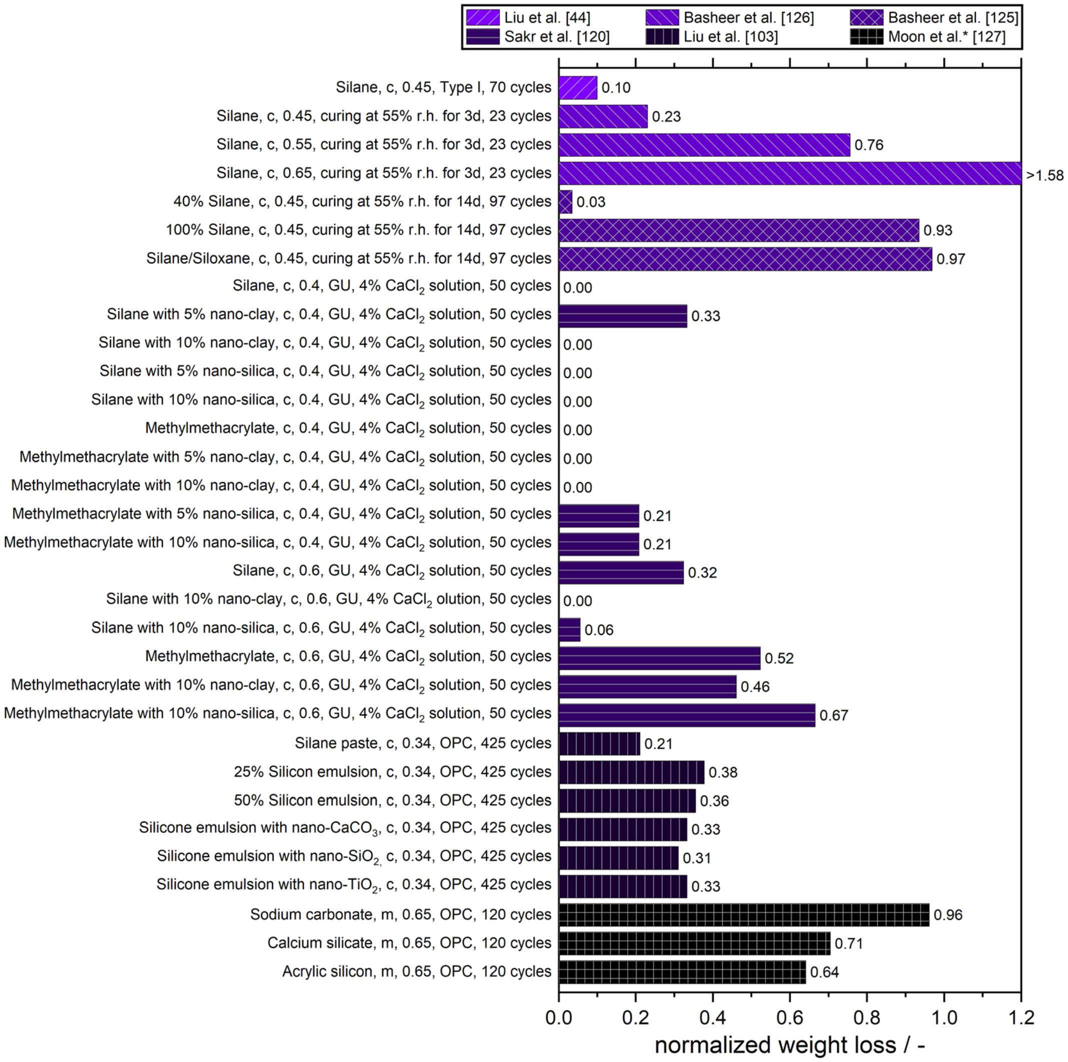


Fig. 10 Comparison of normalized weight loss of cementitious construction material with surface treatment after freeze-thaw attack. For each literature source, the values are normalized on untreated cementitious material. Given is the type of binder (c = concrete or m = mortar), then w/c-ratio, the type of cement, and additional information where applicable. (* = Normalized coefficient of loss of modulus of elasticity).

under freezing which could be curtailed by the pore lining effect from silanes creating a hydrophobic barrier to the ingress of external liquid. This suppressed growth of ice in the surface region is evidenced by the complete elimination of sub-freezing dilation in a length-change measurement of small-scale concrete specimens with surface treatment. However, internal frost damage is controlled by the universal degree of pore saturation which in turn is dependent on the bulk moisture uptake.[124]

Results by Basheer *et al.* indicate that concretes treated with silane or siloxane not only withstand the freezing and thawing but also improve the freeze–thaw resistance even in the case of the most porous concrete used in their study. Samples, where the surface treatment showed a deeper depth of penetration, withstood more cycles of freezing and thawing compared to the lower depth of penetration of treatment in the case of the salt scaling test.[125] The freeze–thaw salt scaling resistance improved in relation to the untreated reference when the surface treatment was applied on drier concrete. However, the improvement in the salt scaling resistance was only moderate when the initial moisture condition during the application of the pore-liners was high.[126]

Silane mixed with 5% nano-clay or nano-silica mitigated salt-frost scaling damage of sound and pre-cracked concrete, even with inferior quality. Nanoclay showed a relatively better performance due to its unique morphology (interwoven barrier). The combination of the water-repellent action of silane with the barrier/filling/pozzolanic effects of nanoparticles on the concrete surface was the primary mechanism for its enhanced durability under aggravated exposures. Methyl-methacrylate (MMA) with nano-clay or nano-silica failed to maintain the functionality up to the end of the salt-frost scaling exposure due to progressive ingress of salt solution, crystallization of salt built-up, and detachment of coated surface which was aggravated by the cyclic frost action. Sakr *et al.* concluded, that MMA with nanocomposites is suitable for specific conditions (mostly against sulfate attack), but silane with the addition of nanocomposites (especially with the addition of 5% of the nanocomposites) has a wider applicability for concrete. However, even silane with nanocomposites was vulnerable to severe conditions involving salt solutions and cyclic environments like a change of wet and dry state or freeze–thaw.[120]

The addition of nano-materials ($CaCO_3$, SiO_2, and TiO_2) to a silicone emulsion increased the number of freeze–thaw cycles it could withstand by 150 times compared with the reference group. It could withstand more than double the times of cycles of salt freezing than the reference group. It was also reported, that nano-materials can make up for the defect that silicone emulsion cannot fill the pores, and can also construct nano-level roughness on the surface of concrete.[72]

