

Review

Predicted Corrosion Performance of Organofunctional Silane Coated Steel Reinforcement for Concrete Structures: An Overview

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Abstract: This article provides a comprehensive overview of the potential use of organofunctional silane coatings in the corrosion protection of concrete reinforcement in close relation to other commercially used coating technologies—i.e., epoxy coatings and bath hot-dip galvanizing coatings. The application technology of the steel surface is described in detail, and the corrosion performance and bond strength in concrete are compared. The paper also points out the possibility of improving the durability of epoxy coatings by the addition of silanes and, in the case of application to the surface of hot-dip galvanized steel, they can prevent corrosion of the coating by hydrogen evolution. The application potential of organofunctional silanes is also presented in the form of hydrophobic coatings on concrete surfaces or as corrosion inhibitors in simulated concrete pore solutions. The use of a suitable type of modified silane coating on the surface of carbon steel reinforcement can increase the corrosion performance and can also increase the bond strength in concrete. However, these facts need to be experimentally verified.

Keywords: corrosion of steel in concrete; epoxy-coated steel; hot-dip galvanized steel; organosilane coatings; bond strength



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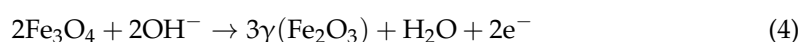
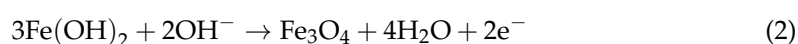
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1. Introduction

The corrosion protection of reinforcement by coatings is often the most economically acceptable option for the construction industry to guarantee the prolongation of the service life of reinforced concrete structures. In contrast, the application of corrosion inhibitors may not always be effective and cathodic protection can only be used in some cases. Organofunctional silane coatings may be a promising alternative to existing coatings applied in practice (epoxy coatings and hot-dip galvanized coatings), the effectiveness of which needs to be experimentally verified. It is clear from the literature that these coatings are able to improve the corrosion protection performance of epoxy coatings, hot-dip galvanized coatings and the surface of the carbon steel without any coatings. This paper studies the relationship between these facts in detail.

The corrosion of the mild steel reinforcement of concrete significantly limits the service life of reinforced concrete structures [1,2]. When reinforcement is surrounded by concrete, the presence of a strongly alkaline pore solution results in forming protective passive layer on the steel surface that leads to a negligible corrosion rate [3–6]. It is generally stated that the passive layer consists (double layer model) of an outer layer (~10–15 nm) rich in Fe^{III} oxo/hydroxides (without significant protective properties due to the very common rough discontinuous morphology structure) and an inner layer (~2–3 nm) rich in Fe^{II} oxo/hydroxides, providing significant protective properties to the mild steel in concrete [6–8]. The magnetite phase (Fe^{II} content in the form FeO) forms a thin, continuous and non-porous protective layer that adheres very well to the steel surface. More detailed studies of the passive layer composition demonstrate the presence of an inner

layer of lamellar phase of magnetite (Fe_3O_4) and an outer layer of hydrous gelatinous $\text{FeO}(\text{OH})$ [9–12]. It is sometimes considered that the lowest layer is composed of FeO and the uppermost layer of Fe_2O_3 [13], while the growth of the outer layer is not homogeneous but is of a topotactic nature [10]. However, in general, it can be summarized that the protective properties of the underlying steel are provided by the magnetite– Fe_3O_4 phase. The final composition of the passive layer in concrete depends mainly on pH and oxygen content. In simulated concrete pore solutions, the mechanism of passive layer formation was described by the initial formation of $\text{Fe}(\text{OH})_2$ (see reaction (1)). Subsequently, $\text{Fe}(\text{OH})_2$ is electro-oxidized to Fe_3O_4 —this is described by reaction (2). The magnetite phase subsequently undergoes further chemical reactions (or structural rearrangements), which are related to passive layer ageing that leads to the formation of oxo/hydroxide Fe^{III} in the form of $\alpha\text{-FeOOH}$ (goethite, see reaction (3)) or $\gamma\text{-Fe}_2\text{O}_3$ (maghemite, see reaction (4)) [11].



In Figure 1, the real concrete condition within the potential vs. pH diagram (in the potential vs. pH diagram, this region shows a thermodynamically defined environment that takes into account real concrete) is defined for the Fe– H_2O system under the formation of a protective passive magnetite layer (Fe_3O_4) [14]. The double layer composition of the passive film formed on mild steel depends on the pH of the pore solution [15], the temperature of the pore solution [16], the presence/absence of Ca^{2+} [11] and the availability of atmospheric oxygen [17]. In the case of aerated concrete profiles (exposure under atmospheric conditions), the presence of a protective passive layer is detected by relatively noble electrochemical potentials of embedded steel in the range of -100 to $+200$ mV versus the saturated calomel electrode (SCE) [18]. The formation of the protective passive layer is a gradual process that occurs only after longer exposure times to ensure negligible corrosion rates in the concrete environment [19–21]. The development of the protective passive layer has been shown to be very significantly related to the exposure environment, i.e., whether the exposure occurs in real concrete or in a simulated concrete pore solution [7,19,22]. If steel is applied to concrete structures with an already continuous layer of corrosion products (corrosion of the steel surface during storage, transport and/or handling), a sufficiently protective passive layer may not form, providing surface corrosion at an acceptable corrosion rate of up to $1 \mu\text{m}/\text{year}$ (corresponding to a corrosion current density of approximately $0.1 \text{ mA}\cdot\text{m}^{-2}$) [23–26].

The transition step from passive to active corrosion can occur as part of the carbonation of the concrete cover. The carbonation of the concrete cover layer is understood as a decrease in the alkaline buffering reserve (formed mainly by dissolved $\text{Ca}(\text{OH})_2$ and marginally by dissolved KOH and NaOH) of the concrete pore solution due to the penetration of atmospheric CO_2 (and marginally also NO_x and SO_2). $\text{Ca}(\text{OH})_2$ is formed as a by-product of the hydration of clinker minerals to form mainly C–S–H gel and a mixture of KOH and NaOH is present in small amounts in ordinary Portland cement [27–29]. Gaseous CO_2 diffuses mainly through air-filled pores of concrete. The diffusion of dissolved carbon dioxide through water-filled pores and the inherent convection play an entirely marginal role in the rate of carbonation concrete cover [30]. The decrease in the pH of the concrete pore solution is caused by the reaction of consumed $\text{Ca}(\text{OH})_2$ with CO_2 to form a sparingly soluble calcium carbonate (calcite or aragonite)—see reaction (5) and (6). With prolonged exposure, soluble $\text{Ca}(\text{HCO}_3)_2$ is formed, the effect of which is to permeate the carbonation at depth—see reactions (7) and (8) [27,30,31].

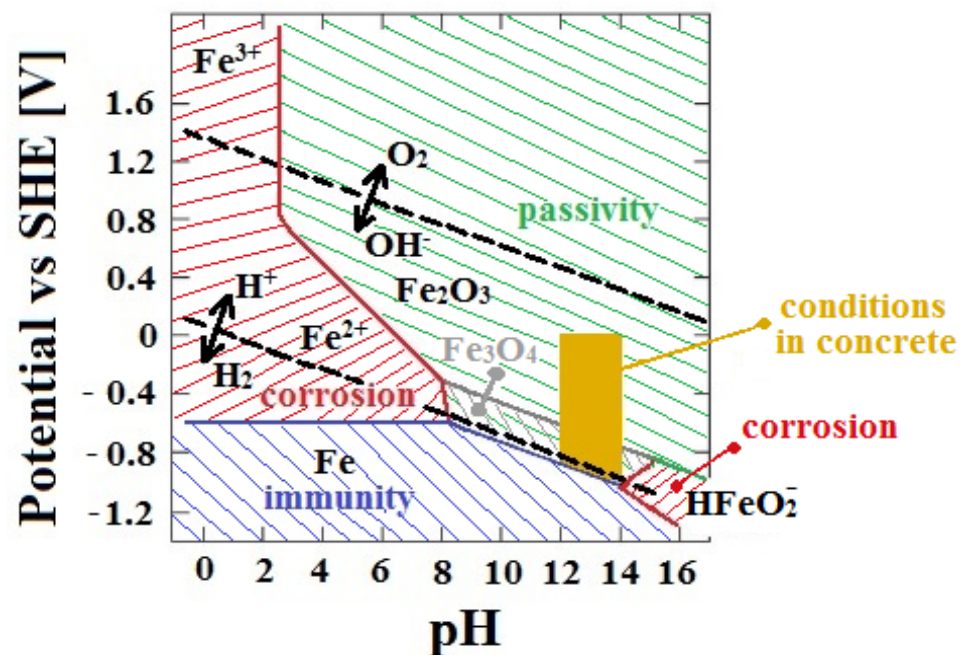
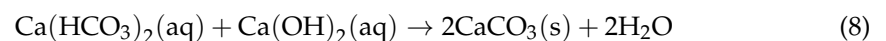
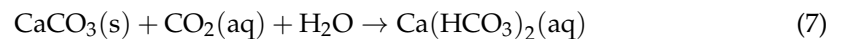
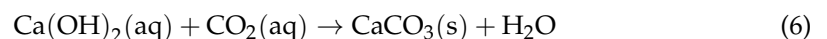
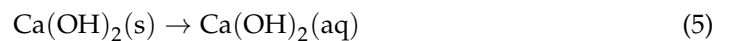
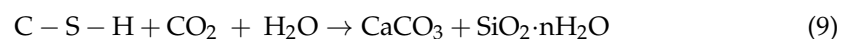


Figure 1. Potential-pH (Pourbaix) diagram for Fe-H₂O at 25 °C and [Fe²⁺], [Fe³⁺] and [HFeO₂[−]] = 10^{−6} M, SHE—standard hydrogen electrode (reprinted from [14]).



The rate of diffusion and reactivity of CO₂ within the carbonation of concrete depends on temperature, relative pore humidity and degree of carbonation [30]. The usual pH of concrete pore solution formed from ordinary Portland cement (OPC) is higher than 13 [32]. However, due to carbonation, it may gradually decrease to values that clearly cause the transition step of corrosion of the mild steel surface from a passive to an active state. This is usually reported to occur at a concrete pore solution pH between 10.0 and 9.4 [33], but results from other work indicate that it can appear as low as pH 11.5 (starts to depassivate) [32]. The overall decrease in the pH of the concrete pore solution (OCP) due to carbonation can reach a limiting value of 8.3 [33]. The permeation of gaseous CO₂ through the concrete cover layer can also react with C-S-H gel (exact stoichiometric relationships are unknown) to form crystalline CaCO₃ and amorphous hydrated SiO₂ (simplified reaction can be written according to Equation (9)) [30,34,35].



This reaction, however, does not affect the alkalinity of the concrete pore solution and therefore does not affect the actual corrosion damage to the steel reinforcement in the concrete. Due to carbonation, the concrete cover layer becomes denser (decrease in concrete permeability and increase in concrete hardness). It is usually reported to be less porous (the increase in volume when converting Ca(OH)₂ to calcite is approximately 11%, when converting to aragonite is approximately 3%) [30,35,36]. Although the carbonation process improves the mechanical properties of the concrete cover, it has a negative effect on the freeze–thaw resistance or shrinkage behavior of the concrete [31,35]. In general, however, it can be summarized that the effect of the carbonation of the concrete cover layer on the

inherent corrosion damage of conventional concrete reinforcement is more gradual and less significant than the effect of chloride anions [31].

Chloride anions from seawater or de-icing salts (NaCl , CaCl_2) cause localized corrosion damage (pitting corrosion mechanism) by breaking down of the protective passive layer. Due to corrosion damage caused by chloride ions ingress, porosity of the concrete cover is dominantly affected by the capillary pores between the hydrating C-S-H gel particles (up to $1\ \mu\text{m}$ in diameter); the gel pores in C-S-H (around $2\ \text{nm}$ in diameter) are less significant. A representation of these two groups of pores is shown in Figure 2 [37,38]. Bulk and transverse cracks resulting from mechanical damage, faulty transport operation, deposition, or concrete treatment have the most significant effect on the transport of chloride anions to the surface of steel reinforcement [38,39]. The transport of chloride anions through the concrete cover layer is provided by diffusion (according to concentration gradient), migration (by the electric field) and water flow (influence of pressure gradient). The rate of transport of chloride anions through the concrete cover layer is mainly influenced by the thickness and quality of the concrete cover, as well as by humidity, temperature and other parameters.

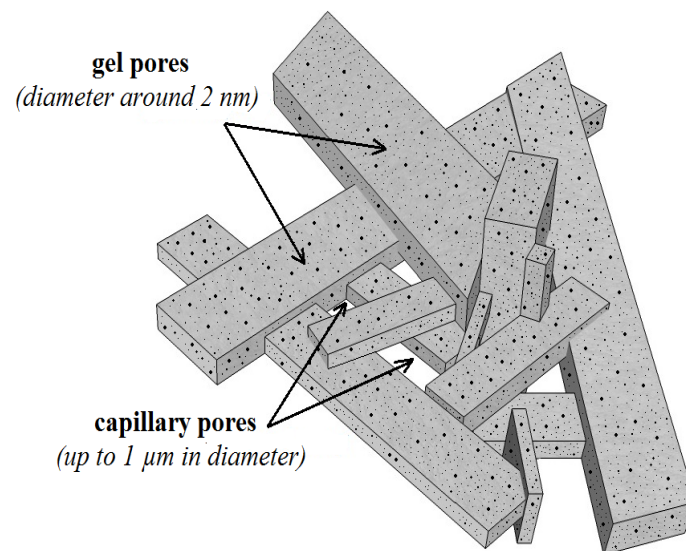
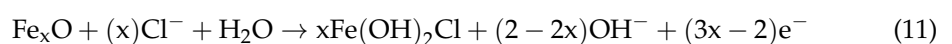
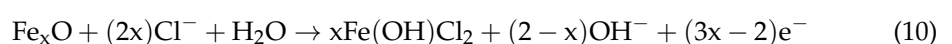


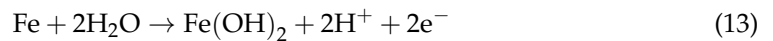
Figure 2. Representation of two common pores in concrete cover formed by hydrated C-S-H gel (reprinted from [37]).

It has been shown that the actual corrosion damage induced by chloride anions is very significantly influenced by the quality of the phase interface (ITZ—interfacial transition zone, area in the concrete close to the surface of the steel reinforcement), with the most vulnerable areas of the steel surface without the presence of cementitious sealant (cavities formed by sealed air, or e.g., by not well mixing of cement paste), cracks and defect in the steel scale [38,40,41]. A thin layer of calcium hydroxide (portlandite) with a pH buffering effect usually forms around the surface of steel reinforcement, aggregates, fibers, etc. [42,43]. The mechanism of intrinsic highly localized corrosion damage to the surface of mild steel in concrete (pitting corrosion mechanism) is two-stage and involves pit nucleation and pit growth [38,39,44]. Pit nucleation involves the local dissolution of the protective passive layer, where the subsequent repassivation process is not conducted to the extent required for surface re-passivation—pit stabilization and subsequent pit growth occurs. The actual description of the passive layer breakdown can be described by Equations (10)–(12). The resulting compounds containing chloride anions are well soluble [13].





It is assumed that, due to the action of chloride anions, oxo/hydroxide Fe^{II} in the inner layer of passive film is transformed under sufficient oxidizing power into oxo/hydroxides Fe^{III} , which no longer bear the protective properties of the underlying steel [13,44,45]. It is apparent that the local pH decrease in the microanode region plays an essential role in the stabilization of the pit nucleation—see Equation (13), which leads to the destabilization of the passive layer and limits the possibility of repassivation (buffering effect of local cement paste) [38,40,46,47]. This equation occurs mainly due to the rapid consumption of the present oxygen by the cathodic corrosion reaction (see Equation (14)).



The scheme of chloride-induced corrosion of mild steel reinforcement after breakdown of the passive layer and pit stabilization is shown in Figure 3.

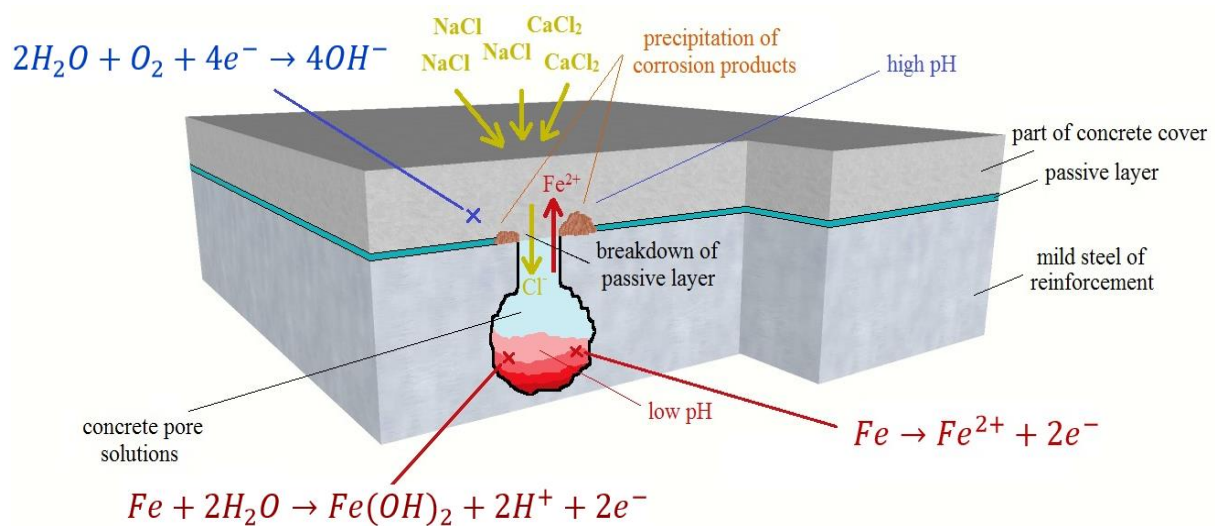
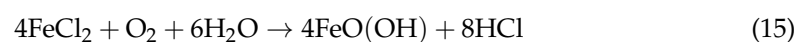
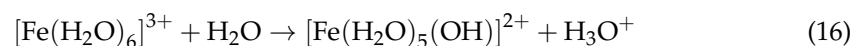


Figure 3. Schema of chloride-induced corrosion of mild steel reinforcement in concrete with breakdown of passive layer and stabilization and acidification of inner pit area.

If sufficient oxygen availability of the corroding steel surface is ensured, the catalytic effect of chloride ions for the corrosion stimulation (pit acidification) of mild steel in concrete can occur by reaction breakdown of the chloride iron complex—see Equation (15) [40,41].



The local decrease in the pH of the pore solution may also be due to hydrolysis of the formed Fe^{3+} cations, which is more extensive than Fe^{2+} (see Equation (16)) [48].



