RILEM Technical Letters (2026) 11: 117-129
https://doi.org/10.21809/rilemtechlett.2026.246

Article of RILEM TC 313-MMS: Importance of moisture for corrosion-related concrete durability

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This article has been prepared within the framework of RIELM TC 313-MMS. The article has been reviewed and approved by all the members of the TC 313-MMS.

Received: 19 May 2026 / Accepted: 03 August 2026 / Published online: 27 August 2026

Abstract

The durability of steel-reinforced concrete is significantly influenced by moisture, which governs the transport of aggressive agents, and the initiation and propagation of reinforcing steel corrosion. Both carbonation- and chloride-induced corrosion are largely related to water penetration, with corrosion rates increasing significantly upon the arrival of waterfront to the steel surface. As the construction sector transitions toward low-carbon binders and concrete with reduced carbonation resistance, understanding internal moisture state and its transport is essential to ensuring concrete durability. This letter critically reviews the multifunctional role of moisture in corrosion-related durability, encompassing carbonation, chloride ingress, and steel corrosion. Key moisture-related mechanisms at the steel-concrete interface (SCI), differences between carbonation- and chloride-driven corrosion, and limitations in current moisture characterization methods - both experimental and modeling - are discussed. The letter concludes by outlining research needs and opportunities.

Keywords: Moisture, Concrete durability, Steel corrosion, Carbonation, Chloride ingress.

1 Background

Modern buildings and infrastructures are commonly constructed using steel-reinforced concrete. Although this composite material is very durable in many exposure environments, corrosion of the embedded steel reinforcement is the most common cause for structural damage, safety concerns, and substantial economic burdens associated with repair and maintenance. One of the key factors needed for steel corrosion is moisture in concrete. As highlighted by the connection of keywords in numerous studies in the literature (see Figure 1), moisture in concrete is closely related to steel corrosion, as well as the durability of steel reinforced concrete. Moisture influences different aspects of steel corrosion, including the transport of corrosive

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agents [1,2], corrosion initiation [3], corrosion propagation [4], and the distribution of corrosion products in concrete [5].

Owing to the unique properties of water, such as its small molecular size, high surface tension, low saturated vapor pressure, and polarity, water can penetrate the porous matrix of concrete; then, it is able to interact with cementitious chemical phases, such as calcium silicate hydrates (C-S-H). The movement of liquid water by capillary forces significantly enhances the transport of corrosive aqueous species such as Cl-, namely by advection, thus markedly accelerating chloride ingress with respect to diffusion. Moreover, pore solution in concrete, generally with high ionic strength, serves as aqueous electrolyte, which enables the electrochemical processes required for corrosion to occur. Empirically measured corrosion rates, either for carbonation- or chloride-induced corrosion, increase with the moisture content or relative humidity (RH) up to partial immersion conditions [4,6–8], but may decline if the material is submerged in water for a long time [7]. Studies have reported that corrosion rates in carbonated concrete are negligible under low RH [4,6,9], whereas they increase markedly when the concrete is exposed to liquid water [10].

In recent decades, due to the urgent need to reduce carbon footprint of the construction sector, many low-carbon binders have been developed and used, such as cements with supplementary cementitious materials. However, most of these binders have lower carbonation resistance than the conventional ordinary Portland cement (OPC) materials, which mainly results from the lower alkalinity or the lower buffer capacity to maintain a high pH [11,12]. This creates a severe dilemma, because the prevailing paradigm in ensuring the durability of reinforced concrete is to avoid that the carbonation front reaches the reinforcing steel within the design service life. Hence, in recognition of the important role that moisture in concrete plays in controlling corrosion, an alternative or complementary route to limiting carbonation is to control the moisture state [11,13]. If the moisture content inside low-carbon concrete can be maintained at a low level, corrosion would be at a negligible level and thus the durability of carbonated steel reinforced concrete is ensured. This requires a better understanding the moisture transport process in the modern low carbon cementitious materials.