Moon *et al.* assessed surface treatment by the modulus of elasticity and found less reduction in the coated specimen than in the untreated reference materials, concluding that the tested surface treatment improved the resistance against freeze–thaw attack with acrylic silicon showing the best performance.[127]

Not shown in Fig. 10 are the results by Dang *et al.* and Mamaghani *et al.* Dang *et al.* reported that 90% or more of the salt scaling of the tested concrete was avoided by the surface coatings after 15 freeze–thaw and wet–dry cycles. Epoxy-based sealers and silane-based water repellents provided the best performance. They concluded, that high resistance to both gas and water penetration is a crucial property for a good surface treatment applied to concrete.[128] An epoxy sealer had the greatest effect in resisting deterioration of concrete properties due to freezing and thawing cycles when exposed to potassium acetate as a deicing chemical in the study by Mamaghani *et al.* The other investigated sealers (a low-viscosity, low-surface-tension, rapid-curing methacrylate reactive resin, a biochemically modified silicate solution, an isobutyl-trialkoxy silane in an alcohol carrier, and one based on special polymers and concrete saturants) had only a minor effect on the resistance to rapid freezing and thawing.[129]

4 Organic coatings

The application of coatings on its surface represents a powerful approach to augment the intrinsic characteristics of concrete and cater to specific requirements.[130,131] Depending on their type, coatings can serve a multifaceted purpose, shielding the surface from moisture infiltration, chemical corrosion, and abrasive wear, all while offering an avenue for creative aesthetic designs.[132–137] In the subsequent sections, we delve into distinct realms of organic surface coating applications, drawing insights from the illustrative examples provided in Table 1. Additionally, in Section 5 we explore emerging materials that hold promise for the future of concrete surface coatings, with a particular focus on graphene-infused coatings, before entirely inorganic coatings are discussed in Section 6.

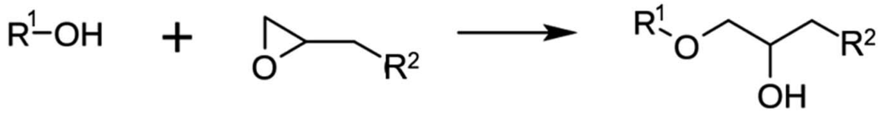
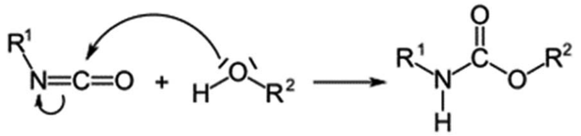
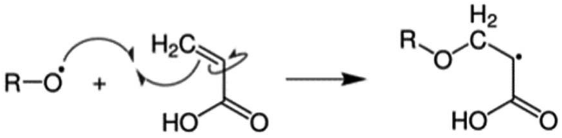
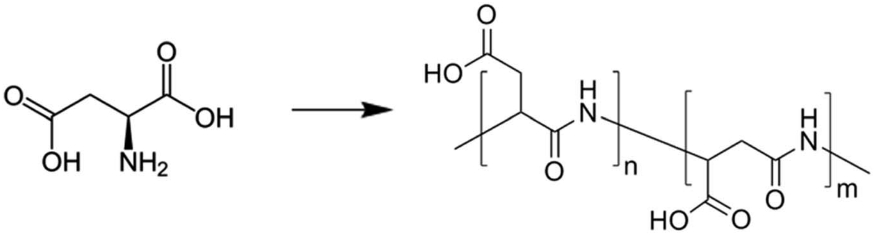
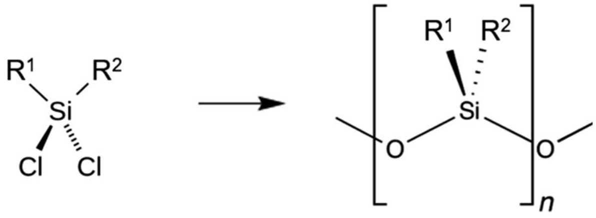
Table 1 showcases a diverse array of organic surface coatings, each tailored to address unique challenges and objectives. For instance, anti-corrosion coatings like epoxy are indispensable in environments where concrete structures are subjected to aggressive chemicals or saline conditions. These coatings form a protective barrier, mitigating the detrimental effects of chemical exposure and prolonging the service life of concrete components. In addition, there is also surface treatment material based on bitumen.[138] Furthermore, decorative coatings offer a canvas for architectural creativity, transforming ordinary concrete surfaces into aesthetically pleasing elements. These coatings come in a spectrum of colors, textures, and patterns, enabling architects and designers to craft visually appealing structures that seamlessly blend with their surroundings.

4.1 Epoxy resins

Epoxy resins are utilized as coatings for concrete due to their exceptional mechanical resistance. Their high hardness, strength, and abrasion resistance make them an effective protective layer that protects the concrete from mechanical stress. Epoxy resins are composed of molecules with a chemical structure containing at least one epoxide group (oxirane ring).

The general chemical formula for epoxy resins is $R–(O–CH_2–CH)_n–O–R'$, where R and R′ represent different organic groups and n indicates the number of epoxy groups. Typical pre-

Table 1 A diverse array of organic surface coatings. Given is in each case the polymerization reaction to form the coating material

Organic coating	The chemical reaction of polymerization	References
Epoxy resins		139–147
Polyurethane		148–151
Acrylic polymers		152–156
Polyaspartic polymers		157,158
Silanes		44,151,159–162

treatment steps before the application include cleaning the concrete surface by dusting, grinding, or blasting to remove loose particles and create a rough surface that allows for better adhesion. Degreasing and de-oiling the surface is also important to remove any oil- or grease-based contamination. The bond between epoxy resins and concrete occurs through a combination of chemical and physical mechanisms.[140] First, the epoxy resin molecules can chemically react with the hydroxyl-rich surfaces of the concrete due to their reactive epoxy groups leading to the formation of covalent bonds between the epoxy resin and the substrate. This chemical reaction between the epoxy groups of the resin and the hydroxyl-rich areas of the concrete creates a strong chemical bond.[163] In addition, physical adhesion plays an important role in building this interface since due to their low surface tension and liquid consistency, epoxy resins can penetrate the pores and microcracks of the concrete and physically adhere there. Therefore, the physical adhesion of the liquid epoxy resin enables a tight connection between the surfaces and the formation of mechanical interlocking. The combination of chemical and physical adhesion ensures good adhesion and effective stress transfer between the epoxy resin and the concrete, resulting in a strong and durable bond.[141–146]

There are also novel epoxy-based coatings where a reactive solvent containing carbonyl groups and the epoxy can react with amines to form a network. Using such carbonyl solvents provides an effective strategy for preparing high-performance epoxy coating for concrete.[147]

4.2 Polyurethanes

Polyurethanes are used as coatings for concrete due to their excellent chemical resistance.[150] Their chemical structure allows for high resistance to a wide range of chemical substances, including acids, alkalis, solvents, and harsh chemicals. This is due to the inertness of polyurethanes, which is achieved through the use of special chemical components. The polyurethane molecules have low polarity, making them resistant to polar and non-polar chemicals.