At the same time, it should be noted that a decrease in the pH of the pore solution at the phase interface due to carbonation or pit nucleation (chloride-induced corrosion) can cause the release of bound chloride anions, which increase the aggressiveness of the condensate at the phase interface [32,49,50]. The pit growth rate (after stabilization of the pits) is subsequently related to the rate of O_2 and H_2O transport through the concrete cover [38]. The stimulation of intrinsic corrosion damage is due to the quite typical ratio of small anode area to large total cathode area [38,41]. To evaluate the level of risk of corrosion damage of conventional mild steel reinforcement due to the action of chloride anions, the

level of contamination of the concrete cover layer by these anions (by weight of dried cement) is usually verified; this particular value is called chloride threshold value or critical chloride content [18,38,40,41]. Chloride-induced corrosion of reinforcement in concrete is observed when a chloride threshold value (free chloride anions contaminating the concrete cover layer) of 0.20 wt. % is reached [18,38]. If the chloride threshold value is exceeded and under easy oxygen access, the corrosion current density (corresponding to corrosion rates up to 1 $\mu\text{m}/\text{year}$) can significantly exceed $0.1 \text{ mA}\cdot\text{m}^{-2}$ and locally up to 1000 times [38,41]. In simulated concrete pore solution (saturated calcium hydroxide) would be damaged the passive film as the $[\text{Cl}^-]/[\text{OH}^-]$ ratio in the solution reaches 0.6 [51,52].

The resulting corrosion products of concrete reinforcement have a significantly higher relative volume than the original mild steel ($\alpha\text{-Fe}$), causing cracks in the concrete cover and subsequently spalling. The progressive exposure of more reinforcement surfaces to the atmosphere accelerates and extends corrosion damage [53–57]. The corrosion of reinforcement also decreases bond strength with concrete [57–59].

Because the costs associated with repairing buildings and bridges due to corrosion damage to reinforcement are significant (in the United States around \$150 million per year), it is necessary to use various corrosion protection measures in an effort to extend the service life of structures [11]. Cathodic protection (electrochemical protection of conventional reinforcement) with a sacrificial anode or a DC current source connection [60–62] or the use of corrosion inhibitors [63–66] is often discussed as corrosion protection. Increasing the thickness and compactness of the concrete cover may be preferred for corrosion protection of concrete reinforcement. Coating concrete reinforcement can be a very practical, simple and economical method of corrosion protection. In actual construction, epoxy-based coatings (usually fusion bonded epoxy coatings) and hot-dip galvanized (HDG) coatings have already been used, with the practical application of epoxy coatings being more significant in this case. Organosilane coatings are an interesting option from the perspective of corrosion protection of mild steel reinforcement of concrete, as they can not only be applied to the steel surface but can also substantially improve the corrosion protection properties of hot-dip galvanized steel, even when used in concrete. This paper details the inherent chemical behavior of organosilane coatings with respect to the application to mild steel and hot-dip galvanized steel surfaces, corrosion performance in real concrete and simulating concrete pore solutions and bond strength properties. The information provided is put into a comparative concept discussion of the corrosion performance and bond strength characteristics of epoxy-coated reinforcement and hot-dip galvanized reinforcement as the prominent representatives of coated concrete reinforcement used in real structures.

2. Surface Coatings of Reinforced Steel

Applying coatings on the surface of mild steel reinforcement usually does not significantly increase the costs. The effectiveness of many types of coatings, such as phosphate conversion coatings [67,68], bitumen-based coatings [69,70], or stainless-steel reinforcement [71–74], etc., has been experimentally verified. In this paper, however, only coatings that have been found to be applicable in construction practice (epoxy coatings, hot-dip galvanized coatings) are discussed in detail, and then organosilane coatings are compared with these coatings. For each type of coating, general technology aspects of the coating process, corrosion performance and bond strength in concrete are discussed.

2.1. Epoxy Coatings

Epoxy coatings have found widespread application in corrosion protection of conventional concrete reinforcement, especially in bridges, marine structures, parking garages, and tunnel structures, intending to prolong service life with respect to the influence of chloride anions (de-icing salts, seawater environment). From the point of view of coating technology, fusion-bonded epoxy coatings (FBE, FBEC) have found a widespread application, rather than wet (liquid epoxy coatings) coating systems (dipped in a fluidized bed of epoxy powder). The use of liquid epoxy coatings (mixing stoichiometrically balanced proportions of

two-part system, epoxy resin and polyamine) is associated with the formation of a coating with a naturally higher porosity (evaporation of usually contained solvents) and therefore with a lower corrosion performance. Compared to FBE, the application technology of liquid epoxy coatings is economically less demanding. This is mainly due to applied lower energy intensity. In FBE coating process, the surface of the reinforcement is first blasted and then the epoxy powder is applied to the steel surface by electrostatic spray. The steel is preheated to a temperature of around 230 °C. The electrically charged powder particles are attracted to the preheated steel and melt to form a continuous film. Then, the system is quenched to form a solid coating [75]. The fusion-bonded epoxy coatings provide the formation of a coating with higher thickness, a more uniform manner and fewer defects (cracks, pinholes, holidays). Such a coating is also cost-effective (the cost associated with the use of FBE is approximately double that of uncoated steel reinforcement). Epoxy-coated reinforcement was first used in a bridge in Pennsylvania (USA) in West Conshohocken in 1973 [35,76–79]. Generally speaking, it is the United States and Canada where epoxy-coated reinforcing steel is most widely used (used in the construction of, e.g., Bay Bridge in California, Wacker Drive Downtown Chicago, Biloxi Bay Bridge in Mississippi, Aqua Building in Chicago, Denver Union Station Redevelopment, etc.) and in the range of 550,000–600,000 t/year. Epoxy-coated reinforcing steel is also widely used in Japan, India, China and the Middle East (especially the Arabian Gulf region) [76,80,81]. As of 2013, it has been reported that epoxy-coated reinforcement has been used to construct of over 80,000 bridges in the USA and Canada [76]. The number of construction projects in the EU using epoxy-coated reinforcement is significantly less than in the previously mentioned countries (Great Belt Bridge/Tunnel in Denmark is an example) [82].

Through field studies, it has been verified on real bridge structures that the use of protective epoxy coatings can extend the service life of structures from 35 years (uncoated steel) to 70 years and in some cases up to 100 years. It has been shown to theoretically increase chloride threshold value over uncoated steel by 2–4 times. For economical reasons, very often this surface treatment is used in critical areas of the structure (especially considering the presence of chloride anions) [81,82].

2.1.1. General Technology Aspects

Epoxy coatings exhibit high chemical and corrosion resistance, good mechanical and thermal properties, outstanding adhesion to various substrates, low shrinkage upon cure, good electrical insulating properties, and the ability to be processed under various conditions. On the other hand, these coatings are usually brittle and temperature-sensitive, and high relative humidity and the presence of CO₂ negatively affects the curing process [83,84]. Although epoxy coatings contain hydrophilic chemical group (cured epoxy structure usually includes a hydroxyl group (-OH), a carboxyl group (C=O) and an amino group (-NH₂)), they are preferably used in steel surface protection and marine environment [85–87]. The most commonly used in metal surface treatment is 2,2-Bis(4-(2,3-epoxypropyl)phenyl)propane, widely known as bisphenol A diglycidyl ether (DGEBA/BADGE)—see Figure 4. This substance is formed by reacting one mole of bisphenol A with two moles of epichlorohydrin. The pure form of bisphenol A diglycidyl ether is a crystalline material with a melting point of 40–44 °C [87,88]. The excellent strength of adhesion to steel surfaces (also to aluminum and magnesium alloys) is mainly due to the presence of hydroxyl groups and aromatic rings (strong attractive interactions). It is evident that the flat-laying orientation of the epoxy coatings on the Fe surface is significantly more stable than the standing-up orientation [89,90]. Curing of epoxy resins (curing agents) is mediated by labile proton-containing compounds such as amines, amino alcohols, carboxylic acids, phenols, thiols, imidazoles and poly(amidoamine)s, including Lewis acids and bases. In practice, amines (amino alcohols) are most commonly used, and their reactivity for opening oxirane (epoxy) rings varies. Aliphatic polyamines are very reactive and cause curing of epoxies at ordinary temperatures but produce thermosets with low heat distortion. Conversely, aromatic polyamines cause the curing of epoxies up to and at higher temperatures but produce

thermosets with high heat distortion temperatures [91–94]. A partial illustration of the mechanism of curing of epoxy resins by polyamines (polyamino alcohols) is shown in Figure 5 [95,96].

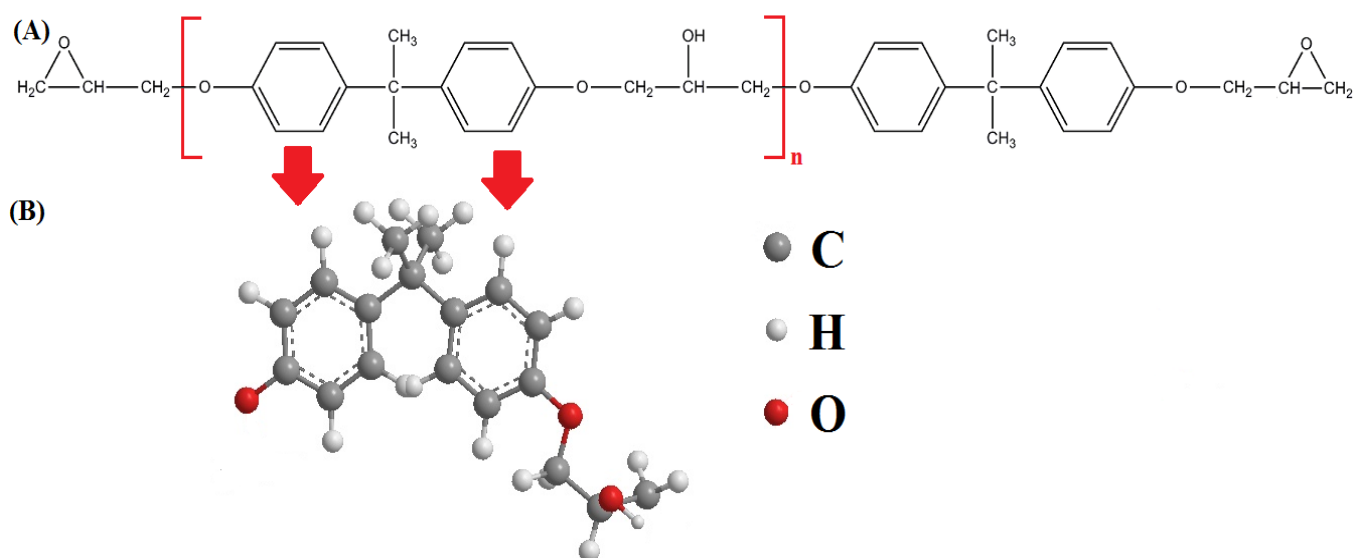


Figure 4. (A) Chemical structure of the diglycidyl ether of bisphenol A. (B) 3D chemical structure of monomer component of bisphenol A.

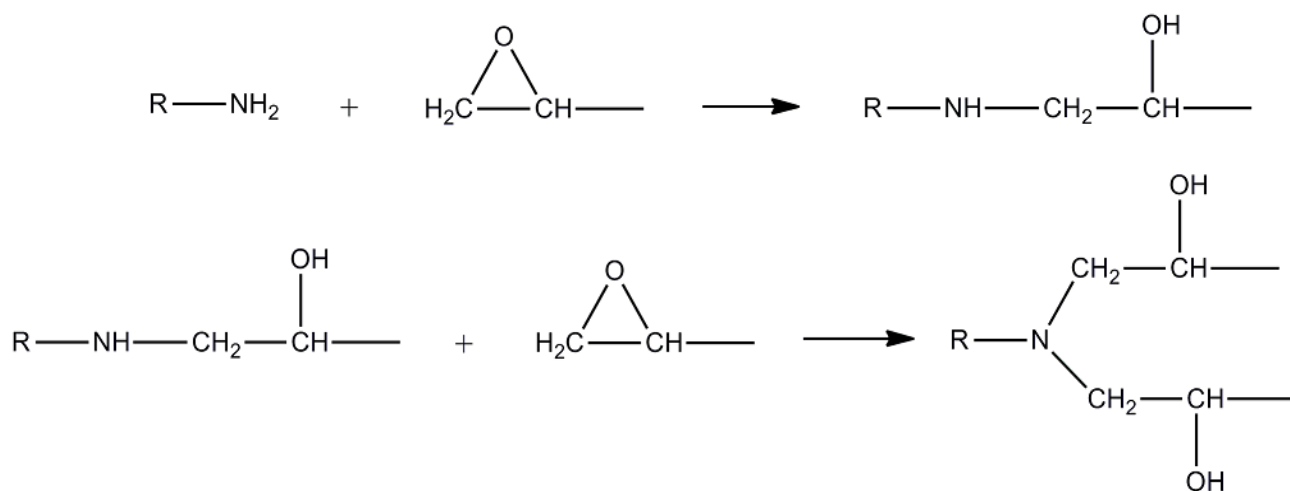


Figure 5. Demonstration of a partial epoxy resin curing mechanism using aliphatic polyamines and polyamino alcohols (oxirane ring-opening).

The most significant failure mode of epoxy coatings is poor resistance to sunlight (low resistance to UV, absorption of aromatic structure of the epoxy coating)—formation of chalky material. This fact may not only reduce the adhesion of the eventual topcoat, but also influence the formation of cracks in the coating, which may condition the corrosion damage of the underlying steel [97,98]. Prolonged exposure of epoxy-protected concrete reinforcement to solar radiation, especially during the summer months (prolonged storage or delayed/staged construction, longer than a month), can cause shrinkage-induced cracking of coatings and a significant weakening of the barrier-protective function of the coating. Oxidation and formation of carbonyl groups occur in areas of damage [98,99]. To increase the resistance of the coating to UV radiation, additives based on ZnO, TiO₂ and carbon black nanoparticles (0.7 wt. % to 2.5 wt. %—increases the resistance approximately twice) are added [100–103]. Cracking of the epoxy coatings can also cause heating–cooling cycles [98].

The addition of small amounts of nanostructured Fe_2O_3 or nanostructured halloysite clay ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O} + \text{SiO}_2$) can significantly increase the corrosion resistance of the coating (providing denser microstructure—enhance the packing of epoxy coating) [104,105]. Additions of barium sulfate improve the tensile strength of the coating and can also strengthen bonding among steel and coating [106,107] and additions of barium titanate improve dielectric and surface properties [108]. Additions of organic substances can also enhance the properties of epoxy coatings—e.g., additions of polyamide could increase the density and resistance to wear [109].

2.1.2. Corrosion Performance

Based on most of the results of laboratory corrosion tests and observation of field performance, it is reported that an adequately made fusion bonded epoxy coating (without defects) and of sufficient thickness significantly prolongs the service life of reinforced concrete structures [81,110–112]. However, it should be noted that proper handling of such coated reinforcement on site is crucial, as significant damage to the coating (imperfection) can occur, especially at the tops of the ribs (dragged) [113,114]. Due to coating damage leading to premature corrosion, it is necessary to strictly limit metallic tie wires and needle vibrators with metallic vibrating heads for compacting the concrete in construction practice [98]. However, excessive bending of epoxy-coated reinforcement can damage the coating even more significantly than dragged (for typical coating damage, see Figure 6) [114]. Such coated reinforcement cannot be joined on site by welding, and joining can only be conducted with coated connecting wire or sleeves [115]. Any minor coating defects can be repaired on the construction site (using an acceptable epoxy resin repair system) [81,114]. As part of adequate corrosion protection, especially against the action of supercritical amounts of chloride anions, it is essential to ensure sufficient coating thickness, with recommended thicknesses in the range of 175–350 μm (ASTM A775 and IS 13620) [114,116,117]. In the case of an average thickness of 100 μm and below, sufficient protective properties of the coating are not ensured and premature corrosion may occur [118]. It is sometimes reported that epoxy coatings with a thickness of not less than 200 μm have significant protective properties [113,119].

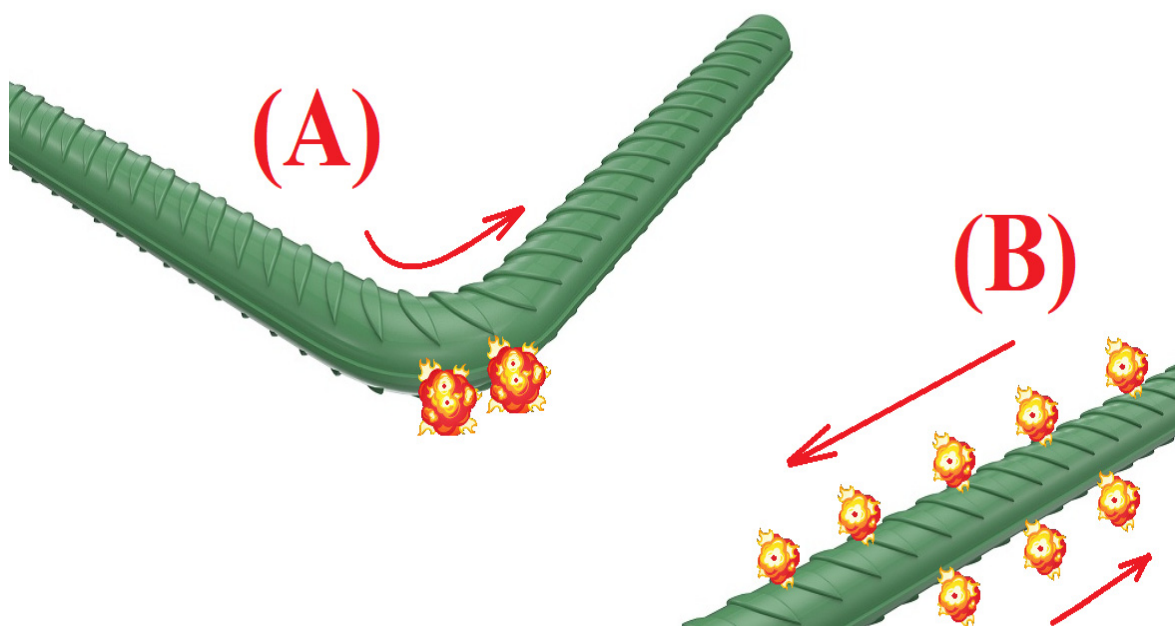


Figure 6. Typical examples of epoxy coating damage: (A) damage/cracking of coating by bending (using metallic levers); (B) scratch damage on the top of the ribs due to dragging of rebars at construction sites (reprinted from [114]).

Epoxy coatings of sufficient thickness (without cracks, holidays and pinholes) can protect the underlying mild steel against corrosion damage by several mechanisms [109,114,120]:

- (a) providing a physical barrier from the surrounding environment;
- (b) limiting the formation of anodic and cathodic sites;
- (c) restricting the ionic conduction between anodic and cathodic sites at the steel surface.