This letter provides a critical analysis of the various roles of moisture for corrosion-related concrete durability. It delves into the specific effects of moisture on steel corrosion mechanisms, including its general influence on corrosion rate, its critical impact at the SCI, and its distinct roles in carbonation- and chloride-induced corrosion. Furthermore, the letter examines the inherent challenges in current moisture determination methods, encompassing both modeling and experimental approaches, and finally concludes with a summary of key findings and recommendations for future research.

2 Role of moisture on steel corrosion

2.1 Effect of moisture at the SCI on corrosion

The SCI is the transition area between the steel and the bulk concrete [14–18]. Conditions in this zone decisively influence whether steel corrosion initiates, at what rate it propagates, and to what extent corrosion products precipitate. The thickness of the SCI varies from 5-40 μm to 100-200 μm (if the bleeding water zone is included), depending on factors such as rebar casting direction and water-to-binder ratio [19,20]. Moisture conditions specifically at the SCI are of great importance, as only water at this interface directly controls both corrosion initiation and corrosion rate. The microstructure and moisture properties of the SCI are often distinctly different from those of the bulk concrete [18,21], making localized moisture assessment at this critical boundary essential.

2.1.1 Moisture transport and distribution at the SCI

The distinctive microstructure of the SCI leads to significantly different moisture transport, sorption properties and moisture distribution from the bulk concrete. In general, porosity tends to be higher at the SCI, and pore sizes are larger than the bulk concrete. When reinforced concrete is exposed to water, the large pores and voids at the SCI are partially filled with water, as illustrated in Figure 2. Due to the low water retention capacity of the porous matrix with macroscopic voids, the degree of moisture saturation (S, defined as the ratio of water volume to the total volume of pores) at the SCI is generally below 100%. Even though concrete is submerged in water, capillary pressure cannot let the porous SCI be fully filled with water in a short time because of trapped air and changes in the microstructure. This was apparent from a study combining experiments by means of neutron imaging and numerical modeling, which reported that S at the SCI is lower than that in the adjacent bulk concrete [10]. Furthermore, numerical simulations have shown that during capillary water absorption into a complex porous system, air can be trapped in the pore network, particularly in large pores and voids [22]. With the persistence of capillary forces, the trapped air may slowly dissolve and diffuse outwards, a process that requires very long time (in the order of years, even decades) until completion, that is, achieving water filling of these macroscopic voids [23,24]. The heterogeneous microstructure and the uneven moisture distribution at the SCI play important roles in corrosion initiation and propagation.