Polyurethanes consist of a polymer chain in which urethane and organic groups alternate in the repeating units. The general chemical formula for polyurethanes can be represented as [R–NHCOO–($C_6H_4O_2$)]$_n$, where R represents various organic groups and n indicates the number of repeating units. The connection between polyurethanes and concrete occurs mainly through physical interactions at the interface. Due to the flexible nature of the polyurethane molecules, they can conform to the rough surface of the concrete and cling to it through physical adhesion forces. The flexible chains of the polyurethane penetrate the pores and microcracks of the concrete and adhere there through various intermolecular interactions such as van der Waals forces and surface tension effects. While there is no direct chemical reaction between polyurethanes and concrete, certain polyurethane coatings can hydrolytically degrade in the presence of water or moisture, which can affect adhesion and durability. Overall, the adhesion of polyurethane coatings to concrete surfaces occurs primarily due to physical interactions and mechanical interlocking at the interface between the materials. The flexibility and resilience of polyurethanes allow them to adapt well to the movements of the concrete, helping to form a stable and durable coating.

4.3 Acrylic polymers

Acrylic coatings are used as coatings for concrete in the field of waterproofing due to their excellent water–repellent properties.[153] The chemical structure of acrylic polymers (polyacrylates) allows them to form a dense and impermeable barrier on the concrete surface and due to the low polarity of acrylic molecules, they have a natural repellency to water, preventing moisture penetration.[154] Additionally, acrylic coatings can be manufactured in various formulations specifically tailored to the needs of the application, including the ability to withstand UV radiation and provide resistance to weathering. With their water-repellent properties, acrylic coatings help to maintain the integrity of the concrete and prevent water ingress as well as associated damage.

Polyacrylates consist of polymer chains in which the repeating units are acrylic acid esters. The general chemical formula for polyacrylates can be represented as $[\mathrm{R{-}COO{-}CH_2{-}CH(COOR')}]_n$, where R and R′ represent different organic groups and n indicates the number of repeating units. The connection between polyacrylates and concrete is based on a combination of chemical and physical adhesion. The carboxyl groups of the polyacrylate molecules react with the hydroxyl-containing groups on the concrete surface to form ester-like bonds, leading to a stable and permanent bond at the interface. In addition, the physical interactions, such as van der Waals forces and surface tension effects, contribute to mechanical adhesion. Overall, chemical bonding provides strong adhesion, while physical interactions add stability and durability.

It was shown, that near-infrared spectroscopy (NIRS) as a fast, non-destructive, and portable method can be used to monitor the deterioration of acrylic coatings in building components. With this method, early signs of deterioration of acrylic coatings like the decomposition of a C–H bond of CH_2 in a linear alkyl group of the coating material can be identified.[155]

4.4 Polyaspartic polymers

Polyaspartic coatings are used as coatings for concrete due to their outstanding surface protection properties. Due to their chemical structure, they offer high resistance to UV radiation, chemical attacks, abrasion, and atmospheric agents. The polymer chains of the polyaspartic coatings are flexible and have high elasticity, which allows them to adapt to the movements of the concrete and minimize cracking. In addition, the coating hardens quickly, which leads to a quick start-up of the treated surface. The combination of these properties makes polyaspartic coatings ideal for protecting concrete surfaces and increasing their durability and service life.[158]

These polyaspartic coatings consist of polymer chains in which the repeating units are aspartic acid ester groups. The general chemical formula for polyaspartic can be represented as $[\mathrm{R{-}CH_2{-}CO{-}NH{-}(CH_2{-}COOR')}]_n$, where R and R′ represent different organic groups and n indicates the number of repeating units. The connection between polyaspartic and concrete occurs through a combination of chemical reactions at the interface and physical adhesion. The amino groups of the polyaspartic molecules react with the hydroxyl-containing groups on the concrete surface to form amide bonds resulting in a strong and stable bond at the interface. Physical interactions, such as van der Waals forces and surface tension effects, contribute to mechanical adhesion. To sum up, chemical bonding provides strong adhesion, while physical interactions add stability and durability, leading to effective protection of the concrete surface.

4.5 Silanes/siloxanes

Because of their hygienic properties, silane coatings are used as coatings for concrete. Silanes can form a hydrophobic surface that repels water and other liquids. This reduces the adhesion of dirt, dust, and microorganisms on the surface and makes cleaning easier.[160] In addition, certain silanes can exhibit antimicrobial properties that inhibit the growth of bacteria, mold, and other harmful organisms. By providing a stain-resistant and hygienic surface, silane coatings help to maintain a clean and hygienic environment, particularly in areas where hygiene requirements are high, such as hospitals, food processing plants, and public facilities.[161,162]

Silane coatings consist of silanes, which are organic compounds with a silicon atom group. The general chemical formula for silanes can be represented as $\mathrm{R}_x\mathrm{Si}(\mathrm{OR}')_{4-x}$ where R and R′ represent different organic groups and x represents a variable number. The interface between silane coatings and concrete relies on a combination of chemical and physical adhesion.[164] Silane molecules react with the hydroxyl-containing groups on the concrete surface to form silanol groups, which can then further react with the silane molecules.[162] The chemical bonds between the silanol groups of the silane molecules and the hydroxyl-containing groups of the concrete contribute to chemical adhesion, while the physical interactions, such as van der Waals forces and surface tension effects, lead to mechanical adhesion.[165]