However, regardless of the thickness, the dielectric epoxy coating is partially permeable to oxygen and moisture. If a layer of condensate forms on the steel surface below the coating, corrosion damage will occur, which is limited by oxygen access to the metal surface. Two-component epoxy coatings can absorb water molecules in the range of about 1 wt. %–7 wt. % by weight of coating [121,122]. However, it is mainly the curing agents that affect the ingress of the water molecules in the polymer structure [123,124]. From the concrete/epoxy coating phase interface, water molecules reach the epoxy coating/steel interface by diffusion, and they not only condition the electrochemical corrosion process but can also induce water-induced adhesion loss (it is a reversible process that causes water film many monolayers thick) [125].

In the presence of sufficient amounts of chloride anions on the steel surface, corrosion damage is stimulated and localized (see above). However, the average value of the chloride diffusion coefficient of fusion-bonded epoxy coating ($D_{cl,coating}$) was determined to be approximately 10^{-20} m²/s, which is significantly less than that of the trough of concrete coating (approximately in the range of 10^{-8} to 10^{-12} m²/s) [113,114,126,127].

The actual electrochemical mechanism of corrosion of the underlying steel in the area of defects in the coating in the presence of chloride anions is based on anodic blistering (breaking of the adhesion of the organic coating through hydrolysis reactions) near and along the defects and cathodic delamination (in scribes) around the anodic blistering and away from the defects. Anodic blistering occurs through two processes—anodic sites' localized corrosion and a subsequent blistering effect based on the osmotic pressure mechanism [128,129]. Crevice corrosion and underfilm corrosion mechanisms have also been described around defects in the coating [113,130].

The improvement of the corrosion performance of epoxy coatings on reinforcing bars can be ensured by using Cr^{VI}-based conversion coatings (formed between steel surface and epoxy coating). Still, the use of these chromate coatings is currently significantly limited due to environmental and health risks [131,132]. Other coatings include phosphate-based conversion coatings [133], zirconium-based conversion coatings [134] and cerium-based conversion coatings [135].

Recently, the significant anti-corrosion properties of epoxy coatings modified with nano-clay or tung oil microcapsules have been experimentally verified. It was found that the coating modified with nano-clay particles exhibited enhanced toughness and barrier-protective effect. The addition of tung oil microcapsules imparts self-healing capabilities to the coating [136,137]. A significant anti-corrosion effect is also achieved by completely alternative smart coatings based on molybdate-loaded halloysite nanotubes (phytic acid and polyvinyl alcohol formed a graphiting solution) [138].

While many research results show very good corrosion performance (a prolonged service life compared to uncoated steel), the use of epoxy-coated reinforcement is banned (in, for example, Florida) or not recommended (Virginia, Ontario, Quebec) in some states of the USA and Canada [114]. The reason for this was the previously unproven insufficient corrosion performance of epoxy-coated reinforcement in concrete (significant extension of service life), especially against exposure to environments with a substantial presence of chloride anions—e.g., the Long Key Bridge in the Florida Keys [81,112,139]. But the bars used in this structure were not manufactured to represent acceptable practice.

The effective use of epoxy-coated reinforcement is linked to using quality coatings of sufficient thickness with quality control of the coating (good handling and transportation on the construction site) during construction.

The stability of epoxy coatings in the alkaline environment of concrete pore solution is related to the choice of epoxy type. However, the resistance of epoxies to alkaline

environments is excellent, hence the application of epoxy polymer concrete. This building material is more stable in alkaline environments than polyester polymer concrete.

2.1.3. Bond Strength in Concrete

The use of epoxy-coated reinforcement is often not recommended not only because of the often observed (observation of field performance) poor corrosion performance but also because of the observed reduced bond strength between reinforcement and concrete [140–142]. The bond between steel reinforcement and concrete is a crucial property for the load-bearing capacity of a reinforced concrete structure [143–145]. In experimental verification, it has been found (compared with uncoated steel) that the reduction in bond strength of epoxy-coated reinforcement in concrete can be 15–50%, with important roles played by coating thickness, bar size and location, deformation patterns, concrete properties, casting conditions, testing method, and ambient temperature during testing and the adopted test method [80,146–151]. Epoxy coating of reinforcement initiates bond-splitting failure mode at lower loads [142].

The presence of an epoxy coating may reduce the adhesion coefficient, i.e., reduce the adhesion of the cement paste to the surface of the reinforcement [150]. It has been experimentally verified that for plain bars the epoxy coating does not affect the friction coefficient for plain bars. Still, for deformed bars, the coating significantly reduces the bar friction coefficient—which has the effect of reducing bond strength [151]. With respect to the bond strength of epoxy-coated reinforcement, the effect of coating thickness is very often discussed—with increasing coating thickness, corrosion performance usually increases, but bond strength with concrete decreases [81,114]. It is usually stated that there is a significant decrease in bond strength with epoxy coating thicknesses greater than 350 μm [114,119] or greater than 420 μm [118]. This is because with increasing bond strength, the surface smoothes (change of rib geometry—a decrease in relative rib area) of the ribbed reinforcement [152,153]. This is particularly evident in reinforcements with a diamond rib pattern rather than an inclined or perpendicular rib pattern [152,154]. A sufficiently thick epoxy coating can reduce rib face angle [152] and rib height [155], and decreases in either parameter reduce the bond strength of epoxy-coated reinforcement on concrete. The effect of epoxy coating thickness on the decrease in the bond strength of deformed bars is less significant for larger relative rib areas [156]. To minimize the decrease in bond strength of epoxy-coated rib reinforcement, it is recommended to use reinforcement with a steeper rib face angle and high deformed steel [151]. From this point of view, it is necessary to add that the effect of coating thickness on the bond strength is also related to bar size in the case of epoxy-coated steel [157]. It is often stated that, in general, the bond strength of epoxy-coated reinforcement decreases with increasing bar size (identical coating thickness). At the same time, it has been experimentally verified in the past that the bond strength also decreases with increasing coating thickness (for one type of bar size), but this has its limits. For a sufficiently large bar size the effect of increasing coating thickness on bond strength already has little effect [148,155,158].

The influence of concrete related parameters has a significant effect on the bond strength of epoxy-coated ribbed reinforcement (bearing capacity of concrete in front of the bar ribs). These are mainly the depth of concrete cover, concrete strength and types, concrete slump and concrete consolidation [155,158–160]. These parameters can significantly influence the bond strength and the overall load-bearing capacity of the reinforced concrete structure as a whole.

Because the corrosion effect of the epoxy coating thickness (175–350 μm) reduces the cohesion of the coated reinforcement, the length of the bar embedment is usually increased to compensate for this. For example, in the ACI 318 standard, the embedment length is multiplied by a factor of 1.50 for epoxy-coated bars with a coverage less than 3 d_b (d_b is the bar diameter) or a clearance between bars less than 6 d_b and a factor of 1.20 for other cases [149,161]. In the AASHTO bridge specification, these factors are 1.50 and 1.15 [149,162].

2.2. Hot-Dip Galvanized Coatings

Applying protective properties of hot-dip galvanized coatings on the surface of reinforcing bars in construction practice is less important than epoxy coatings. Nevertheless, it has been used in a considerable number of structures (bridges and other transport infrastructure construction, marine and offshore structures, chemical and processing plants, power generation and water treatment facilities), mainly due to resistance to the carbonation of concrete cover and due to significantly higher chloride threshold value [81,163,164]. From the perspective of the corrosion protection of concrete reinforcement, the hot-dip galvanizing (HDG) technology is mainly considered. Still, currently the continuous hot-dip galvanizing (CGR) technology is discussed for this purpose [81]. Hot-dip galvanizing involves immersing reinforcement bars in a molten zinc bath at a temperature of 450–470 °C (the immersion time varies from a few minutes for a light section to 20–30 min for heavy structural section) [81,163]. The continuous galvanizing coating is an in-line process, where blast cleaned and preheated bar is fed through a molten zinc bath at speeds higher than 10 m/min such that the bar remains in the zinc bath for no more than 1–2 s, and the total time at temperature including the preheating stage is not more than 4–5 s [81,165]. The thickness of the coating formed depends on many parameters, the technology of galvanizing, bath parameters, time of immersing, type of cooling process, microstructure and chemical composition of steel, the wall thickness of the coated part and, e.g., surface condition. The HDG coating shows a thickness strongly dependent mainly on the wall thickness of the coated part—usually in the range of 50–180 µm, whereas the CGR coating is around 50 µm [163,165]. The HDG coating consists of an inner Fe-Zn alloy layer and usually an outer pure zinc (eta phase) layer [163]. Hot-dip galvanized reinforcement was first used in the 1930s in the USA [81]. The use of hot-dip galvanized reinforcement is associated with the prominent large-scale example of many reinforced structures in Bermuda (the most notable example from this group is a pair of bridges: Longbird Bridge and New Watford Bridge), and it has been partially used in the realization of prominent buildings: Sydney Opera House, National Theatre London, New Parliament House Canberra, Parliament House Wellington and others. It has also been used for bridge structures in Florida, Iowa, Michigan, Minnesota, Vermont, Pennsylvania, Connecticut, Massachusetts, Ontario and Quebec. Bridge structures in France (Toutry Viaduct, Pont d'Ouche Viaduct) or offshore piers at Ominichi (Japan) are also well known [163,164,166]. Hot-dip galvanized reinforcement is approximately 50% more expensive than plain uncoated bar, as far as the economic case for galvanized reinforcement is concerned it can be summarized that the total cost is about 0.25–1.00% of the total capital cost of a typical building project [163,167].

Based on many field studies, hot-dip galvanized coating has been shown to extend the service life of reinforced concrete. This has been confirmed on several bridges in Iowa, Florida and Pennsylvania, as well as bridges in Bermuda. However, in some cases with very high levels of chloride anion-contaminated concrete, or high cracked concrete, the life extension may not be significant. Some field studies confirm that the chloride threshold level for hot-dip galvanized reinforcement is reported to be 2 to 2.5 times higher than that for uncoated steel, in some cases even 2.6 to 3 times higher [81,163,168,169]. Some field studies have shown that, because the significant contamination of the concrete cover layer by chloride anions, epoxy coating (sufficient coating thickness without defects) rather than hot-dip galvanized coating provides significant life extension [170,171].

2.2.1. General Technology Aspects

When steel profiles are dipped in a bath of molten zinc (batch hot-dip galvanized reinforcement), an alloy diffusion coating is formed on the steel surface. The inner layer of the coating is composed of Fe-Zn intermetallic phases, and the outer layer usually consists of a solid solution of iron in zinc (η -phase, 0.03 wt. % Fe). The coating layers differ in chemical composition, morphology, thickness and mechanical properties (mainly hardness). The iron content of the individual coating layers decreases towards the outer surface [172,173]. The composition of the hot-dip zinc coating on the surface of conventional

carbon steel is shown in Figure 7. The inner layer of the coating is composed of iron-rich phases (Γ phase). This group of phases is divided into Γ ($\text{Fe}_3\text{Zn}_{10}$, 23.5–28.0 wt. % Fe) and Γ_1 ($\text{Fe}_5\text{Zn}_{21}$, 17.0–19.5 wt. % Fe). Both of these phases crystallize in cubic systems, but the Γ phase is cubic space-centered (bcc) and the Γ_1 phase is cubic area-centered (fcc). The Γ phase is formed by a peritectic reaction between α -ferrite and zinc melt at 782 °C (see Equation (17)), but the Γ_1 phase is formed by a reaction between two intermetallic phases, Γ and δ (see Equation (18)), at a temperature of about 550 °C [172,174–176].

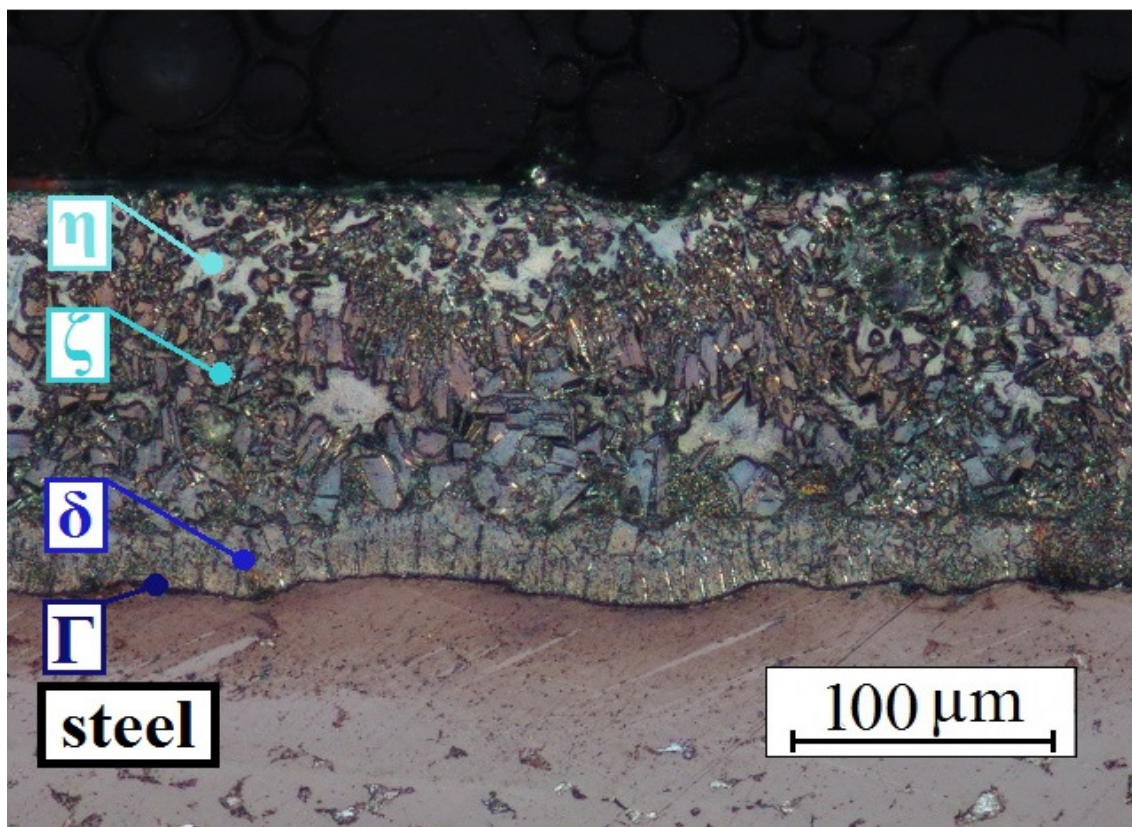


Figure 7. The structure of the usual hot-dip galvanized coating on the surface of mild steel. (Reprinted from archive of CTU—Klokner Institute.)

Above the cluster of gamma (Γ) phases are the delta δ phases, also in this case a cluster of δ_{1k} and δ_{1p} phases. The δ_{1k} (or δ) phase corresponds to the FeZn_7 crystal structure, and the δ_{1p} (or δ_1) phase corresponds to the FeZn_{10} (or $\text{Fe}_{13}\text{Zn}_{126}$) crystal structure. These intermetallic compounds form a hexagonal crystal structure with a $P6_3/mmc$ symmetry group and exhibit iron contents in the range of 7.0–11.5 wt. %. However, from a crystallographic point of view, there are differences between the two compounds. Both intermetallic compounds are formed by peritectic recombination of the gamma (Γ) and melt (L) phases. These facts are considered by Equation (19) [172,177–179].



In the hot-dip galvanized coating, the two phases are indistinguishable. However, the δ_{1p} phase has more palisade morphology and, conversely, the δ_{1k} phase is more compact in nature [177,178]. Above the delta (δ) phase grouping, the ζ phase (FeZn_{13} , 5.0–6.2 wt. %

Fe) appears, which usually has the most significant thickness in the HDG coating itself. It crystallizes in a single-clone basally centered system with a $C2/m$ symmetry group and has a typical palisade morphology in the hot-dip galvanized coating. This phase forms via a peritectic reaction between the delta phase (δ) and the zinc melt (L) at a temperature of approximately 530 °C—see Equation (20) [172,180–182].



The composition of the coating and its thickness is significantly influenced by the composition of the steel—especially the silicon and phosphorus content (however, the surface condition and thickness of the coated profile also have a significant influence). The most important thing from this point of view is the silicon content, in the case of Si content in carbon steel in the range of 0.03–0.12 wt. % (Sandelin region—gray coating) there is a dramatic increase in the thickness of the layer (even more than 1500 μm) and it is formed only by non-oriented monoclinic crystals of the zeta (ζ) phase (FeZn_{13}). Due to the dominance of this phase, the coatings are very fragile and susceptible to mechanical damage [172,183].

In the case of silicon content in the Sebysti region of the steel (0.15–0.25 wt. %), the hot-dip galvanized coating (the grouping of the Γ phases may not be noticeable) contains a grouping of the δ phases (δ_{1k} and δ_{1k}). Above the δ phases, a very thick ζ phase (FeZn_{13}) appears—see Figure 8. The thickness of the whole coating is significantly higher than in the case of non-silicon killed steel but not as significant as in the case of coating mild steel with silicon content in the Sandelin range (0.03–0.12 wt. %). The best structural differentiation (bright coating) occurs in steels with low silicon content (<0.03 wt. %). With increasing silicon content (>0.25), the level of differentiation of the individual layers of the intermetallic phases may decrease (again in favor of the ζ phase) and the overall coating thickness increases. Steels with silicon content above 0.28 wt. % cannot be recommended for galvanizing, as the coating is again only composed of non-oriented monoclinic crystals of the zeta (ζ) phase with already large coating thickness and brittleness [172,183].