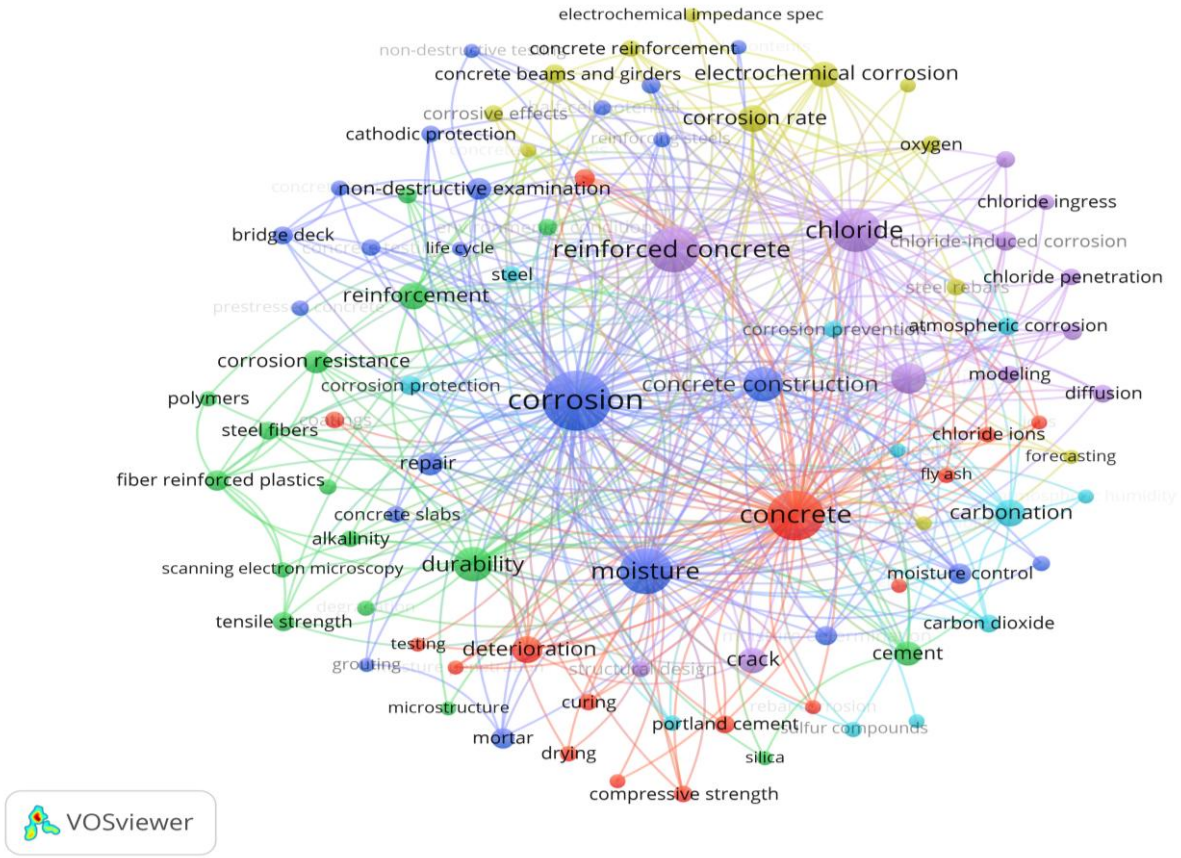

Figure 1. The network of keywords related to moisture in concrete (created by VOSviewer based on the keywords search "moisture" + "concrete" + "corrosion" in Scopus from 2005-2024). The keywords include both "Author Keywords" and "Index Keywords" in about 770 publications. The size of circle represents the occurrence of a keyword in these publications, and the lines connect the keywords mentioned in the same publication. To have a better view, we limited the occurrence to 17, the number of keywords to 90, and the minimum link of each line.

2.1.2 Effect on corrosion initiation

The presence of pore solution at the SCI acts as the electrolyte for electrochemical corrosion reactions. At the anode on the steel surface, the dissolution of metal happens ($Fe \rightarrow Fe^{2+} + 2e^-$), where solid Fe transitions across the metal-electrolyte interface into pore solution as dissolved iron. Meanwhile, at the cathodic site, aqueous species gain electrons from the metal such as oxygen reduction ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$). In sound concrete, these reactions happen in negligible rates (<0.1μA/cm2). However, changes in the pore solution at the SCI (e.g., the drop of pH, the ingress of aggressive ions, etc.) can shift the anodic polarization curve to much higher corrosion densities; therefore, active corrosion initiates. In these processes, water is required as a reactant and as the aqueous environment for the transport of ions and chemical reactions.

From the micro-perspective, steel corrosion initiates at the steel surface where liquid water is present [4,8], known as electrochemically active area. While dissolved oxygen is generally expected to exist in concrete pore solution, initially at a concentration equal to the equilibrium with air, oxygen may be consumed during the cathodic reduction reaction. In this case, the presence of trapped air nearby may resupply the dissolved oxygen and thus contribute to maintaining the corrosion process. Therefore, the presence of large pores and voids at the SCI leads to non-uniform moisture and oxygen distributions, promoting non-uniform corrosion on the steel surface.

In carbonated concrete, with low pH compared with non-carbonated concrete, the locations of the low pH pore solution on the steel surface determine whether the anodic and cathodic reactions are expected to happen. In non-carbonated concrete, on the other hand, steel corrosion is triggered by more complex combinations of parameters. A common cause for localized corrosion is chlorides, generally combined presence of interfacial voids and moisture [16]. However, the underlying physico-chemical processes still need further research to well understand [25], which will be discussed in detail in Section 2.3.