Silanes are one of the most commonly used hydrophobic products. Their properties depend on the molecular structure: the larger the molecule of the alkyl group, the better the water repellency of the silane for the hydrophobic products.[166] Silane molecules are very small (1.0–1.5 nm) and can thus penetrate a highly dense concrete substrate of more than 5 mm.[167] Some silanes with alkoxy groups can polymerize during the application if they come in contact with water.[43] There are reports, that silane impregnations still provide a residual hydrophobic effect 20 years after the application.[168]

Beside silanes, there are also hydrophobic products which consist of siloxanes (oligosiloxanes) or a mixture of silanes and siloxanes. Siloxanes react with the silica contained in the cementitious material to form a hydrophobic layer. Siloxane molecules are oligomers (1.5–7.5 nm) and therefore larger than the silane molecules. These products cannot penetrate the surface of concrete as deeply as silanes and may therefore not be suitable for the protection of dense concrete substrates.[52,53] Silanes are more efficient in penetrating concrete ($w/c = 0.6$ and $w/c = 0.7$) than siloxanes due to the lower dimension of the molecules. Penetration depth for $w/c = 0.6$ and 0.7 is 3 mm and 7 mm respectively for siloxane as well as 4–6 mm and 10–17 mm respectively for different concentrations of silane (40–99%).[43]

The dimension of the molecules plays a crucial role in determining the penetration depth of the hydrophobic product.[52,169] Also the water-to-cement ratio influences the penetration depth whereas a higher w/c is related to deeper penetration of silanes. The surface water content has also a remarkable influence on the silane impregnation depth of cement-based materials. As the initial moisture content at the surface of mortars increases, the depth of surface silane impregnation gradually decreases. Therefore, the initial water content (determined by water-to-cement ratio and environmental conditions) affects the water repellency of surface impregnation of cement-based materials.[69]

The surface water repellent treatment can achieve a larger impregnation depth of silane in recycled aggregate concrete than in natural aggregate concrete due to the higher porosity of the former. Hence the durability enhancement of recycled aggregate concrete subjected to surface water-repellent treatment is more significant than that of natural aggregate concrete.[62] Silane, siloxane, and a mixture of these two components are the most commonly-used hydrophobic impregnation. They can react with hydrated cement particles in the pores of cement and concrete, and form a hydrophobic lining of silicon resin on the surface of cement hydration products, enlarging the contact angle and coarsening the pore surface.[122]

Silanes can also be used to form a hydrophobic surface on geopolymers to inhibit the efflorescence typical for these kinds of materials.[170,171] Silanes even reduce the water absorption of a highly porous structure like foamed concrete.[172]

MALDI-TOF can be applied to investigate these substances: time-of-flight mass spectrometry (TOF/MS) is used to analyze monomeric alkyltrialkoxysilanes and by matrix-assisted laser desorption ionization (MALDI) the reaction products resulting from hydrolysis and condensation are characterized.[173] Micro X-ray fluorescence (μ-XRF) can be used to indirectly determine the depth of penetration of silanes on profiles of drill cores.[174]

Besides the application on the surface of hardened cementitious material, there are also studies that added fluorinated silanes (1*H*,1*H*,1*H*,2*H*-perfluorodecyl triethoxysilane, PFDTES) during the curing of cement paste resulting in a superhydrophobic surface.[45] This was obtained by an introduction of PFDTES on the surface and a modification of the nanostructure of the hydration products. The ethanoic solution of PFDTES is also used to modify the surface of silica particles, creating the roughness leading to superhydrophobicity. This was done for example with rice husk ash and the obtained silica particles were sprayed on a layer of commercial adhesive coated on a concrete surface resulting in a very high water contact angle of 152.3° and a cumulative water uptake reduced by 40%.[175]

5 Coatings based on nanomaterials

In the realm of surface coatings, the predominant focus in both research and application has traditionally revolved around organic materials. These organic coatings have offered a plethora of advantages, such as facile synthesis, versatility, and excellent adhesion to various substrates. However, organic coatings have not been without their limitations. They are susceptible to degradation under harsh environmental conditions, possess limited thermal stability, and may exhibit restricted durability over extended periods. Moreover, concerns regarding their ecological impact have stimulated the exploration of alternative coating materials.

As we embark on this scientific journey, our attention is redirected towards a promising frontier in surface coatings: nanomaterial-infused formulations, most notably those incorporating graphene. The integration of nanomaterials, such as graphene, into coatings has ignited a new wave of research and development. These nanomaterial-infused coatings hold the potential to offer an array of benefits, including exceptional mechanical strength, superior electrical and thermal conductivity, and heightened chemical resistance. Nevertheless, challenges persist in harnessing these advantages, with issues related to dispersion, scalability, and environmental sustainability necessitating thorough investigation.

In this transition, we navigate from organic surface coatings to nanomaterial-infused formulations, delving into the inherent advantages and disadvantages of both approaches. This exploration not only paves the way for innovation but also underscores the importance of balancing performance with sustainability in the quest for advanced surface coatings. Hybrid nanocomposites of organic–inorganic materials give a possibility to combine the characteristics of both groups of material generating opportunities to prevent biofouling.[176]

In 2010, Andre K. Geim and Konstantin S. Novoselov were awarded the Nobel Prize in Physics for the discovery and characterization of graphene. Graphene is a two-dimensional structure of carbon in which the individual atoms are connected to each other in a hexagonal pattern. The material has attracted much interest in recent years due to its exceptional mechanical, electrical and other properties. For a long time further exploration of the area was limited by the production of enough material. This point has been overcome and attempts are now being made to combine graphene with other materials – such as polymers. Many studies show positive effects on mechanical properties and corrosion resistance.[177,178]

In the realm of emerging materials, graphene-based coatings have garnered considerable attention. Graphene, with its exceptional mechanical, electrical, and thermal properties, holds the potential to revolutionize concrete coatings. Graphene-infused coatings exhibit enhanced strength, electrical conductivity, and barrier properties, making them ideal for applications ranging from anti-static flooring to advanced sensors.