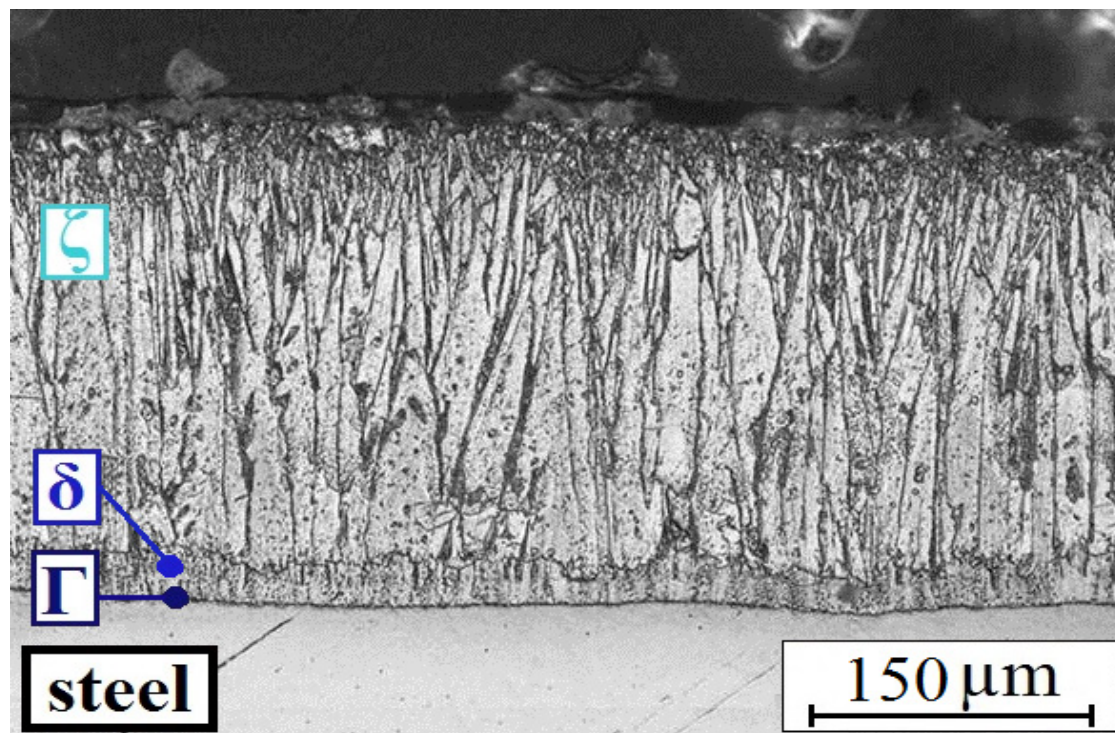
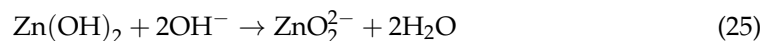
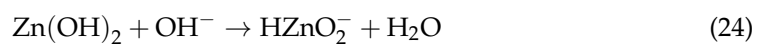
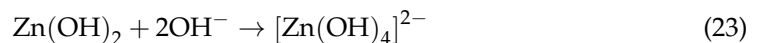
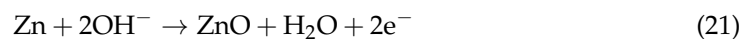


Figure 8. Example of hot-dip galvanized coating on silicon-killed mild steel (the silicon content of the steel is in the Sebysti region; reprinted from archive of CTU—Klokner Institute).

Metallic element additives are added to the molten zinc bath in relatively small amounts to affect the formation of the coating. These are mainly Ni and Al, which reduce the reactivity of silicon-killed steel and limit the formation of Fe–Zn intermetallic phases. The additives lead, bismuth and tin affect the shaping of the outer layer and the smoothness of the coating [184,185]. However, these additions can significantly affect the corrosion performance of HDG coatings in concrete.

2.2.2. Corrosion Performance

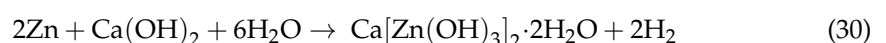
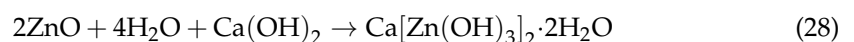
The corrosion behavior of zinc depends mainly on the pH of the electrolyte. Since it exhibits amphoteric behavior, it dissolves intensively both at low pH values of the electrolyte (under Zn^{2+} formation) and at high pH values of the electrolyte—when ZnO , Zn(OH)_2 , Zn(OH)_4^- , HZnO_2^- and ZnO_2^{2-} are formed (see Equations (21)–(25)) [163,186].



At pH 11.0 to 12.0, localized corrosion attack occurs on the zinc surface, associated with forming porous non-adhesive layer of ZnO-based corrosion products. However, at pH 12.0–12.8 there is a decrease in the corrosion rate of zinc associated with the formation of an adherent and non-porous passive ZnO layer with isolated Zn(OH)_2 crystals. An increase in the pH of the exposure solution above 12.8 leads to corrosion under hydrogen evolution and prolongation of the time to surface passivation forming $\epsilon\text{-Zn(OH)}_2$. The cathodic corrosion reaction associated with hydrogen evolution is described by Equation (26) and the actual anodic corrosion reaction—zinc oxidation is defined by Equation (27).



At pH above 13.3, a continuous passivation coating no longer forms on the surface of the exposed zinc and the corrosion rate increases rapidly with a further increase in pH [186–188]. The presence of Ca^{2+} (simulated concrete pore solutions and real concrete) in an alkaline exposure electrolyte with pH higher than 12.5 fundamentally changes the corrosion behavior of zinc and hot-dip galvanized steel. In the case of HDG samples, the corrosion of the coating occurs under hydrogen evolution with the significant formation of $\text{Ca}[\text{Zn(OH)}_3]_2 \cdot 2\text{H}_2\text{O}$ ($\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$). The formation of calcium hydroxyzincate on the surface of hot-dip galvanized steel is described by Equations (28)–(30) [163,168,189,190].



It is reported that the crystalline $\text{Ca}[\text{Zn(OH)}_3]_2 \cdot 2\text{H}_2\text{O}$, which covers the entire surface of the coated steel in a continuous well-adhered layer, is responsible for the observed transition of the hot-dip galvanized coating to corrosion in the passive state. With increasing pH, the calcium hydroxyzincate layer gradually coarsens and its barrier-protective effect decreases (time to surface passivation increases). If the pH of the exposure medium is higher than 13.3, then a continuous layer of $\text{Ca}[\text{Zn(OH)}_3]_2 \cdot 2\text{H}_2\text{O}$ is no longer formed and complete dissolution of the hot-dip galvanized coating occurs [191–194]. However, the

results of some papers point to the fact that the presence of Ca^{2+} destabilizes the formation of corrosion products ($\text{ZnO}/\text{Zn}(\text{OH})_2$) associated with the transition of zinc corrosion from the active to the passive state in alkaline environments ($\text{pH} > 12.5$). The conclusions of these papers admit the corrosion of the hot-dip galvanized coating at a significant corrosion rate even in the presence of a continuous layer of corrosion products with a majority of calcium hydroxyzincate [195–197].

In the case that chloride anions are present in the simulated concrete pore solution (or in the real concrete), the formation of a passive layer of corrosion products from $\text{Ca}[\text{Zn}(\text{OH})_3]_2 \cdot 2\text{H}_2\text{O}$ may be slowed down [198]; however, according to another source, chloride anions may accelerate the passivation process, but with the formation of a less protective (porous) passive layer of calcium hydroxyzincate [199]. According to other authors, chloride anions may cause passivation due to the formation of corrosion products based on $\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2$ [186], or $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ (simonkolleite), which has a significant volume compared to other zinc corrosion products and therefore may disturb the concrete cover [200,201].

In the case that the simulated concrete pore solution is melted with a ζ phase (FeZn_{13} —usually silicon-killed mild steel), the time to surface passivation is prolonged (lower zinc content in the outer layer). Moreover, when exposed at pH around 13, transverse cracks are observed through the entire coating to the underlying steel surface [202]. It has also been experimentally verified that the hydrogen overvoltage on the surface of the ζ phase is lower than on the surface of the η phase in simulated concrete pore solutions, as well as the fact that the corrosion of the FeZn_{13} phase under hydrogen evolution cannot be prevented even by surface treatment by chromating [203]. Also, the results of other works indicate a lower resistance of Fe-Zn intermetallic phases in alkaline environments in the presence of calcium cations [204–206]. Due to the ease of corrosion transition of the hot-dip galvanized coating in real concrete, a coating with a minimum external η phase thickness of 10 μm (consumed by the corrosion process under $\text{Ca}[\text{Zn}(\text{OH})_3]_2 \cdot 2\text{H}_2\text{O}$ formation) is recommended [81,163,189,207].

The HDG coating prepared from Zn-4.9 Al-0.1 misch metal bath shows higher resistance in the alkaline environment of simulated concrete pore solution also to the action of chloride anions (2.5 times better) [184]. For high alkaline concrete matrices, HDG coatings formed from Zn-Ni-Sn-Bi baths show lower corrosion resistance than HDG coatings formed from Zn-Ni-Bi and Zn-Pb baths. On the contrary, for the low-alkali concrete matrix the % Cl^- by weight of cement at the concrete cover for localized corrosion initiation was 1.36 (Zn-Ni-Bi) and 1.73 (Zn-Pb), respectively, but for coating formed from Zn-Ni-Sn-Bi bath significantly more, i.e., 4.02 [208].

Chromate-free conversion coating can improve the corrosion performance of HDG coatings in simulated concrete pore solution and in real concrete. From this perspective, coatings based on cerium (mainly composed of $\text{Ce}^{\text{III/IV}}$) [209], lanthanum (composed mostly of La^{III}) [210], tin ($\text{ZnSn}(\text{OH})_6$) [211], molybdate (Mo^{VI}) [212] and others have been successfully tested.

2.2.3. Bond Strength in Concrete

Since the corrosion of the hot-dip galvanized coating in real concrete (pH typically >12.6) is accompanied by hydrogen evolution, there may be an increase in the porosity of the cement paste at the phase interface [81,150,153,163,189,196]. In some cases, hydrogen has been verified to increase the porosity of cement paste up to 400 μm from the surface of the coated reinforcement [213]. The pores in the cement paste formed by hydrogen evolution have a diameter of 3 μm [214] and 10 μm [215,216] according to mercury porosimetry or 10–20 μm according to electron microscopy images [217]. It is sometimes reported that these pores are later filled with zinc corrosion products. After 28 days of concrete ageing, the porosity of the cement paste affected by hydrogen evolution is no longer evident [163,218]. However, according to some papers, pore filling by zinc corrosion products does not occur even after six months of concrete maturation [217,219] or even after four years [214].

Increasing the porosity of the cement paste at the phase interface may decrease the adhesion factor (i_{fad}). The adhesive factor is one of the factors affecting the bond force $T_{\text{c,i}}$, expressed according to Equation (31) [150,220]. In this equation, i_{ff} is a factor accounting for friction, and $i_{\text{f}\sigma}$ is a factor of bearing capacity (mechanical resistance of concrete cover layer) of ribbed steel (in detail, the individual variables are described in Table 1).

$$T_{\text{c,i}} \approx i_{\text{fad}}^{A^b, A^r} + i_{\text{ff}}^{A^b} + i_{\text{f}\sigma}^{A^r} \quad (31)$$

Table 1. Description of individual variables from Equation (31).

Symbol	Property	Unit
$T_{\text{c,i}}$	bond force	N
i	contribution of force	N
f_{ad}	completed adhesion force	N
f_{f}	friction force	N
f_{σ}	force of mechanical resistance of specific concrete cover layer	N
A^b	total area of bar body	m ²
A^r	total area of bar ribs	m ²

It is usually reported that zinc corrosion products in real concretes with a majority of $\text{Ca}[\text{Zn}(\text{OH})_3]_2 \cdot 2\text{H}_2\text{O}$ growing perpendicularly from the surface increase the surface roughness, and this fact contributes to the increase in the overall bond strength [221,222]. The findings of some papers point out that calcium hydroxyzincate crystals form preferentially over portlandite ($\text{Ca}(\text{OH})_2$) crystals, which could contribute to increasing the bond strength of hot-dip galvanized reinforcement with concrete [223]. This is because portlandite crystals grow longitudinally with the surface, which in turn contributes to reducing the adhesion (adhesion factor) of cement paste with uncoated steel [224,225]. It has been experimentally verified that the addition of CaCO_3 to cement increases the bond strength of hot-dip galvanized reinforcement with concrete, which probably results in the stimulation of $\text{Ca}[\text{Zn}(\text{OH})_3]_2 \cdot 2\text{H}_2\text{O}$ formation [226]. However, it has been experimentally verified that a significant thickness of calcium hydroxyzincate on the surface of hot-dip galvanized reinforcement significantly reduces the bond strength with concrete [227]. Figure 9 shows the changes on the surface of the hot-dip galvanized reinforcement and the cement paste at the phase interface due to the corrosion of the coating in the concrete.

Adding certain substances directly to the mixing water for concrete preparation can prevent the corrosion of the coating under hydrogen evolution and thus contribute to increasing the bond strength of the hot-dip galvanized reinforcement with the concrete. It is generally accepted that the addition of 70 ppm CrO_4^{2-} to the premixed water reduces the risk of coating corrosion during hydrogen evolution in concrete [204]. However, for environmental reasons, chromates (Cr^{VI}) cannot be used for this purpose [132]. Therefore, other substances such as H_2O_2 [228] and KMnO_4 [220] have been successfully tested for this purpose. However, the practical use of H_2O_2 is not possible because it decomposes in concrete to form O_2 , resulting in an overall increase in porosity.

Since the bond strength of ribbed reinforcement with concrete is mainly determined by the factor of bearing capacity ($i_{\text{f}\sigma}$ —see Equation (31)), it is vital to check whether the hot-dip galvanizing process does not affect the geometry of the reinforcement surface (especially the possible reduction in the height of the ribs or the depth of the indentations). However, it is usually considered that this only occurs significantly for reinforcements with nominal diameters $d < 16$ mm. For reinforcements with larger diameters, it is no longer significant (greater coating thickness in the form of a thicker phase η at the heel of the ribs). It has been reported that for reinforcements with smaller diameters, the reduction

in the height of the ribs due to hot-dip galvanizing is about 10% [150,229]. According to some authors, rib smoothing is one of the significant factors reducing the bond strength of hot-dip galvanized ribbed reinforcement with concrete [150,230,231].

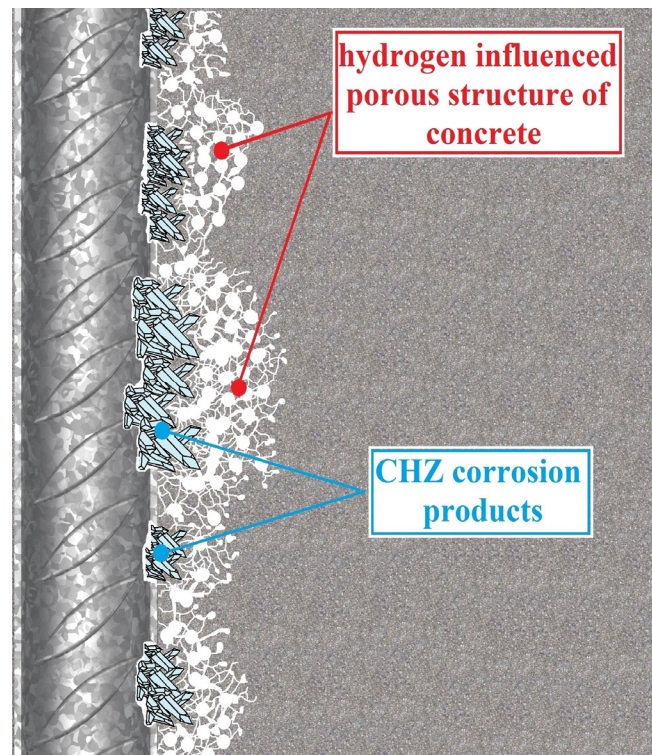


Figure 9. Scheme of changes in the ITZ due to corrosion of the hot-dip galvanized coating in concrete (the scheme takes into account the conclusions of the article [227]).

From 1920 [232] to the present, many comparative bond strength tests have been conducted on hot-dip galvanized reinforcement and uncoated reinforcement of different geometries (pull-out test and beam test). The results of some tests indicate that plain and ribbed hot-dip galvanized bars have comparable bond strength with concrete as uncoated steel with the same surface geometry [153,233,234]. However, the results of other works (again plain and ribbed bars) indicate reduced bond strength of hot-dip galvanized reinforcement with concrete [227,235,236].

The results of the bond strength of hot-dip galvanized reinforcement with concrete are often contradictory. The main reason for this is the necessity to observe all the parameters affecting bond strength during testing (especially the composition of the coating and the type of concrete used), to ensure perfect axial anchorage of the test reinforcement to the concrete bodies and to correctly interpret the bond strength results (bond strength and slip characteristic).

2.3. Organofunctional Silane Coatings

Practical application of organofunctional alkoxysilane (organofunctional silane, organosilane, very often simplistically defined only as silane) in the framework of corrosion protection of reinforcement in concrete found the concept of application of waterproof performance coating on the surface of concrete (wide practical extension), or the concept of application of organosilanes as electro-migration inhibitors, or in coating fibers (fiber-reinforced concrete). So far, the use of organofunctional alkoxysilanes directly on the surface of steel reinforcement is theoretical. However, it has been experimentally verified that silanes can improve the adhesion of epoxy coatings (binding bridge) on steel [237,238], or prevent the corrosion of hot-dip galvanized coating in simulated concrete pore solution by hydrogen evolution [239,240].

Small molecular organosilanes applied in the form of solutions in water or organic solvents to the concrete surface enter through the capillary pores, react with the hydrated silicates and remain bonded to the pore wall (surface concrete as well), exposing hydrophobic alkyl groups (see Figure 10) [35,241,242]. The low molecular weight of silane-based materials means better penetration ability to improve the durability in the surface zone and keep the substrate breathable [243]. Hydrophobic non-polar organosilanes with low surface energy applied to the surface of concrete can be included in the surface treatments in terms of penetrants, sealers or impregnation [242–246]. These coatings can inhibit water intrusion but allow vapor in or off the concrete—to freely “breathe” (the ability to transport water vapor remain entirely unaffected—no internal tension occurs) [247–249]. Concerning the corrosion protection of concrete reinforcement, silanes applied in this way ensure a significant reduction in the water capillary absorption coefficient and, of course, the chloride ion diffusion coefficient [250–252]. The use of hydrophobic organosilanes on the surface of concrete also increases the resistance of concrete to carbonation [253,254]. This application of organosilanes is beneficial for the corrosion resistance of conventional concrete reinforcement. It has been proven that, in the case of the application of an external electric field using iso-octyltriethoxy silane, the penetration depth of silane into mortar increased from one to four times compared to the dipping method, the surface angle increased by 5–15° and the water absorption coefficient was reduced by 25–30% [255]. Successful performance of silane on the surface of concrete in different environmental conditions was observed for 9–15 years [256,257]. With an average thickness of the silane coating, it is recommended that they be reapplied at intervals of 10–20 years to stay effective [258,259]. In terms of data, very little is known about the effectiveness of reapplied silane coatings on the concrete surface to increase the corrosion resistance of conventional concrete reinforcement. The degradation of silane coatings on the surface of concrete is caused by ultraviolet light, physical abrasion, weathering and alkaline attack of hydrophobic molecules [260,261].

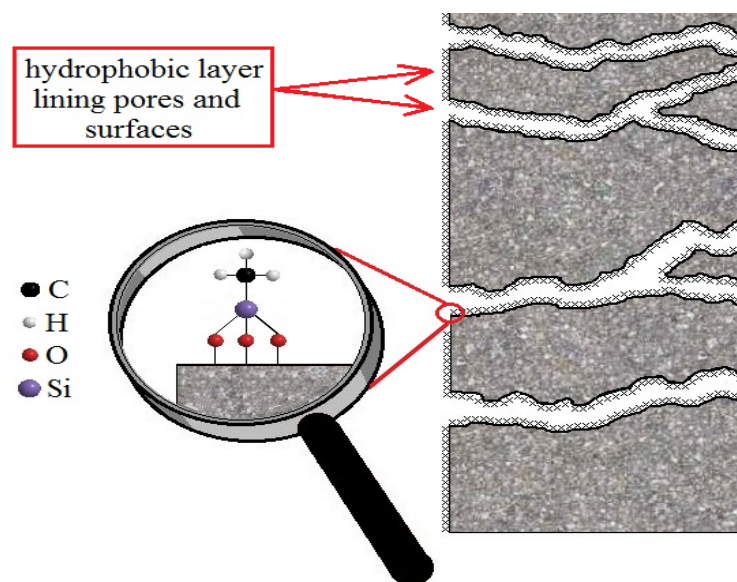


Figure 10. Hydrophobic layer of penetrants (sealers) on concrete based on organosilane lining pores and surfaces (reprinted from [242]).