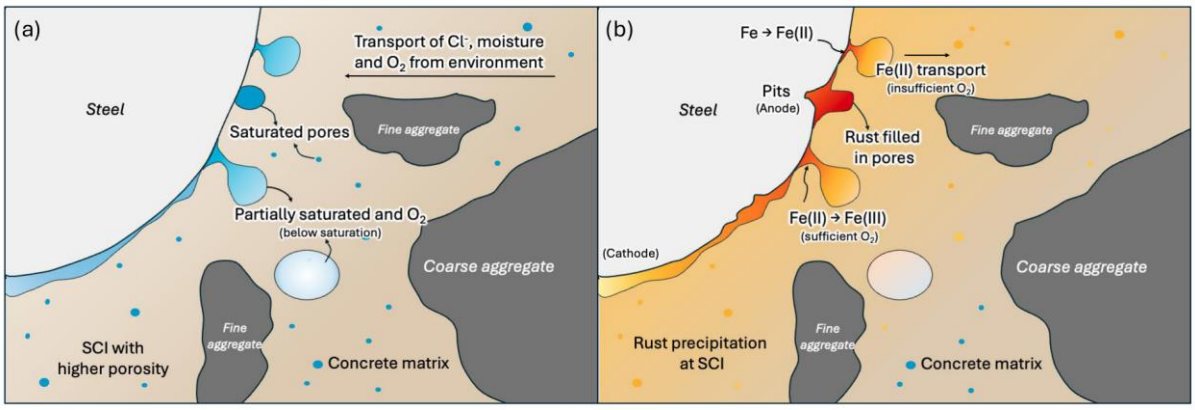

Figure 2. An illustration of the SCI with macro-cell corrosion. (a) The porous SCI before steel corrosion, with saturated pores (blue) and partially saturated pores filled with air and water vapor (light blue). (b) The porous SCI after steel corrosion, with Fe dissolution in the anodic regions, Fe(II) oxidation to Fe(III) (with sufficient O_2), diffusion (without sufficient O_2) and then precipitation. Rust (reddish color) primarily accumulates in the pores at the SCI and may also enter the concrete matrix with water as indicated by the color gradient.

2.1.3 Effect on corrosion propagation

Once corrosion is initiated, moisture continues to play a crucial role in the propagation process. The released Fe(II) ions may undergo different processes, including diffusion, hydrolysis, oxidation, and precipitation, which all happen in pore solution [26]. Moreover, when anodic and cathodic sites are spatially separated (see an example in Figure 2), which is primarily the case in chloride-induced corrosion, the presence of a continuous electrolyte in the pore system establishes the electrolytic connection, thereby enabling macro-cell formation [27,28]. Moisture thus contributes to macro-cell corrosion, particularly by enabling the involvement of large cathode surfaces, which results in a high cathode:anode area ratio and accelerates iron dissolution [29,30].

In recent years, research has increasingly highlighted the effect of moisture on corrosion products transport and distribution in the cementitious matrix. Based on numerical simulations (reactive transport modeling) and experimental observations, various studies found that corrosion products do not only precipitate close to the steel bar but can diffuse far away from the steel into the bulk concrete (in the order of mms) [8,20,26,31–33]. During the transport process, Fe(II) ions may be oxidized to Fe(III) compounds and precipitate as ferric oxides (α- and γ-Fe_2O_3) and/or oxyhydroxides (α-, γ-, δ- and β-FeOOH) or mixed-valence oxides (magnetite, Fe_3O_4) [34–37] depending on the pH, concentration of oxygen, and other factors such as the presence of additional ions [38].

When macroscopic voids are present close to the steel surface, corrosion products preferentially precipitate in a unique pattern. SEM images reveal that these voids can accommodate a large amount of corrosion products, which grow specifically along the void walls inward towards the center of the void, rather than outward into the concrete matrix [20,31,39,40]. This inward growth is hypothesized to continue until the void is filled or until the pore solution can no longer reach the anodic site due to the accumulation of corrosion products. The presence of an aqueous phase within the void is crucial for this hypothesized precipitation mechanism, involving processes like oxidation, diffusion, hydrolysis, and (ad)sorption of iron ions.