2021, a composite from polyaniline and graphene oxide-hydrotalcite hybrid (PAN–HG) was fabricated by direct polymerization of aniline using ammonium persulfate as an oxidant in the presence of a HG hybrid.[179] As new materials are designed and brought into use, it is important to understand their potential mobility and impacts in and across air, water, soil, and biota.[180]

One of the biggest challenges is the homogeneous distribution of the mixed graphene in the polymer. The homogeneous distribution and alignment of reduced Graphene Oxide (rGO) within polymers is governed by the presence of functional groups on the surface of the rGO material.[181–183] The effects of rGO on the diffusion of ions in a polymer can cause both reduction and improvement, depending on the specific properties of the rGO and the polymer matrix (see Fig. 11). In some cases, the incorporation of rGO into a polymer can lead to blockages. The rGO can partially or completely block the pores and channels of the polymer, which impedes the diffusion of ions. These blockages can mean that the ions can only move slowly or not at all through the material. On the other hand, rGO can also act as an 'ion highway' since the rGO can have high electrical conductivity and serve as an electrically conductive network. This network can facilitate the transport of ions by providing an efficient pathway for ion movement which means that the ions can diffuse faster and more efficiently along the rGO network. Reduced graphene oxide has a high conductivity because functional groups and oxygen atoms are removed during the reduction process of graphene oxide (GO) to rGO. As a result, rGO acquires a conductive structure that enables a high mobility of the electrical charge carriers (electrons). The exact effects of rGO on the diffusion of ions depend on several factors, including the concentration and distribution of the rGO in the polymer, the interaction between the rGO and the polymer, the size and shape of the rGO, the ion species, and other material parameters. It is important to note that these effects can also depend on the specific needs of the application.

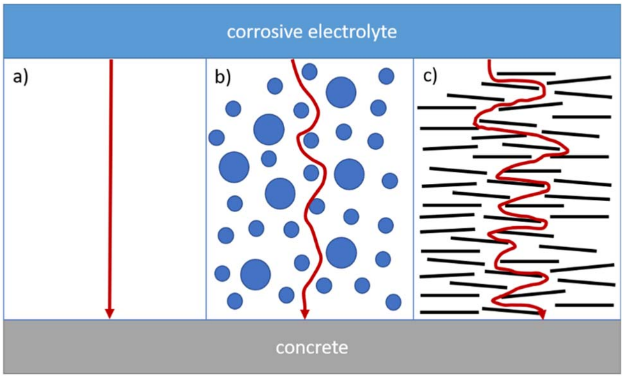


Fig. 11 (a) The red line represents a direct and thus short diffusion path of harmful ions such as chloride for a coating without nanomaterials. (b) The coating has been filled with nanoparticles and the diffusion path is extended. (c) Schematic for the mechanism of improved anti-corrosion in epoxy coatings with reduced Graphene Oxide (rGO).

Graphene has been demonstrated as an excellent protection material for metals because of its complete impermeability. Unfortunately, graphene fails to prevent metal corrosion in the long term because its essential conductivity promotes the electrochemical reaction between the graphene and the metals.[184] However, the addition of certain chemicals like boron nitride nano sheets (BNNS) to the rGO can improve the interaction and thereby the structure.[185]

However, rGO can also be used an integral component to modify the bulk properties of cementitious materials, and not only as part of a coating of the surface (see Fig. 12). For that, rGO is mixed directly with the cement before hydration. First investigations have shown the interactions.[186–190] Theoretical studies calculated positive effects on the mechanical properties of such a material. However, it is doubtful whether such a large quantity of rGO, as would be required for an application as an admixture in concrete, could ever be produced at a reasonable price.[191–195]

There are also reports where nanoparticles are added to organic surface treatments to improve their properties. For example, nano-materials can make up for the defect that silicone emulsion cannot fill the pore, and can also construct nano-level roughness on the surface of concrete. Therefore, the protective property of concrete impregnated with silicone emulsion modified by the addition of nano-materials ($CaCO_3$, SiO_2, or TiO_2) can be improved.[72] Also submicron/nano-carbon can be added to epoxy surface treatments resulting in a composite coating with improved properties. A share of 1% of these particles showed the best performance. This is attributed to the capability of the carbon particles to densify the epoxy matrix thereby decreasing the diffusion of the aggressive agents to the concrete substrate as indicated by the mineralogical composition and results of the durability evaluation.[196]

6 Inorganic coatings

Inorganic coatings on mortar and concrete surfaces play a crucial role in enhancing the durability, performance, and aesthetic properties of these materials. The application of inorganic coatings involves the deposition of non-organic compounds onto the surface of cementitious substrates, creating a protective layer that shields against various environmental factors. Unlike their organic counterparts, inorganic coatings are characterized by the absence of carbon–hydrogen (C–H) bonds, relying instead on mineral-based compounds for their protective functionality. Inorganic coatings predominantly utilize minerals, silicates, aluminates, or metallic oxides, while organic coatings rely on carbon-based polymers, resins, and additives. Since for the manufacturing process and especially during coating works volatile organic compounds are used, a decisive shortcoming of organic coatings is the air-pollution