The results of some professional studies point to the fact that the most significant damage to organosilane coatings is caused by the alkaline pore solution of concrete, with loss of Si-O and Si-O-Si bonds [262,263].

Organofunctional silane (3-aminopropyl)-triethoxysilane or similarly named gamma-aminopropyltriethoxysilane (APS, APTS) was successfully tested as a corrosion inhibitor of mild steel in simulated concrete pore solutions and against the action of chloride anions (admixed inhibitor) [264,265]. It was found that the inhibition efficiency of this organosi-

lane in a simulated concrete pore solution of pH 12.5 with the addition of 3.5% NaCl is better than that of N,N'-dimethylethanolamine (DMEA) by approximately 27%. Compared to this alkanolamine inhibitor, APS inhibitor has a stronger adsorption ability and has a higher inhibition effect on the anodic dissolution of iron and cathodic reduction of oxygen. Compared to DMEA adsorption (adsorption to the surface takes place with a lone pair of electrons of nitrogen and/or oxygen atoms donate to the vacant d-orbital of an iron atom—i.e., coordination bond or in other words donor–acceptor relationship), silane adsorption is based on promoted hydrolysis by alkaline media and stable Si-O-Me bonds are formed (the detailed mechanism will be described below) [264–267]. Adsorbed molecules of both substances are shown on the mild steel surface in Figure 11. It turns out that the inhibitory effect of APS is more significant in carbonated concrete pore solution (lower pH solution—content of e.g., $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$) than in the usual simulated concrete pore solution (saturated $\text{Ca}(\text{OH})_2$ sometimes with additions of NaOH/KOH). In the case of carbonated concrete pore solution, there is physical adsorption and at the same time chemical adsorption of APS on steel surface (adsorption energy is relatively high), while in simulated concrete pore solution there is only physical adsorption such as van der Waals force and electrostatic force (adsorption energy is low) [265].

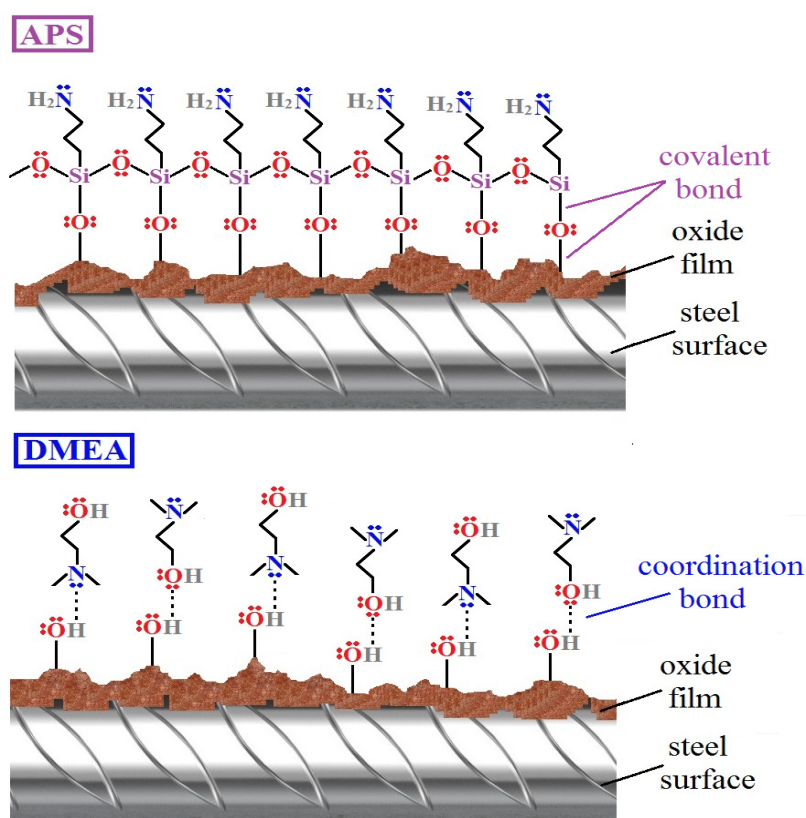
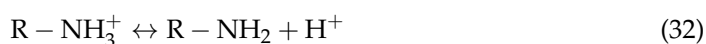


Figure 11. Schematic diagram of APS and DMEA inhibitor adsorption mechanism on reinforcing steel rebar in simulated concrete pore solution (reprinted from [264]).

APS functional solutions can also be used as an electro-migrating (EM) inhibitor (cationic inhibitory chemicals) in the form of protection of concrete reinforcement [268,269] as part of electrochemical treatments, both in the ERA method (electrochemical re-alkalization, i.e., re-increasing alkalinity of the pore solution of carbonated concrete at the phase interface of reinforcing rebars and cement paste) [270,271] and the ECE method (electrochemical chloride extraction, i.e., removal of chloride anions in contaminated concrete at the phase interface of reinforcing rebars and cement paste) [272,273]. APS has been confirmed as a multifunctional inhibitor, providing corrosion resistance for steel rebar and hydrophobicity on the cement mortar surface after electro-migration treatment (inhibitor injection) [268,269,274]. From

the point of view of EM treatment, APS shows a good effect of electrochemical chloride extraction (ECE) and electrochemical re-alkalization (ERA) and remarkably increases the resistance of the mortar bulk [268]. In addition, it can be summarized that the alkaline environment concrete pore solution and the formation of OH^- due to cathode reaction through electrochemical treatment can promote the condensation reaction between Si-OH groups (in detail see below) [269]. Electromigration properties, in this case, are provided by the amino group in the silane chain, because amines, amino alcohol and quaternary ammonium salts can exist as cations in a relatively high pH (can migrate in the alkaline concrete matrix to the cathode—embedded reinforced bars and can form on the surface steel by monolayer protection) [268,275,276]. These substances containing amino groups in aqueous solutions are protonated to an extent governed by the solution pH and the dissociation constants (K_a) of their conjugate acids, as represented in Equations (32) and (33) [276–279].



$$K_a = \frac{[\text{H}^+][\text{R} - \text{NH}_2]}{[\text{R} - \text{NH}_3^+]} \quad (33)$$

For comparison, dissociation statistics (pK_a) for the most commonly used amine-based inhibitors of steel in concrete (application in alkaline media)—guanidine ($pK_a \sim 13.6$), hexamethylenediamine ($pK_a \sim 11.8$), and ethanolamine ($pK_a \sim 9.5$)—can be compared to (3-aminopropyl)-triethoxysilane—APS ($pK_a \sim 9.5$) [268,269,277,278,280]. According to the obtained results, it was even verified that commercial organofunctional silane-based inhibitors could have greater inhibitor efficiency than amino-alcohol-based inhibitors in the protection of reinforcement in concrete in a chloride environment [281].

Another application of organofunctional silanes with regard to cementitious composite materials is the surface treatment of fibers (fiber-reinforced concrete). This application is considered green, simple and cost-effective (free from heavy metal, can work at room temperature) compared to other chemical coatings methods, e.g., zinc phosphating (phosphorus and heavy metal ions can pollute water, high process temperature is required) [282–284]. Applying silane coupling agents on non-metallic fibers improves the bond performance with the cement matrix, which increases the toughness and durability of cement-based materials [282,285–288]. The use of silane coating (most notably vinyltris(2-methoxyethoxy)silane) can change the original hydrophobicity of the surface of PE fibers to hydrophilic and increases the bonding between fibers and the cementitious matrix [289]. Silanes have also been successfully used in the surface treatment of basalt fibers to ensure stronger interfacial bonding with the asphalt matrix [290] or better connection between rubber-fibers and the concrete matrix [291]. The application of silane coupling agents to the surface of steel fiber (brass-coated steel fibers) within fiber-reinforced ultra-high-performance concrete (UHPC) can be a crucial process for increasing electrochemical corrosion resistance, chloride ion penetration resistance, frost resistance and sulfate resistance [292]. The overall increase in the durability of UHPC in treating metallic fibers with silane coatings is due to improving the interface bonding performance [282,292–295]. As part of the coating of metallic fibers, tetraethoxysilane (TEOS) functionalized fibers (with final activation in $\text{Ca}(\text{OH})_2$ solution) [291] or APS ((3-aminopropyl)-triethoxysilane) [282,292,293,295] were used. It was verified that the presence of the ($-\text{NH}_2$) group in APS is capable of forming a stronger physical interaction force (“bonded bridge”) with the UHPC matrix due to the excellent hydrophilicity of the surface (the amino functional group ensures the change of the usual hydrophobicity of organosilanes to hydrophilicity performance) [282,292,293,295]. In the case of using TEOS (hydrophobic surface), the chemical affinity between the silane layer and the formation of UHPC hydration products ensures activation in $\text{Ca}(\text{OH})_2$ solution (formation of calcium silicates over the fiber surface) [294]. In general, it can be summarized that using both types of silane coatings is associated with positive chemical interaction caused by the silane film with cement paste. In the case of contact of the surface of the organosilane with the hydrated cement matrix (rich in ions Ca^{2+} , Si^{4+} and OH^-), a diffuse layer can be formed. The organosilane film gradually becomes

solubilized into Si^{4+} and OH^- ions, which leads to C-S-H precipitation. This fact leads to an increase in the C-S-H gel at the phase interface of fibers and UHPC matrix, which results in a fundamental reduction in the porosity of the cement matrix (detected by measuring the Si/Ca ratio in the transition zone) [292,294,296]. Moreover, it was proved that APS coating on the surface of fibers can accelerate cement hydration and the formation of C-S-H gel [293]. An increase in the adhesion of cementitious putty using a silane coupling agent has been shown previously without further explanation of the mechanism [297]. A conceptual model of the silane functionalized fiber–matrix interface in the framework of the early age cement hydration stage and hardened cement paste stage is shown in Figure 12.

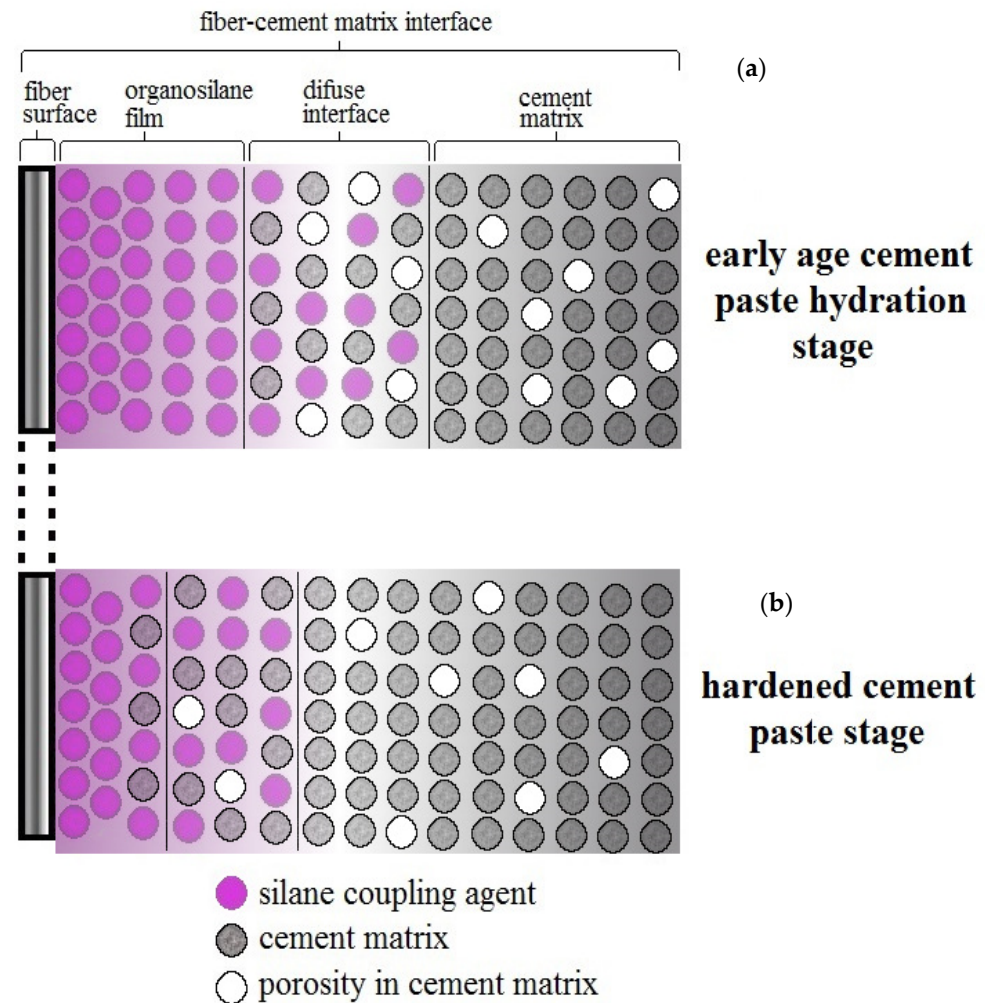
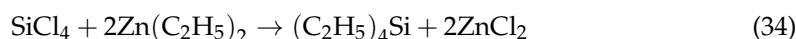


Figure 12. Conceptual model of functionalized fiber–matrix interface in the short (a) and long term (b) (reprinted from [294,296]).

The use of silanes also significantly roughens the surface of metallic fibers, which also leads to an increase in the mechanical properties of UHPC [293,294]. Applying silane coatings on the surface of metallic fibers of UHPFRC can significantly increase the tensile properties of UHPC and increase the resistance of the UHPC matrix to the generation and expansion of cracks [282,295]. In contrast, these properties can significantly strengthen the application potential of UHPC in construction [298–302]. Modifying the surface of steel fibers with nano- SiO_2 [303] and CaCO_3 particles [304] may not ensure such a significant increase in interfacial shear strength and pullout energy fiber-reinforced cement materials as the use of APS.

2.3.1. General Technology Aspects

The term silanes (alkoxysilanes, organosilanes and often organofunctional silanes) refers to compounds of silicon with hydrogen with a limited ability to form chains (up to $n = 8$). The stability of Si-Si chains is lower compared to C-C analogues. All these compounds are very reactive gases (monosilane, disilane) or liquids ($n = 3$ to $n = 8$) with autoignition potential, their stability decreases with increasing silicon chain length [305–307]. A vast range of substances with specific reactivity can be obtained by the adding an alkyl or aryl chain—the so-called organosilanes (organofunctional silanes), whose origin is purely synthetic [308,309]. Organosilane was first prepared in 1863 (Charles Friedel and James Crafts—see reaction 34) by heating diethyl zinc and tetrachlorosilane in a sealed tube at 140–160 °C [310,311].



The organofunctional silane molecule consists of three essential parts. The core of the molecule is of aryl or, more commonly, alkyl $(\text{CH}_2)_n$ origin. On one edge of the molecule there is an organic functional group (most commonly amino, vinyl, alkyl, mercapto, glycidoxy, etc.) which can provide a link to polymeric substances with a hydrocarbon chain—the so-called functional group linkage. The second counterpart of the molecule is an alkoxysilane group $(\text{Si}(\text{OR})_n)$, where n is most often 3, which after hydrolysis and subsequent condensation can form a siloxane bond (Si-O-Si) with inorganic materials [296,312–316]. Organofunctional silanes are usually used as adhesion promoter primers, crosslinkers or coatings with specific reactivity [317,318]. A general example of a graphical representation of an organofunctional silane molecule (mono-functional organosilanes) is shown in Figure 13. However, bis-functional organosilanes (dipodal functional organosilanes) are of practical importance, especially in corrosion protection of metals. Their general molecular formula is $\text{X}_3\text{Si}(\text{CH}_2)_n\text{Y}_m(\text{CH}_2)_n\text{SiX}_3$ —they contain double the number (symmetrical ends of the molecule) of alkoxysilane groups, which leads to more outstanding crosslinking capabilities and the formation of overall thicker coatings. A graphical representation of three representatives of bis-functional organosilanes is shown in Figure 14. In the context of more efficient crosslinking, combinations of silanes as well as, e.g., mono-functional organosilanes with bis-functional organosilanes are particularly suitable.

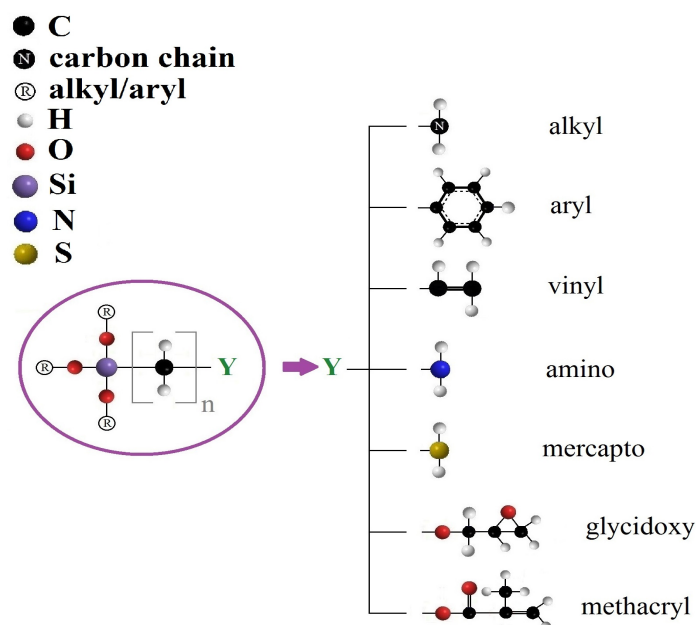


Figure 13. A representation of a conventional organosilane molecule (mono-functional) with an indication of some organic functional groups (Y) and the characteristic alkoxysilane group $(\text{Si}(\text{OR})_n)$.

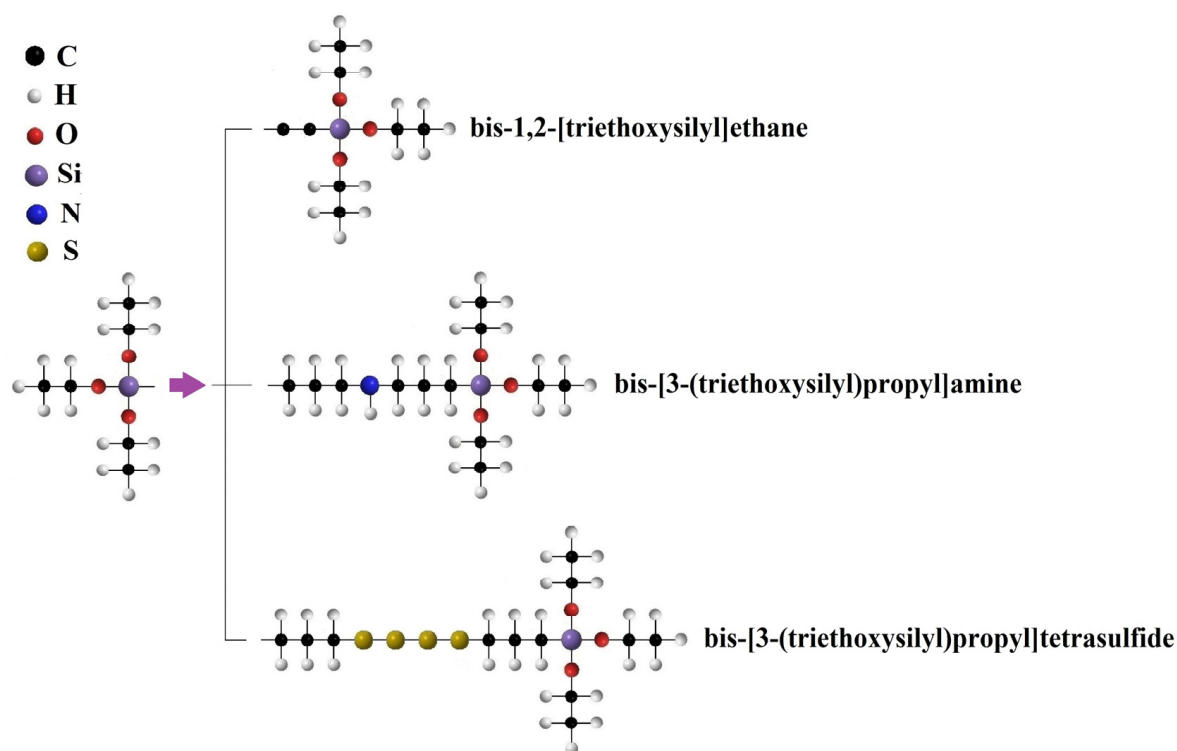


Figure 14. Scheme of three molecules of bis-functional organosilanes most often tested in the surface treatment of metals.

The binding possibilities of silanes are very significant, and they were already used in the Second World War, when, for example, they ensured an increase in the cohesion of fiberglass fibers with the polyester base of this composite [296]. Silanes can form non-selective and permanent covalent bonds (permanent link) with glass [319–321], ceramics [322,323], substances based on cement building materials [241,242,324,325], cellulose [326–331] and by some metal materials such as aluminum alloys [332–334], copper alloys [332,335,336], magnesium alloys [337–340], hot-dip galvanized steel [341] and uncoated mild steel [342–344]. In the case of their modification with a specific organic chain, it is possible to ensure a covalent connection with polymeric substances (coatings, elastomers, etc.). In the anti-corrosion protection of metals, organofunctional silanes have found an irreplaceable place as a replacement for chromate (Cr^{VI}) or phosphate conversion coatings (toxic properties of Cr^{VI} , eutrophication of water in case of use of phosphate coatings) under coating systems when coating hot-dip galvanized steel and aluminum alloys [345–356]. Although organofunctional silanes usually create thinner coatings (~400 nm) compared to Cr^{VI} -rich content chromate conversion coating (~1000 nm, Alodine process) with only a barrier option for surface corrosion protection (without automatic self-healing ability), they often provide extraordinary adhesion properties for organic coating (molecular bridge via covalent bonds) [333,357,358]. The general binding possibilities of silanes are shown in a simplified manner in Figure 15.

Applying organofunctional silanes to the surface of inorganic materials usually cannot be made without pre-treatment of the surface. For the application of organofunctional silanes, the coated surface of the inorganic material must be accessible and rich in free OH groups (OH-rich substrates are essential for the adsorption of organofunctional silanes) [359–361]. Before the actual application, the hydrolysis of these substances or mixtures is necessary—the proper execution of the hydrolysis is also a critical step for the creation of a high-quality surface treatment. During its own hydrolysis, the corresponding alcohols are liberated, and a reactive silanol group is generated. Under the same hydrolytic conditions, the methoxy groups of trimethoxysilane hydrolyze more rapidly than the ethoxy groups of triethoxysilane. In general, it can be summarized that the length of

the chain of alkoxy groups significantly reduces the hydrolysis rate—pentoxy < butoxy < propoxy < ethoxy < methoxy [362–365]. The kinetics of the hydrolysis itself is further strongly influenced by the pH value of the solution, the temperature and the nature of the solvent system. Still, it is also influenced by the molecular structure of organofunctional silane and its concentration [363–367]. Relative silanes effectiveness for application on the surface of various inorganic materials is shown in Figure 16.

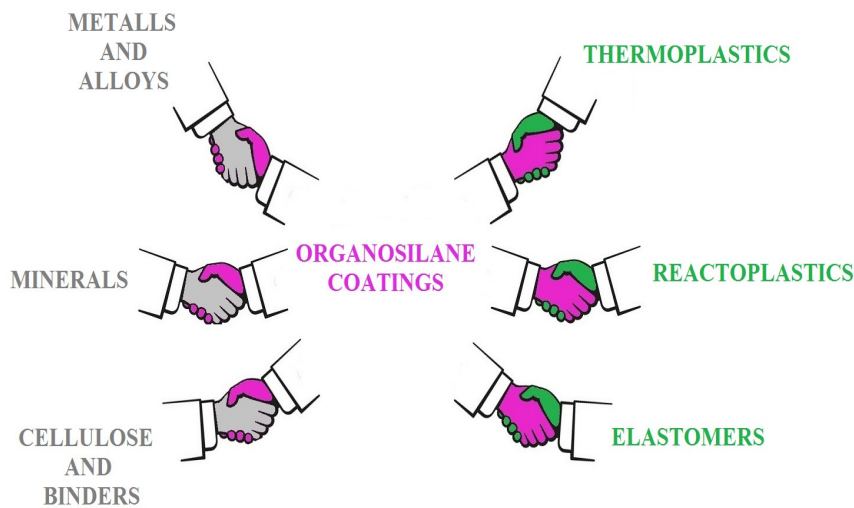


Figure 15. Simplified schematic representation of the binding options of organosilanes–alkoxysilane binding (gray color) and functional group binding (green color).

RELATIVE ORGANOSILANE EFFECTIVENESS

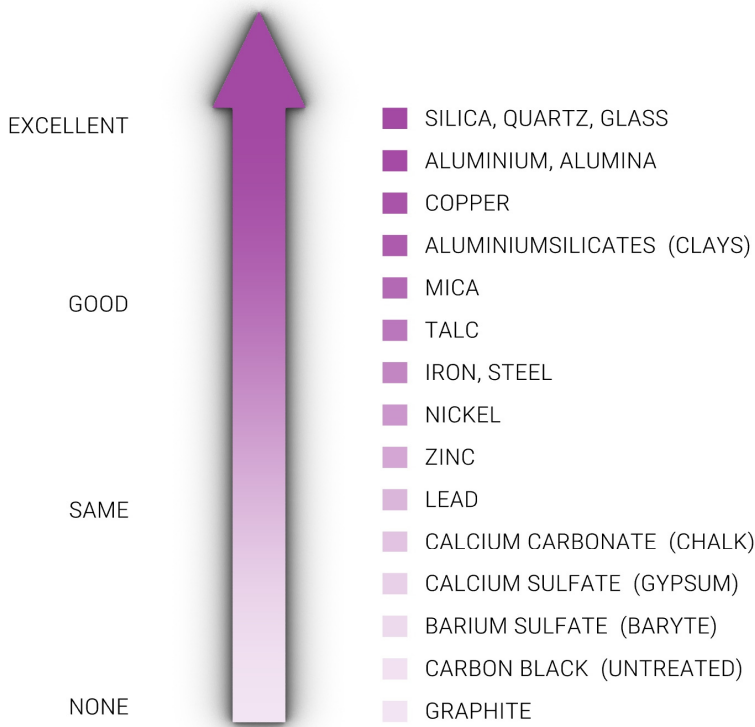


Figure 16. Schematic relative organosilane effectiveness for application on the surface of various inorganic materials (reprinted from [366]).

In the case of alkoxysilanes, the rate of hydrolysis is significant at acidic and alkaline medium but reaches a minimum at neutral pH—this is evident from Figure 17 [366,368,369].

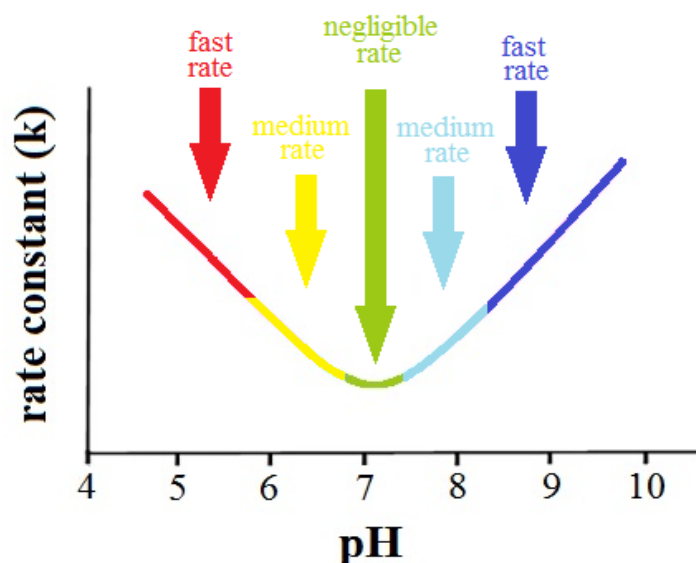


Figure 17. Schematic representation of the effect of pH on the kinetics of hydrolysis of alkoxysilanes (reprinted from [369]).

The mechanism of acid (A) and alkaline hydrolysis (B) is shown in Figure 18. In both cases, the corresponding silanol is formed. However, the acid hydrolysis mechanism is considered to be two-step compared to the one-step mechanism of alkaline hydrolysis. In this case, the reaction center on the oxygen atom is reported [246,296,370–372]. Sometimes, however, a reaction center on the silicon atom is mentioned, where a bimolecular nucleophilic substitution (S_N2) reaction occurs to form a pentacoordinate trigonal bipyramidal transition state. The subsequent reaction system of the breakdown of this complex leads to the formation of the corresponding silanol [366,369]. The necessary presence of alcohol (methanol, ethanol, propan-1-ol) in the hydrolysis solution of some organofunctional silanes is essential not only for the actual course of hydrolysis but also for the stabilizing the solution [366,373].

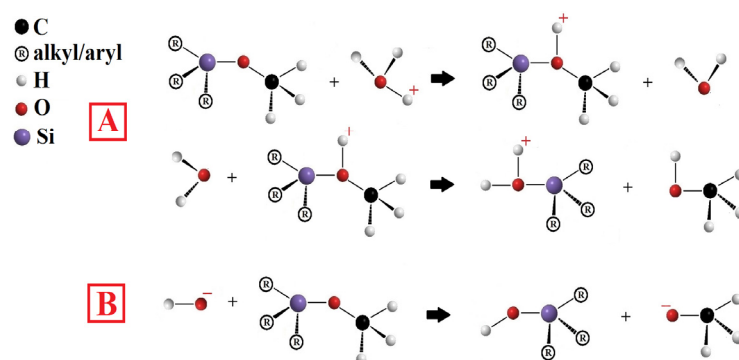


Figure 18. Scheme of the mechanism of acidic (A) and alkaline (B) hydrolysis of organofunctional silanes (reprinted from [246,296]).

The rate of hydrolysis is also significantly affected by temperature, with increasing temperature also increasing the rate of hydrolysis. A plot of log rate constant as a function of $1/\text{temperature}$ gives a straight line according to Arrhenius law (see reaction 35), where k = rate constant, A = Arrhenius frequency factor, E_a = activation energy, R = universal gas constant and T = temperature, in K [366,374].

$$\log k = \log A - \frac{E_a}{2.303RT} \quad (35)$$

The total adhesion strength of organofunctional silanes is dependent on the type of material (see above Figure 16). The most robust adhesion is achieved with silica, glass and quartz, which form strong siloxane linkages (-Si-O-Si-) through the condensation reaction with surface hydroxyl groups. On the contrary, due to the utterly negligible amount of free OH groups on the surface of gypsum, graphite and untreated carbon black, it is complicated to create strong adhesion bonding with organofunctional silane [246,296,363]. Mild adhesion strength is evident for metals and their alloys and is related to the formation of a less stable covalent bond with metals (-Me-Si-O-; metallo-siloxane bond) with a susceptibility to reversible hydrolysis with re-formation of silanol [358,375–378]. Possible enrichment of the surface of OH group metals by immersion in alkaline solutions before the actual coating [377], possibly through cathodic polarization during coating [379–382], can ensure easier adsorption of silanes and the formation of thicker coatings (verified on Al-Cu alloys). Due to cathodic polarization, the surface electrolyte is alkalized according to Equation (14) or (26) and thicker coatings with fewer cracks and pores are formed (alkaline-aided condensation). However, a higher level of cathodic polarization (optimum -0.8V/SCE -critical cathodic potential) supports the formation of a considerable amount of gaseous hydrogen, which can cause the formation of highly porous coatings of organofunctional silanes [383–391]. Possible anodic polarization is usually not as successful in forming thicker non-porous coatings [383,385]. The adsorption mechanism of organofunctional silanes on the metal surface takes place via a hydrogen bond between the OH group of the silanol and the free OH group on the metal surface. The mechanism of adsorption of silanes on the metal surface is shown in Figure 19. The subsequent formation of siloxane linkage (-Si-O-Si-) is usually induced by an increased temperature (usually $75\text{--}120\text{ }^{\circ}\text{C}$, and usual drying time is 20–30 min) and is called condensation (see Figure 20). The subsequent gradual grouping of siloxane linkage into a dense polymer network can be called the polymerization phase. Equilibrium hydrolysis reaction and subsequent condensation and polymerization are shown in Equations (36)–(38) [392–398].

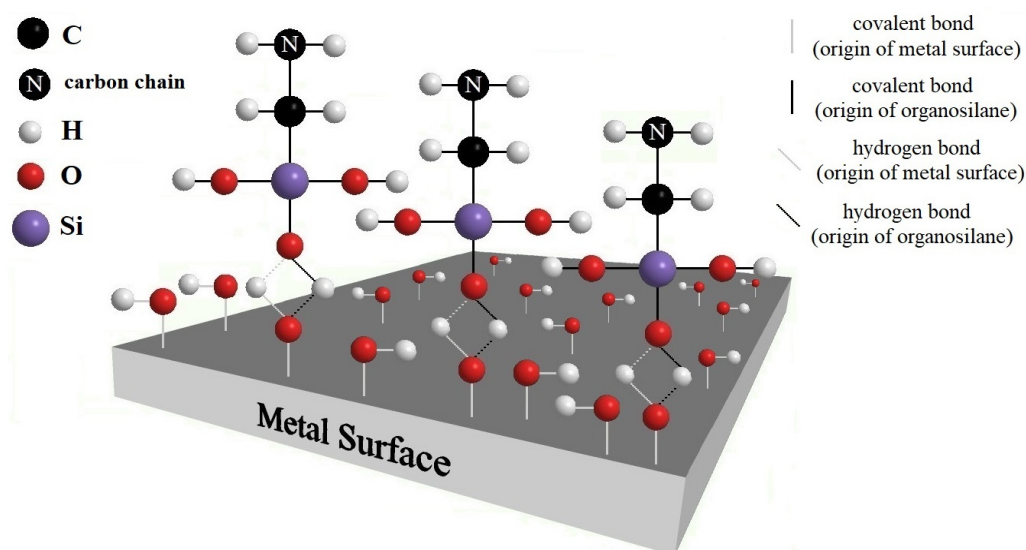
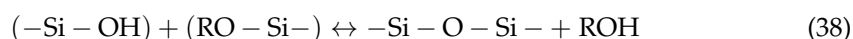
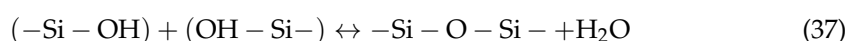
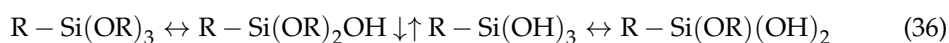


Figure 19. Representation of the mechanism of adsorption of organofunctional silanes on metal surfaces (reprinted from [358,393,397]).

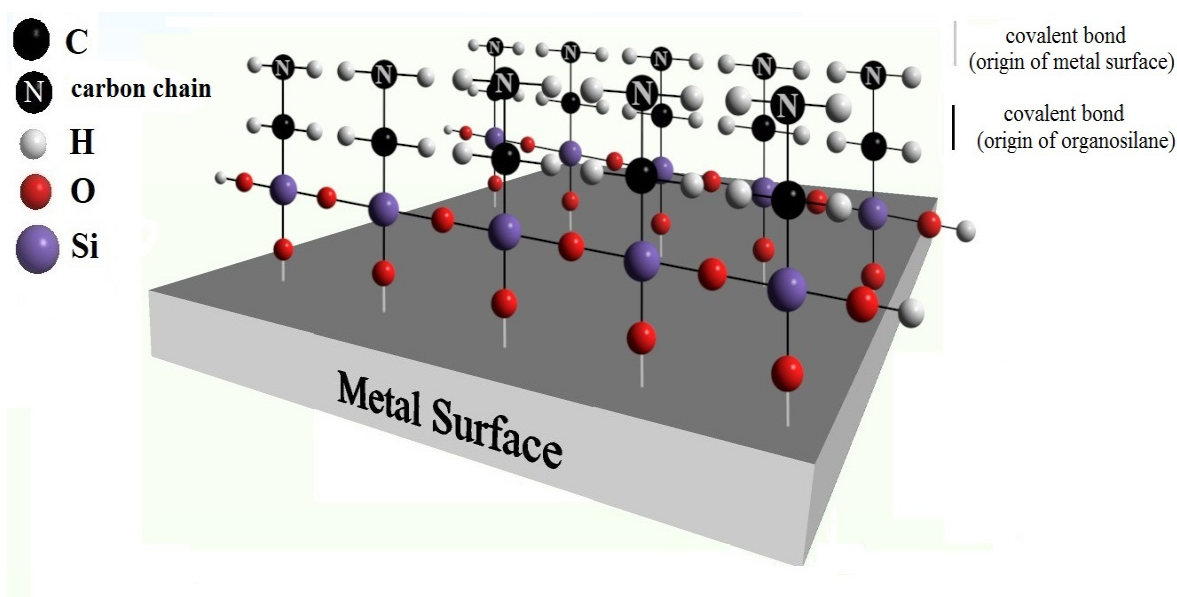
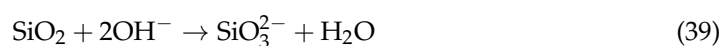


Figure 20. Scheme of adsorbed organosilane molecules crosslinking on metal surface after thermosetting ageing (condensation and polymerization) (reprinted from [358,393,397]).