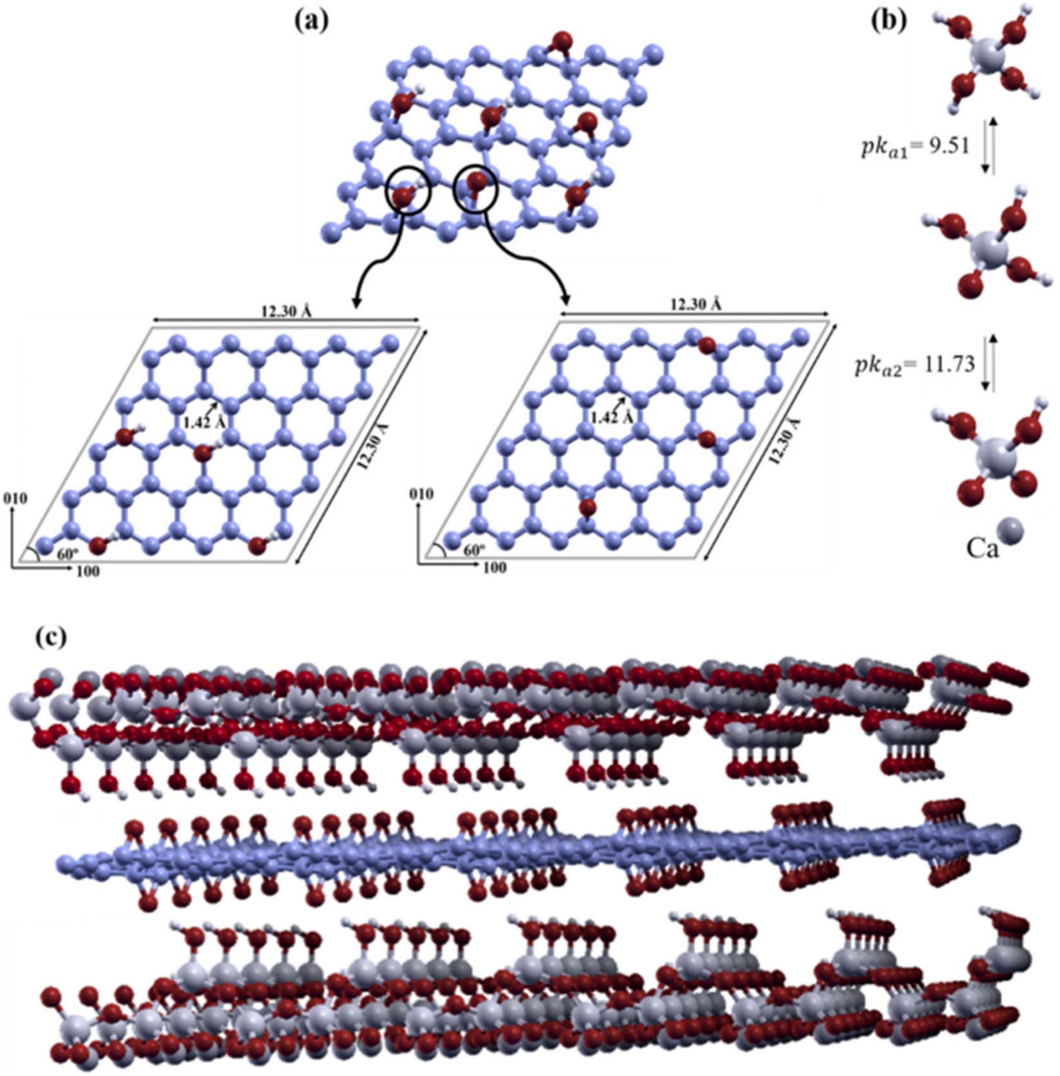


Fig. 12 (a) Reduced graphene oxide with hydroxyl and epoxide groups. The lower, left- and righthand panels show hydroxyl and epoxide surface models, respectively. (b) The p*K* ratios for calcium silicate hydrate gels. (c) Calcium silicate hydrate composites consisting of calcium silicate hydrate gel and epoxide/reduced graphene oxide. Carbon atoms are indicated in blue; oxygen in red; hydrogen in white; silicon in light grey and calcium in dark grey. Reprinted with permission from Nanomaterials. 2021; 11(9): 2248. Copyright 2023 MDPI.

caused by them.[197] The absence of organic constituents in inorganic coatings imparts distinct advantages and challenges to each type.

6.1 Silicates

Silicates are used as coatings for concrete in the field of aesthetics due to their aesthetic properties.[198,199] They show a high transparency, allowing the natural texture and color of the concrete to remain visible.[200] In addition, they offer a matte finish with a natural, mineral look that meets the aesthetic demands of many architectural and design projects. Silicate coatings are available in a wide range of shades, allowing for customization and adaptation to different aesthetic preferences. Due to their water-based formulation and mineral composition, silicate coatings are environmentally friendly and contribute to a healthy indoor climate. They also offer good resistance to UV radiation and aging processes, allowing them to preserve their aesthetic properties over time.

Silicate coatings consist of silicate compounds, especially water-soluble potassium or sodium silicates. The chemical formula for silicate coatings can be represented as $M_2O\cdot nSiO_2$, where M is a metal like potassium or sodium and n is the number of silicon dioxide (SiO_2) units. The aqueous solution of sodium silicate is known as ‘waterglass’. The connection between silicate coatings and concrete occurs through chemical reactions at the interface. The alkaline silicates react with the calcium hydroxide ($Ca(OH)_2$) in the concrete to form water-insoluble calcium silicate hydrates (C–S–H), which form a solid compound. C–S–H gels formed *via* the reaction between the silicates and calcium hydroxide can significantly decrease the concrete porosity in the surface layer and effectively block the micropores and microcracks in the surface layer.[201] The chemical reactions between the alkaline silicates and the calcium hydroxide result in the formation of C–S–H which is bonded to the concrete surface enabling a permanent adhesion and a firm connection of the coating to the concrete.

The water impermeability of concrete sealers like silicates is also determined by their surface tension. Fluorosilicates are used as a pretreatment agent to further improve the effect of silicate treatments, reducing the surface tension of the concrete sealer to an ideally low value.[202]

The surface treatment can also consist entirely of fluorosilicates as an alternative to normal silicates. Magnesium fluorosilicate has been shown to perform mainly at early ages better than sodium silicate, while the effect of the latter lasted longer. Magnesium fluorosilicate, sodium fluorosilicate as well as sodium silicate can reduce the macro and the capillary pores, but slightly increase the volume of pores smaller than 100 nm. Magnesium fluoride can block more macro-pores while waterglass is more effective in blocking capillary pores. The pores on the concrete surface are in each case blocked by insoluble calcium silicate hydrate and silica gel which are generated by reactions between an inorganic surface treatment agent and $Ca(OH)_2$ in concrete.[60]

6.2 Colloidal nano-silica/TEOS

Ethyl silicate, also known as TEOS (tetraethylorthosilicate), the ethyl ester of silicic acid ($Si(OC_2H_5)_4$), is an alkoxysilane compound that is usually applied in solution with low viscosity organic solvents onto mineral surfaces by brushing or spraying.[56] Once penetrated the pores, it undergoes a two-stage curing process: first, a hydrolysis, forming silanol and ethanol, and second a dehydration/condensation of silanol. This leads to the precipitation of amorphous silica gel inside the pores of the substrate.[203]

TEOS is often applied to stone buildings (*e.g.* cultural heritage) for consolidation. In silicate-rich stones like sandstones, silanol binds to the hydroxyl groups present in the silicate phases, thus leading to an appreciable increase in cohesion and mechanical strength.[204] On the contrary, in carbonate stones like marble, the ethyl silicate hardening only results in a pore-filling effect, with limited re-adhesion and consolidation effects.[205] The reasons for the wide use of ethyl silicate for stone consolidation are mainly its small monomer size and low viscosity, leading to deep penetration into the stone, and its hardening byproducts (ethanol and water), which are volatile and do not attack the stone. Moreover, the final reaction product of TEOS is silica gel, which exhibits good compatibility with stone and good durability, unlike many polymeric consolidants. Further advantages are the incomplete reduction of open porosity (which still allows transport of water vapor) of stone as well as the absence of an abrupt interruption between the impregnated and the untreated zones.[56]