2.3.2. Corrosion Performance

In the context of corrosion protection of metals with application potential as adhesion promoters for automotive (aluminum alloy and hot-dip galvanized steel), silanes were proposed as an eco-friendly alternative to conventional chromating as early as 1991 [358,396,399]. Since then, both nonfunctionalized and organofunctionalized silanes (and their combinations) have been tested in the corrosion protection of aluminum alloys (most commonly AA2024-T3, but also Al-Mg, Al-Mn alloys), hot-dip galvanized steel (HDG) but also carbon (plain) steel [358,397].

The coating of organofunctional silanes provides the underlying metal with barrier-protective properties, which can be increased if the coating has hydrophobized the surface (depending on the type of silane used). The coating does not carry inhibitory properties or have a self-healing effect (compared to chromate coatings). However, the addition of certain substances (nanostructured SiO_2 , TiO_2 , Al_2O_3 , ZrO_2 , CeO_2 , etc.) can increase the thickness of the coating and its resistance to abrasive damage [358,397], or be effective corrosion inhibitors (benzotriazole, tolyltriazole, cerium nitrate) [358,400–403], or provide coloration of the coating (xanthene dye does not affect the composition and corrosion properties of bis-sulfur silane coating) [358]. To increase the mechanical properties of the coating (abrasion resistance), silane coatings on metals in Al_2O_3 and SiO_2 nanoparticles were tested. In addition to this, nanoparticles of both substances increase the hardness of the coating and, in the case of the optimum addition of SiO_2 , the corrosion resistance is increased. The increase in corrosion resistance in this case is due to the precipitation of silicates (SiO_3^{2-}) and the decrease in the activity of cathodic sites (local increase in pH by the formation of OH^- ions) according to Equation (39) [333,358].



The optimum amount of SiO_2 nanoparticles in silane coatings to achieve a significant increase in the corrosion resistance of silane coatings (predominantly on aluminum and its alloys) is 5–15 ppm (see Figure 21), and it has also been verified that SiO_2 nanoparticles can engage (via OH groups on the surface) in the Si-O-Si network of silane films (the high reactivity between SiO_2 and silanes is shown in Figure 16). On the contrary, in the case of dosing more significant amounts of SiO_2 nanoparticles, the provided barrier protection

properties are radically reduced due to the formation of an already porous coating. This fact is schematically shown in Figure 22 [333,358].

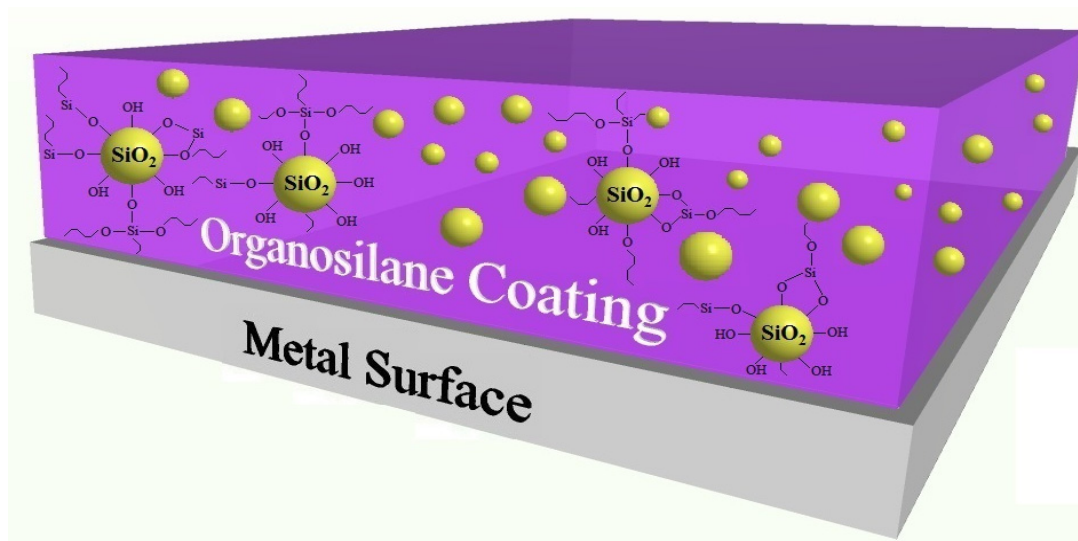


Figure 21. Schematic representation of wiring and enhancement of corrosion resistance properties of organofunctional silane coating by a suitable amount (5–15 ppm) of SiO_2 nanoparticles (reprinted from [333]).

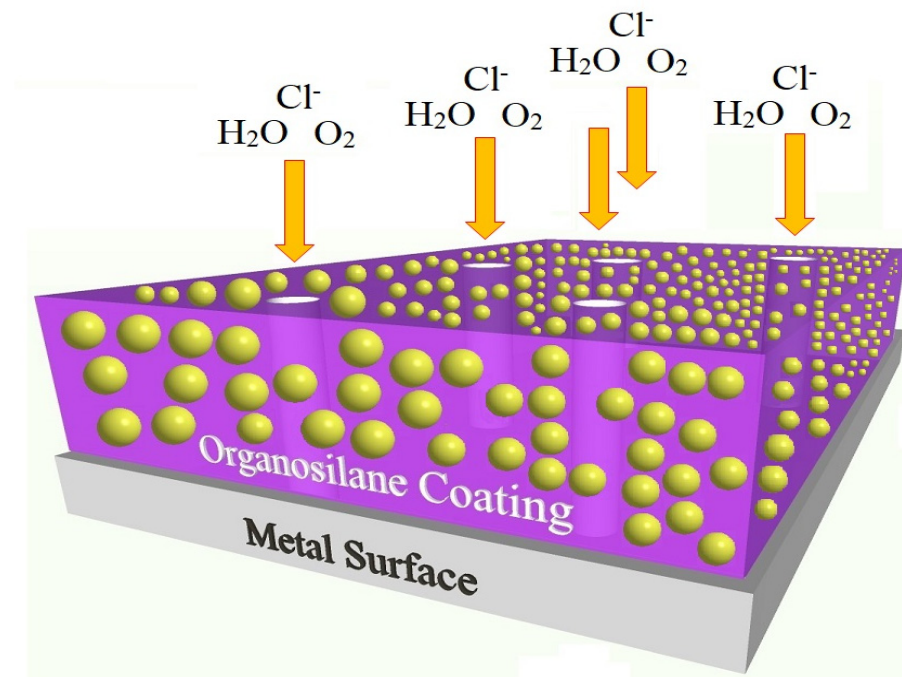
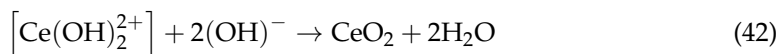
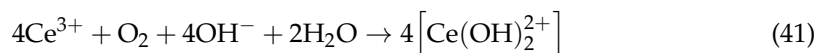


Figure 22. Schematic representation of the formation of cracks in the organofunctional silane coating when supercritical (>15 ppm) amounts of SiO_2 nanoparticles are used (reprinted from [333]).

The addition of sufficient amounts of ZrO_2 nanoparticles apparently results in a pore-blocking effect of the silane coatings. This fact also resulted in a significant increase in barrier protection properties [404,405].

From the point of view of hybrid-silane coatings with inhibition properties, mainly (dopant) $\text{Ce}(\text{NO}_3)_3$ [406–409] or probably less effective $\text{Zr}(\text{NO}_3)_3$ [406,410] have been successfully tested. Cerium nitrate acts mainly as a cathodic corrosion inhibitor (local pH

increase according to Equation (14))—precipitation of insoluble $\text{Ce}(\text{OH})_3$ and CeO_2 compounds occurs (precipitation proceeds according to reactions (40)–(42)) [407,411].



It has been shown that in the application solutions of hydrolyzed silanes, Ce^{III} can be converted to Ce^{IV} via atmospheric oxygen [412,413] and, based on this fact, it can be incorporated in the silane Si-O-Si network (see Figure 23), thereby increasing the coating thickness and decreasing its porosity [414]. Furthermore, it was found that the addition of CeO_2 nanoparticles can increase the thickness of the silane coating up to two times and are good carriers of Ce^{III} particles, which act as a very effective corrosion inhibitor. Silane coatings formulated in this way are called “smart coatings” because they carry self-healing ability and thus provide comparable corrosion protection to Cr^{VI} -based conversion coatings [415–417]. Based on these facts, adding cerium compounds appears to be more effective in providing corrosion protection to metals by silane coatings than adding lanthanum ($\text{La}(\text{NO}_3)_3$) compounds. This is probably due to the higher solubility of lanthanum hydroxides (precipitation of $\text{La}(\text{OH})_3$ occurs at cathodic sites) and the inability to form La^{IV} compounds (La^{III} does not appear to be able to incorporate effectively into silane coatings) [414,418].

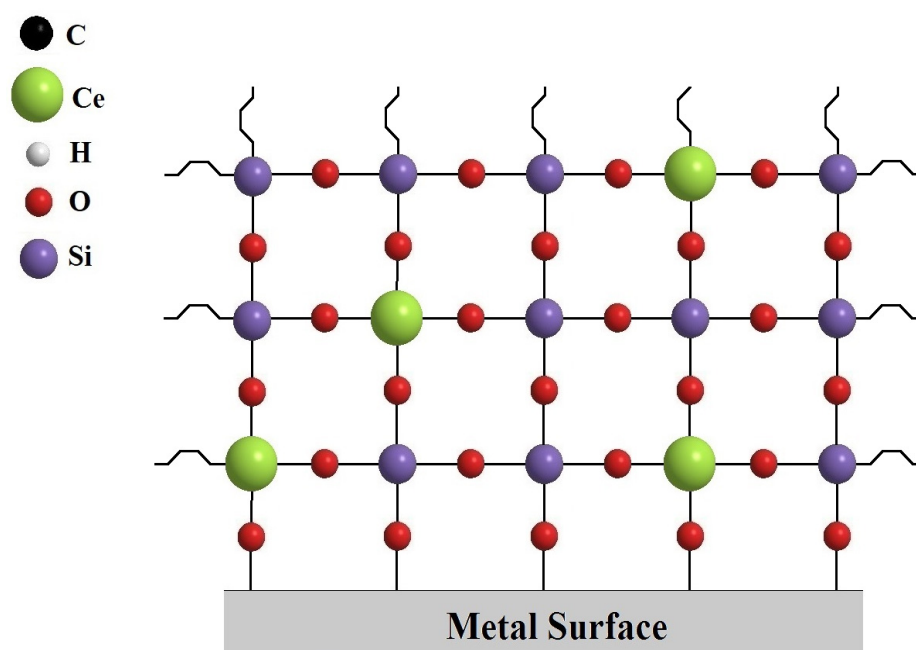


Figure 23. Schematic representation of the integration of Ce^{IV} into the silane network (reprinted from [414]).

Also, the presence of praseodymium in the form of $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ [419,420] in silane coatings leads to an increase in corrosion resistance. The inhibition effect is again based on the reaction of Pr^{3+} with OH^- to form Pr oxide/hydroxide and the effective blocking of active corrosion sites. It has been verified on aluminum alloy AA 7075 that the inhibitory effect of Ce and Pr cations are more significant than that of La and Nd cations [421]. Furthermore, the addition of Y_2O_3 has also been shown to improve the corrosion resistance of silane coatings [422,423]. Concerning the corrosion performance provided, very often

the aim of adding various substances to silane coatings is to limit the crack structure and provide self-healing ability.

The coating of organofunctional silanes is highly unreactive (except for the hydrolysis reaction of metallo-siloxane bond), and it is challenging to perform oxidation or reduction in its components [358,424]. Thus, the thickness of the coating formed on metals is directly related to the type (group) of silane used, with the application of bis-silanes leading to the formation of thicker and less porous coatings [349,358]. Using multiple layers of different silanes with possible modification of the composition of the coatings with other substances can increase not only the corrosion resistance but also the friction resistance and provide antimicrobial ability [425,426]. The silane concentration in the bath has a significant effect on the coating thickness (linear dependence). The uniformity of the resulting coating also increases with increasing concentration, and its porosity decreases. On the other hand, the coating thickness is not affected by the immersion time; it was found that the differences in thickness are insignificant for samples after 5 s and 30 min of exposure [427]. The effect of bath pH (in the case of adequately performed hydrolysis) and its temperature on the silane coating thickness is of little significance. The chosen drying method has a more significant effect on the coating thickness. In the case of high-pressure drying, significantly thinner coatings are formed than in a standard atmosphere or a low-pressure nitrogen atmosphere [358,427]. In particular, it has been verified via FT-IR that even long-lived (high-density siloxane linkage) coatings aged at high temperature and properly hydrolyzed contain non-hydrolyzed groups (e.g., $-\text{Si}-\text{O}-\text{CH}_2-\text{CH}_3$) and non-linkage silanol groups ($\text{Si}-\text{OH}$) [358,427].

Silanes achieve outstanding results for corrosion performance when protecting the surface of aluminum and its alloys. For this reason, they find application as an alternative surface pretreatment (compared to the no longer used chromate conversion coatings with Cr^{VI}) of aluminum alloys in the automotive industry before applying organic coatings. The usually high reactivity (see Figure 16) of silanes to aluminum alloy and Al_2O_3 (usual thickness around 5 nm) ensures the formation of protective coatings of sufficient uniformity and thickness [358,428–431]. The composition of the silane coating on the surface of aluminum alloys tends to be stratified into two layers (directly demonstrated for the application of bis-sulfur silane on the surface of AA 2024-T3)—interfacial layer and outermost silane layer (see Figure 24) [358,432–434]. For intrinsic corrosion resistance, the interfacial layer is the critical layer with most $\text{Al}-\text{O}-\text{Si}$ bonds (metallo-siloxane bond). Still, it also contains a siloxane bond ($\text{Si}-\text{O}-\text{Si}$) [358,432,435,436].

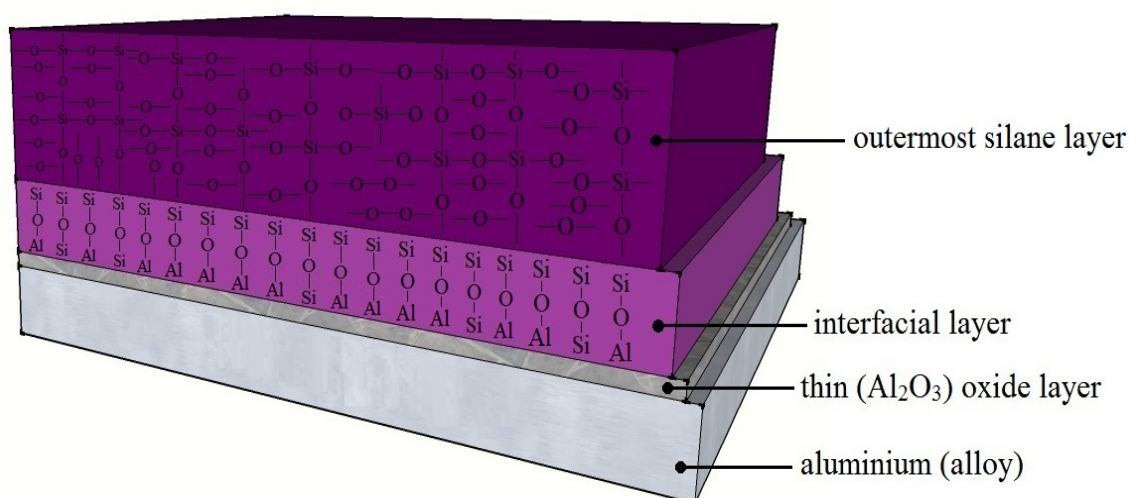


Figure 24. Predicted composition of silane coating on the surface of aluminum and its alloys (reprinted from [430]).

More accessible surface treatment of aluminum and its alloys compared to, for example, hot-dip galvanized steel is not only due to the high affinity of Al_2O_3 to silicates (the effect of the specific arrangement of OH groups) but also to the higher stability of Al_2O_3 (compared to ZnO —pH treatment window is wider), as well as the presence of a less ionic Al-O-Si bond than Zn-O-Si [358]. A significant influence on the higher reactivity of aluminum and its alloys towards silanes is also due to its ability to insert into the Si-O-Si bond (Al is trivalent) [358,432,435].

When applied to concrete, silanes on the surface of hot-dip galvanized steel can have significant potential for application in the construction industry, and not only in the form of reinforcement (wastewater drains, sewer profiles, etc.). The influence of silanes on the prevention of corrosion of the zinc coating during the evolution of hydrogen and the limitation of the formation of the porous structure of the cement sealant at the phase interface is discussed in particular (see Section 2.2) [239,240]. The lower reactivity of ZnO (possibly also $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$) to silanes can lead to the formation of discontinuous coatings that do not provide barrier-protective properties [358,393,437–440]. The combination of bis-amino silane/VTAS [346] and bis-amino silane and bis-sulfur silane (ideal ratio 1:3) has been shown to provide sufficiently protective coatings [358,432]. The separate use of bis-amino silane to protect the surface of hot-dip galvanized steel leads to the formation of an unprotected very hydrophilic coating; it has also been proven that the separate use of bis-sulfur silane cannot perfectly wet the surface and create a continuous protective coating, only a combination of both is suitable. These facts are summarized by a group of projections in Figure 25 [432]. Galvanic galvanized steel can often be more successfully coated with silanes than hot-dip galvanized steel [441]. When applying γ -APS and γ -UPS to zinc substrates, it was shown that the most compact coatings are formed at a deposition pH of 6–9 (near the isoelectric point of ZnO) [441,442]. To increase the corrosion resistance of hot-dip galvanized steel with silane coatings, modified coatings with the addition of other substances are more often proposed with the aim of limiting the formation of natural cracks and inhibiting the corrosion process [406,416,443].