However, TEOS is also used as a surface treatment for cementitious materials.[58,206–208] The application there is expected to have similar effects as for stone consolidation, *i.e.* good penetration depth, good chemical–physical–mechanical compatibility, high durability of the final product (silica), and absence of the pore-blocking effect. This last aspect is very important for the good durability of the surface treatment because the presence of water trapped behind the consolidated layer (*e.g.* from infiltration) might otherwise lead to its detachment, especially in case of freeze–thaw cycles.[209]

The use of TEOS as a consolidant for cementitious materials improves mechanical strength and lowers porosity and permeability, without inducing substantial alteration in color or gloss. The consolidation is the result of the reaction between TEOS and the hydrated phases of the cement, namely portlandite and C–S–H gel.[210] It reduces the susceptibility to carbonation (the higher the porosity of the substrate, the better the effect of the treatment) and therefore also improves the corrosion resistance of the steel reinforcement.[59]

7 Further developments/outlook

Today, organic coatings are a billion-euro-per-year business. Due to the high diversity in organic chemistry, there are tailor-made coatings for almost every situation. However, they have limitations in terms of susceptibility to environmental degradation, reduced thermal stability, and potential for limited long-term durability. There are also concerns regarding their negative environmental impact.

So-called antibacterial coatings are a real bottleneck in surface research. Microbiologically induced corrosion (MIC) describes the negative effects of microorganisms on all kinds of materials. Sometimes the consequences for people, technology, and the environment are dramatic.[211] Today's technical infrastructure is affected by MIC when organic material is used in coatings, thermal insulation, or structural elements. Despite intensive efforts, no effective protection is known to date.[212,213]

However, microorganisms do not always cause negative effects. They can also be used in the form of the so-called microbial-induced calcite precipitation (MICP) as an alternative surface treatment for concrete. Similar to some inorganic coatings, a layer of inorganic crystalline material is deposited on the surface of the substrate to decrease the capillary water uptake.[54] With this environmentally friendly method, calcium carbonate (calcite) is formed (MICP). The use of pure cultures of the species *Bacillus sphaericus* resulted in a decrease in the uptake of water comparable to conventional water repellents.[54] MICP also reduces chloride permeability of concrete with silica fume and other pozzolanic additions.[214]

In contrast to the widespread application of organic coatings, fully inorganic coatings represent an approach that leverages the intrinsic durability and resilience of inorganic materials.[215,216] These coatings are engineered to be highly resistant to chemical corrosion and mechanical wear, making them suitable for critical infrastructure exposed to extreme conditions. Looking ahead, the continued advancement of coating technologies and the pursuit of sustainable solutions are poised to be instrumental in shaping the future of concrete surface applications. As environmental considerations grow in significance, the development of coatings with reduced environmental footprints and improved durability will be imperative. In this context, the convergence of innovative materials like graphene and the evolution of fully inorganic coatings stand as promising avenues to enhance the performance and longevity of coated concrete surfaces, underpinning the quest for sustainable and resilient infrastructure solutions.

Having a look at all types of coatings, they seem very different. However, most of them have an organic group as a carrier of hydrophobicity and polar groups at the interface with the concrete. This always creates a weak point in the interaction with water, reducing the durability of the coatings.[217] Increasing polarity generally leads to increased hydrophilicity and therefore the need for polar groups to ensure bonding with the surface of cementitious materials is an inherent problem for the durability of such surface treatments.

This problem can only be overcome, if the carrier of hydrophobicity is part of the cementitious construction material. However, in order to avoid the downfalls of integral waterproofing concepts, a new type of purposeful inherent modification of only the exposed surface of the cementitious material would be required. A promising approach could be the use of rare earth oxides (REOs) to dope such surfaces. Metal atoms in REOs have an electronic structure in which the vacant 4f orbitals are shielded from interactions with the environment by the full octet of electrons in the $5s^2p^6$ outer shell.[218,219] Consequently, these atoms would be less apt to exchange electrons and not form a hydrogen bond with the water molecules at the interface. Therefore, it should be possible to dope cement-bound materials with REOs to achieve hydrophobic wetting properties.[220]

By adapting the Metal–Proton Exchange Reaction (MPER) to a new mineral synthesis process, Burek *et al.* prepared an intrinsically hydrophobic surface of C–S–H phases at room temperature.[221–223] After growth on silicon wafers, the C–S–H phases were contacted with a Eu(III) solution at room temperature. The surface properties of the C–S–H material change as the ions are exchanged (see Fig. 13). Depending on the type of metal replaced, a completely new platform is created that improves the corrosion resistance of cement and concrete surfaces – called Metal–Metal Exchange Reaction (MMER).[215,224] The presented approach controls the adsorption of liquids into the pore structure through an intrinsic and inorganic modification of the C–S–H linkages. The hypothesis is that the interactions of cementitious materials with aqueous solutions are determined by structure and composition and therefore, the incorporation of ions other than calcium into C–S–H phases has a significant impact on their surface chemistry.

How the hydrophobicity of ceramic surfaces can be changed by doping with rare earth metals was explained by Azimi *et al.* in 2013.[225,226] When doped with oxides, these elements have an octet outer shell that prevents any interaction with water molecules at the interface. The presented doping of rare earth oxides into the C–S–H phases was not driven by temperature as this would destroy the samples and later would not be suitable for commercial cement. The sorption of Eu(III) into C–S–H probably results from a combination of diffusion and capillary transport. In addition, there is an attractive challenge in the