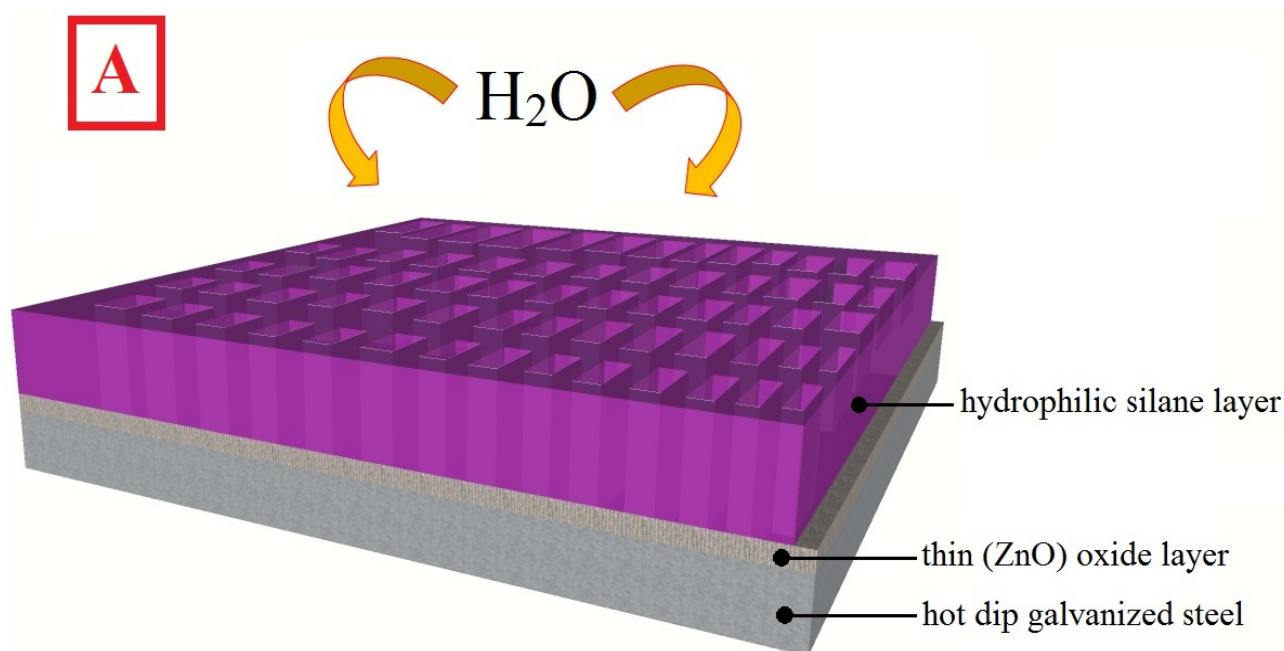


Figure 25. Cont.

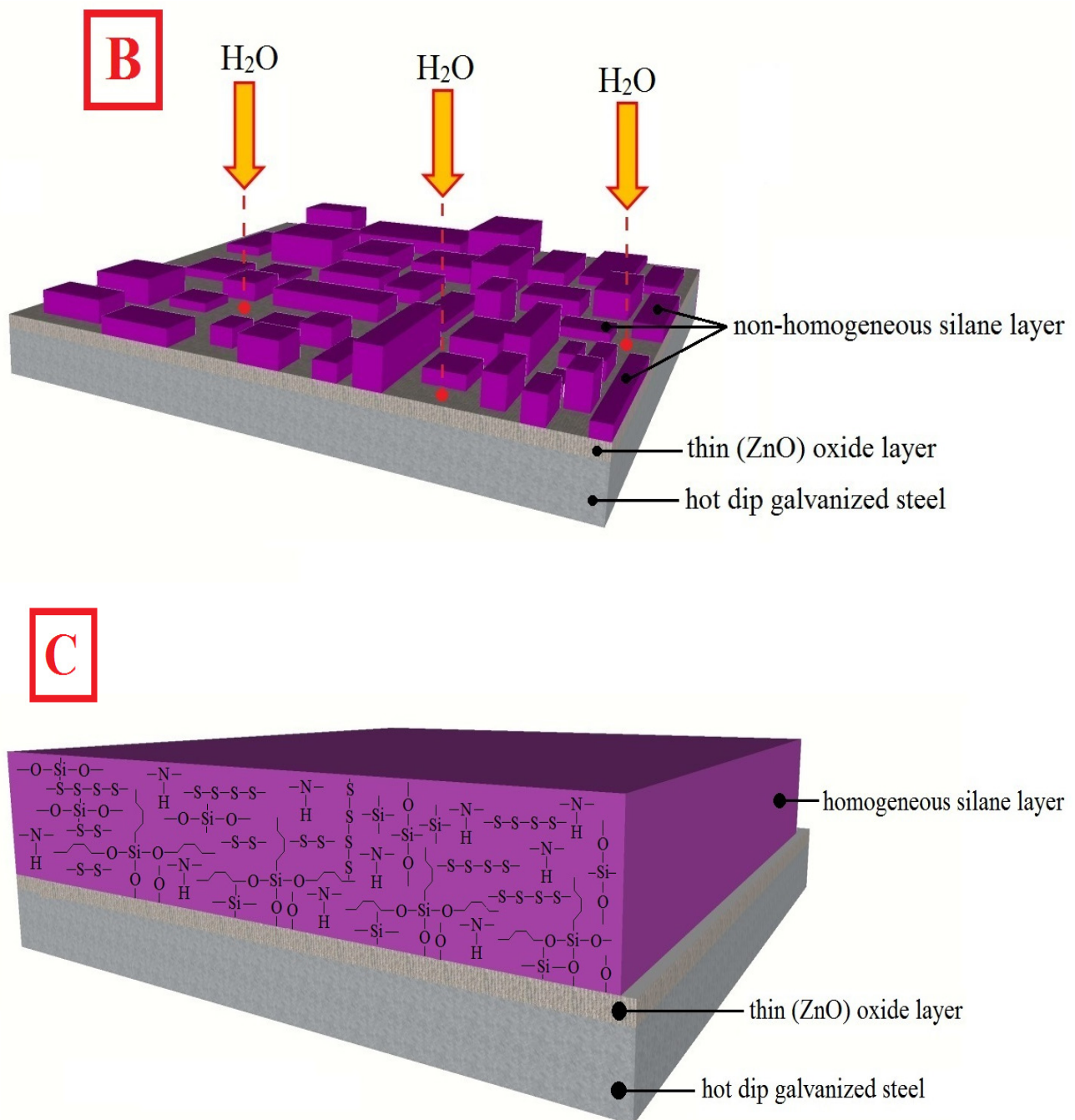


Figure 25. The effectiveness of the application of bis-silanes on the surface of hot-dip galvanized steel: (A) ineffective application of bis-amino silane (hydrophilic coating formation); (B) ineffective application of bis-sulfur silane (formation of discontinuous coating); (C) effective application of a combination of bis-amino silane and bis-sulfur silane (1:3) (reprinted from [358]).

The use of silanes on the surface of carbon steel can be a very interesting matter with regard to extending the life of conventional concrete reinforcement (without additional coatings). The coating could extend the time until the steel surface is activated (reduce the effect of carbonation and chloride anions) and at the same time increase bond strength with concrete [294,298]. It has often been experimentally verified that the application of silanes to the steel surface without pretreatment leads to the formation of coatings with low thickness, poor inhomogeneity and low compactness [410,425]. Such coatings do not provide sufficient anti-corrosion protection [444], and it has also been proven that they do

not provide good adhesion for painting [445]. In the case of coating carbon steel with silanes, for the formation of a homogeneous, continuous and sufficiently strong layer, pretreatment of the surface with the provision of a sufficient amount of free OH groups (hydroxylated metals) is necessary [446,447]. In the case of application to the aluminum surface, it has been verified that surface alkalization or controlled oxidation leads to the formation of stronger and more compact silane coatings [448]. In the case of carbon steel coating, it is evident that pre-treatment of the surface before applying silanes is necessary. The presence of a natural oxidation layer on a carbon steel surface is usually porous, discontinuous and poorly adherent—for these reasons, it is unsuitable as a base layer for the application of silanes [449]. It is usually considered that the presence of FeO(OH) on the steel surface [447], or a more significant proportion of FeO(OH) compared to Fe₂O₃ [450], is necessary to ensure the formation of sufficiently protective silane coatings. In stainless steels, the presence of Cr₂O₃ and Fe₂O₃ plays an essential role in the adhesion of silanes [406,451]. It has been verified that the mere alkaline cleaning of the surface of steel (cold-rolled steel) in a NaOH solution near the IEP (isoelectric point, pH 9.5) leads to an increase in the adsorption of silanes on the surface (tested on a mixture of bis-amino silane/vinyltriacetoxysilane) of steel [450,452]. When cleaning the surface near pH 9.5, a fine, dense and spherical surface oxide morphology with the highest content of FeO(OH) is formed on the surface of the steel compared to Fe₂O₃. Cleaning the steel surface at a pH lower than the IEP leads to a positive charge of the surface (Equation (43)), and if the pH is higher than the IEP it leads to a negative surface charge (Equation (44)) [450,453]. At IEP, the easiest adsorption of the mixture of silanes on the surface of cold-rolled steel occurs (the lowest proportion of polar components on the surface)—see Figure 26. Alkaline surface pretreatment was also successfully used as a pretreatment of the surface of ZE41 magnesium alloy before the application of bis-1,2-(triethoxysilyl)ethane and provided an increase in the corrosion resistance provided by the silane coating [454].

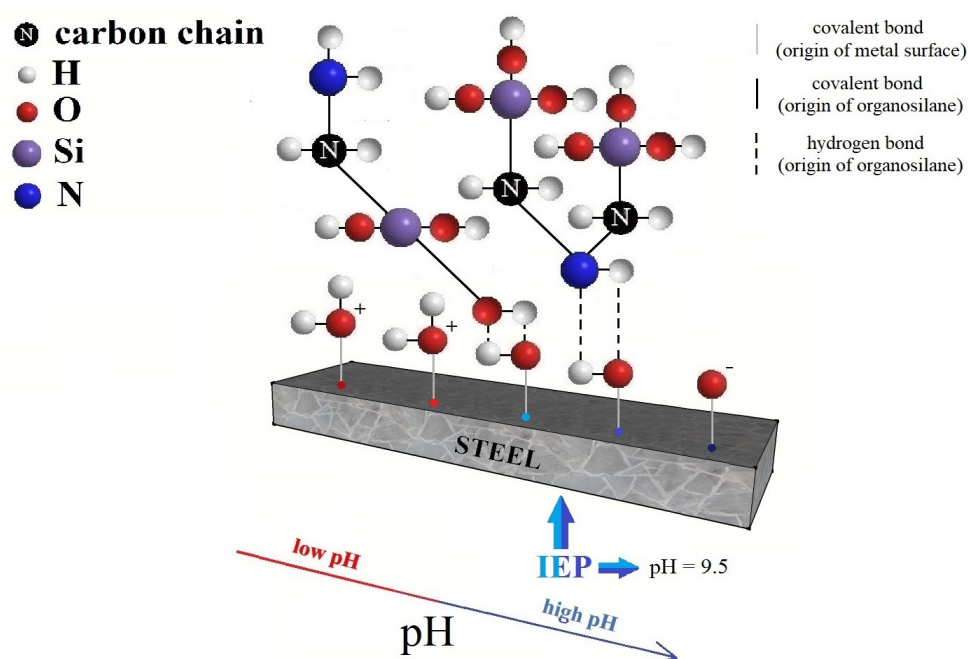
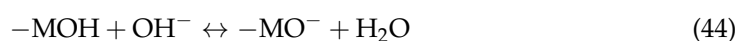


Figure 26. Schematic diagram of the mechanism of bis-amino silan/vinyltriacetoxysilane mixture adsorption on cold-rolled steel (reprinted from [450]).

According to the results of other professional works, acid pickling appears to be more suitable for preparing the surface of metals before application (increasing the presence of OH groups on the surface) of silanes. It was verified on magnesium alloy AZ31 [455] and steel [456–458]. In the case of pretreatment of the steel surface before the application of silanes, sulfuric acid (with the addition of benzothiazole) is suitable, and ideal results for subsequent Si-OH adhesion were achieved by pickling at pH 3.0 [455]. Pretreatment of the steel surface with sulfuric acid is more suitable for forming an oxide coating with the highest hydroxide/oxide ratio than using hydrochloric or phosphoric acid [457]. Additions of H_2O_2 (optimum amount 150 ppm) [458] or $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [459] to the H_2SO_4 pickling solution can lead to an increase in the corrosion resistance of the applied silane coating. Industrially conventional conversion surface treatments can also be used to increase the adhesion of silanes to steel—e.g., zinc phosphating [460] or Zr-based coatings [461,462]. Molybdate solution can also be used as a suitable pretreatment of the steel surface to increase the amount of free OH groups on the surface (hydroxylated metals) [447,463,464]. Controlled anodic oxidation also leads to the formation of ferric hydroxide (FeOOH) on the steel surface and significantly improves the adhesion and subsequent corrosion resistance of silane coatings [384,447]. Conventional immersion application of a combination of TEOS (tetraethyl orthosilane) silanes with, e.g., 3-methacryloxy-propyl-trimethoxysilane [465] or (3-glycidyloxypropyl)trimethoxysilane [466] has been shown to provide a significantly higher level of corrosion protection for carbon steel than a coating with only TEOS or a lower proportion of the main organofunctional silane. Bis [3-(triethoxysilyl)propyl]tetrasulfide (TESPT) achieves excellent results in the provided anti-corrosion protection of carbon steel, especially concerning the significant hydrophobization of the surface [467].

The stability of silane coatings in an alkaline environment is limited [294,296,358] and the same can be expected in the simulated concrete pore solution. It can be assumed that as the pH of the simulated concrete pore solution increases, the stability of the silane coating will decrease; however, it is likely that coatings of sufficient thickness stabilized by the addition of corrosion inhibitors (primarily Ce-based substances) can be durable in the long term [296,358].

2.3.3. Bond Strength in Concrete

It is not clear from the professional literature that there would be verification of changes in the bond strength of reinforcements (mild steel, hot-dip galvanized steel) of arbitrary surface geometry (plain bars, ribbed bars) with an external coating based on silanes in concrete. The potential of applying silanes, ideally in the form of their mixtures, can not only stabilize corrosion products, but also have a positive effect on its bond strength in concrete. In the case of the presence of corrosion products on the steel surface (see Section 1), when embedded in concrete (taking into account the presence/absence of condensate on the steel surface), corrosion may not occur in a passive state at an acceptable corrosion rate [23–26]. The presence of a coating of silanes can ensure the corrosion of the coating in a passive state without the need for demanding scraping of the surface (removal of corrosion products) of the steel. At the same time, the observed increase in the adhesion of fibers coated with aminosilane (see Figure 27) suggests that the application of specific silane coatings can increase the bond strength (physical bonding) of mild steel in concrete [282,295] (this fact was observed on originally brass-coated fibers in the case application to UHPC). It is necessary to verify these facts experimentally.

All the coatings mentioned in this paper have advantages and disadvantages when applied to the surface of steel reinforcement, which are summarized in Table 2 (the use of organofunctional silane in practice is currently the only theoretical base).

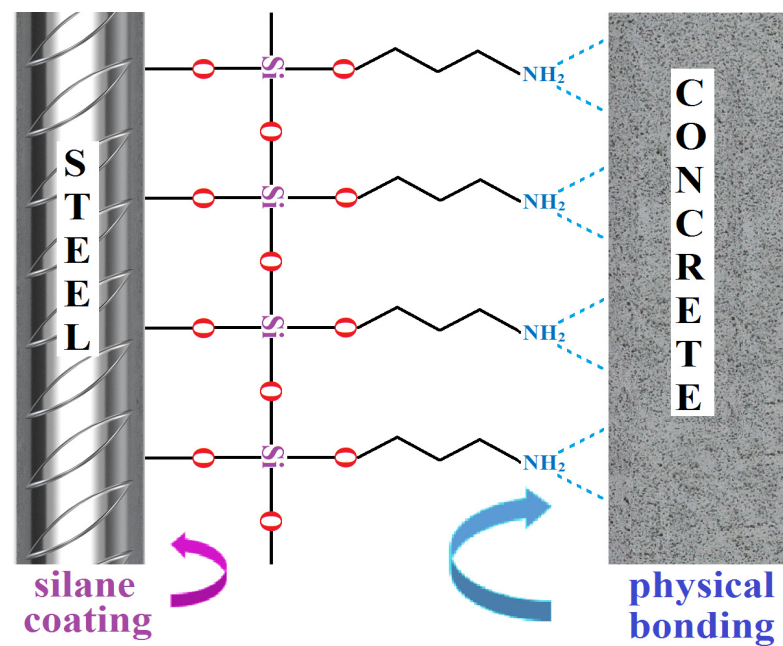


Figure 27. Presumed formation of a “bonded bridge” between conventional steel with organofunctional aminosilane and concrete [282,295].

Table 2. Comparison table describing the advantages and disadvantages of these types of coatings as well as an estimate of their financial requirements.

Type of Coating on Steel Surface	Advantages	Disadvantages	Estimation of Financial Requirements	Notes
epoxy coatings	large coating thickness, do not react with fresh concrete	low bond strength in concrete, more complex manufacturing process, the coating can be abrasively damaged	probably the most financially demanding technique	the necessity to control the coating thickness and its porosity
hot-dip galvanized coatings	hard coating, high resistance to carbonation damage	lower coating thickness, reactions with fresh concrete with hydrogen evolution	financial costs are lower than in the case of epoxy coatings	the need to control the composition of the outer coating layer
organofunctional silane coatings	probable large bond strength with concrete, the possibility to implement a higher coating thickness	poorer applicability to the surface, reactions with fresh concrete	cannot be said in this time	none

3. Conclusions

This paper primarily evaluates the potential of using silane coatings as an external protective layer on conventional carbon steel for application in concrete with the aim of extending the service life of reinforced concrete structures. Research in this particular case is in the early stage; however, applying silane coatings (amino-based silanes) on the surface of metal fibers in UHPC points to the improvement of adhesion properties. Moreover, modified silane coatings are a green alternative to chromate conversion coatings (Cr^{VI}) in the automotive industry. It has been experimentally verified that they provide comparable or in some cases higher corrosion resistance in solutions containing NaCl. However, this article compares the application potential of already used coated reinforcements with the use of epoxy coatings and hot-dip galvanized coatings to the same extent. When added

to epoxy coatings, silanes can improve their resistance. When applied to the surface of hot-dip galvanized steel, they can prevent corrosion of the coating by hydrogen evolution. Therefore, from this point of view, they can also be interesting for construction practice. In the case of their application as external layers on HDG or carbon steel, it is necessary to examine their stability in the environment of the concrete pore solution in more detail. It is also required to verify their specific effect on bond strength, especially with normal-strength concrete (NSC). Furthermore, it is necessary to experimentally verify the applicability of individual organofunctional silanes in practice based on the selection of the most suitable candidate for the most effective corrosion protection. It would also be appropriate to verify in detail the provided corrosion protection using, e.g., the resistometric method, EIS or others. For the application of these coatings on the surface of carbon steel, it is necessary to verify the influence of their chain length (-C-C-) and the presence of specific functional groups on the thickness of the coating and the provided corrosion protection. Research in this area should be focused on verifying the durability of the coatings exposed in simulated concrete pore solution containing chloride anions, or in a simulated concrete pore solution representing carbonated concrete (saturated CaCO_3 solution—pH 8.1). Various organofunctional silanes can also be combined with each other and with corrosion inhibitors. Subsequently, the provided corrosion protection must be verified in real concrete. The last part of the research must be to verify the bond strength of the coated reinforcements in the concrete.

This paper provides a comprehensive overview of the potential use of silanes in the anti-corrosion protection of concrete reinforcement in close connection with other coating technologies already in commercial use. In this case, however, silane coatings are also evaluated as hydrophobizing coatings on the surface of concrete or as corrosion inhibitors (comparison with conventional amines) in simulated concrete pore solutions. These applications are also interesting for construction practice.

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