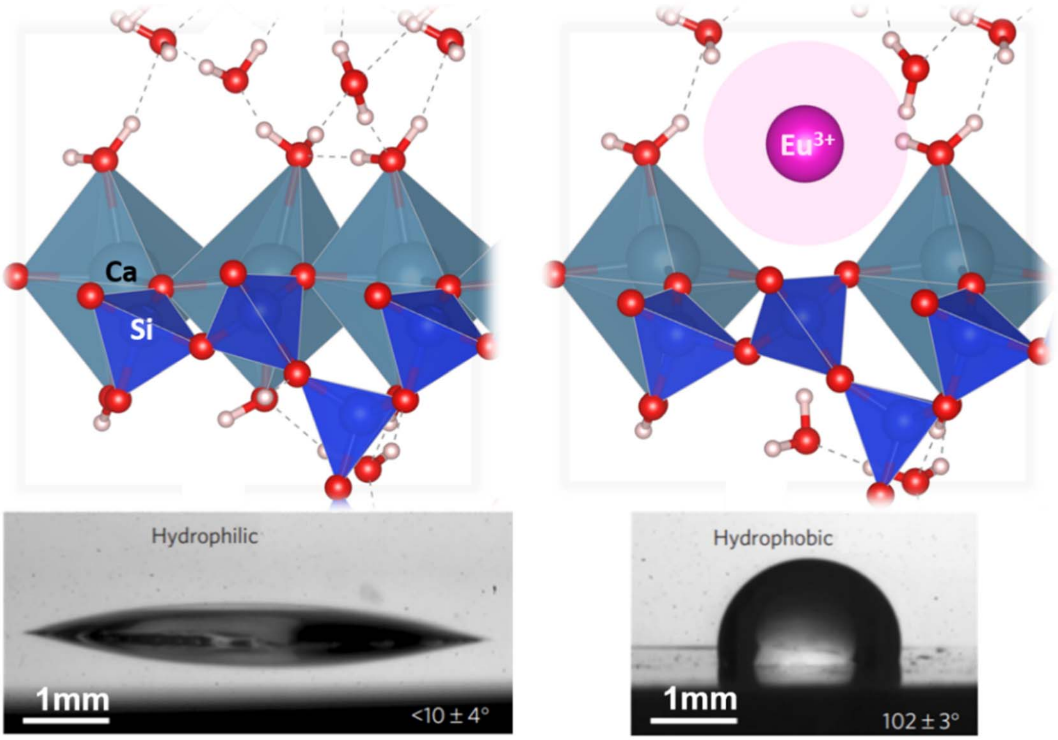


Fig. 13 Upper part: on the left, the atomistic model shows how water molecules form a dense 3D network at the tobermorite/water interface. On the right, a calcium atom in the tobermorite model has been exchanged for europium. The water network at the interface is disrupted and the europium appears to form a cavity. The unfilled 4f orbitals of europium are shielded from interactions with the environment by the full octet of electrons in the $5s^2p^6$ outer shell. Lower part: reprinted with permission from Nature Materials 2013, 12 (4), 315-320. Copyright 2023 Springer Nature.

performance-related matching of the surface chemistry of cement-based building materials. Durability needs to be improved without compromising the mechanical strength or temperature resistance of the system. In these points, the inherent water repellency through ion exchange would be far superior to conventional surface protection systems.

8 Summary

In conclusion, this research article aspires to shed light on the pivotal role of surface coatings in transforming the construction sector into a more environmentally conscious and sustainable industry. By prolonging the service life of cementitious construction materials, not only the need for excessive cement production is reduced, but this also contributes to the overarching goal of mitigating global CO_2 emissions, thus paving the way for a greener and more resilient built environment.

Surface coatings play a crucial role in enhancing the performance and durability of cementitious construction materials. Traditionally, organic coatings have been widely employed in the construction sector for protecting and beautifying concrete surfaces. Organic coatings offer several advantages, including ease of application, good adhesion, and a wide range of available formulations, allowing customization for specific needs. However, they have limitations in terms of susceptibility to environmental degradation, microbiologically influenced corrosion, reduced thermal stability, and potential for limited long-term durability under respective exposure. Furthermore, concerns regarding the environmental impact of organic coatings have prompted researchers to explore alternative solutions.

One prominent area of research involves nanomaterial-based coatings for surfaces made of cementitious construction materials. Nanomaterials, such as graphene or nano-silica, have garnered significant attention due to their potential to impart exceptional mechanical strength, improved resistance to environmental factors (*e.g.*, moisture, UV radiation), and even self-healing properties. Despite these remarkable advantages, challenges persist, including achieving uniform dispersion of nanomaterials in the coating matrix, ensuring scalability for large-scale applications, and addressing potential environmental concerns associated with nanomaterial release during manufacturing or service life.

An alternative avenue is the utilization of inorganic coatings, which offer their unique set of benefits. Inorganic coatings, such as silicate-based or mineral-based coatings, are known for their outstanding chemical resistance and long-term durability even under severe exposure conditions. They provide robust protection for cementitious construction material surfaces, especially in aggressive environments where organic coatings may falter. However, they may be less flexible than organic counterparts and can exhibit limitations in terms of aesthetic options.

Finally, a completely novel approach was introduced. Incorporating rare earth metal ions in the surface of cementitious construction materials could combine the advantages of organic and inorganic surface treatments as well as integral waterproofing. With this procedure, the inherent properties of the surface of cementitious construction materials could be modified and since the rare earth metal ions would be part of the structure, it is expected that this modification would last for a long time despite weathering effects.

In conclusion, surface coatings for cementitious construction materials encompass a diverse landscape, from traditional organic coatings to emerging nanomaterial-based solutions and resilient inorganic alternatives. Each category presents its own set of advantages and challenges, and ongoing research seeks to optimize these coatings for specific applications while considering environmental sustainability and long-term performance.

Abbreviations

c	Concrete
CC	Calcium carbonate
CH	Calcium hydroxide
CS	Calcium–silicate
C–S–H	Calcium–silicate–hydrate
CEM I, II, III, IV, V	Types of cement according to EN 206-1
D	Diffusion constant
FA	Fly ash
IR	Infrared
m	Mortar
MMER	Metal–metal exchange reaction
MPER	Metal–proton exchange reaction
OPC	Ordinary portland cement
p*K*	Strength of an acid on a logarithmic scale
PMC	Polymer-modified cementitious material
POA	Palm oil ash
PUR	Polyurethane
REOs	Rare earth oxides
rGO	Reduced graphene oxide
RHA	Rice husk ash
TEOS	Tetraethoxysilane
ToF-SIMS	Time-of-flight secondary-ion mass spectrometry
UV	Ultraviolet (light)
w/c	Water-to-cement ratio
γ_{SL}	Surface free energy of solid into contact with liquid
γ_{SV}	Surface free energy of solid into contact with vapor
θ	Contact angle
ξ	Bjerrum constant
μ-XRF	Micro X-ray fluorescence

Conflicts of interest

The authors declare no competing financial interest.

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