The moisture condition at the SCI is complex and significantly affects both initiation and propagation of steel corrosion. A better understanding the mechanisms will help us develop predictive models and corrosion management strategies. Therefore, continuous research in this area is essential for enhancing the durability of reinforced concrete structures.

2.2 Carbonation of cementitious materials

2.2.1 Effect of moisture on carbonation

Carbonation is a natural process that atmospheric CO_2 reacts with calcium hydroxide (CH), C-S-H and other hydration products. These reactions induce a significant pH reduction in concrete, from the highly alkaline state (typically between 12.5 and 14) to below 9, often around 8.5 [41,42], which causes the depassivation of steel rebar and steel corrosion.

Concrete carbonation is characterized by distinct processes, including diffusion of atmospheric CO_2 gas through the empty pore space and the reactions of dissolved CO_2 with Ca^{2+} from hydration products in aqueous alkaline pore solution, in which moisture plays a key role. The dry concrete is in favor of CO_2 diffusion as the CO_2 diffusion coefficient in air-filled pores is about four orders of magnitude higher than that in water. Conversely, the wet concrete promotes CO_2 dissolution in pore solution and provides an electrolyte for carbonation reactions. With the competition of two processes (diffusion vs. reaction), an ideal RH environment exists, providing the optimal condition for carbonation. Based on the literature data, the optimal RH range is typically reported between 50% and 80% [43–46]. The specific optimal RH for a given material depends on the microstructure of concrete. For the more porous concrete, the optimal RH is higher, while for the less porous concrete, the optimal RH is lower. The field observations further support the key role of moisture in concrete carbonation. Under the conditions with similar CO_2 concentration, sheltered concrete (35-60 % RH) generally shows a higher carbonation depth than the

unsheltered concrete that was exposed to rainfall and dry events [47,48].

Different moisture conditions during carbonation may affect the phase assemblage of carbonation products. It was reported that the microstructure of carbonated concrete at low RH (e.g., 60%) is denser than that at high RH (e.g., 90%) due to the formation of polyhedral vaterite particles [43]. The precipitation and transformation of calcium carbonate polymorphs strongly depend on RH: higher RH (75%-90%) is in favor of the formation of stable calcite, while amorphous calcium carbonate (ACC), aragonite and vaterite are generated at lower RH (33%-54%) [49]. The formation of ACC is generally considered the first step of $CaCO_3$ precipitation and in high RH ACC transforms into crystalline polymorphs within several minutes, whereas its transformation is much slower in lower RH conditions [50]. Regarding the carbonation of C-S-H, both RH and the Ca/Si ratio in C-S-H have effects on the polymorphs of $CaCO_3$ [51]. C-S-H composed of a Ca/Si ratio of 1.5 decomposed at 57% RH, to form amorphous silica gel, which indicated that Ca^{2+} from C-S-H is more susceptible to carbonation reaction than Ca^{2+} from CH. Stable calcite formed from the carbonation of C-S-H with Ca/Si >1.2 at 91% RH, whereas at 57% RH, vaterite and aragonite phases formed. For C-S-H with Ca/Si of 0.7, vaterite and amorphous calcium carbonates are formed at 91% and 57% RH environments, respectively.

2.2.2 Effect of moisture on carbonation-induced corrosion

With increasing water content in carbonated concrete, electrical resistivity decreases because the pore solution acts as a medium for ion transport, allowing current to flow more easily. Since an electrolyte in the concrete pore system is necessary for electrochemical reactions and thus for corrosion to occur (see section 2.1), electrical resistivity of concrete can be considered as a rough indicator of steel corrosion. Therefore, high electrical resistivity generally indicates a low risk of steel corrosion [29]. Conversely, high water content in carbonated concrete generally increases the risk of steel corrosion by reducing the electrical resistivity. This was confirmed by laboratory experiments and practical experience, which have shown that the moisture condition in carbonated concrete is a key factor for corrosion damage as high corrosion rates were only observed when concrete was subjected to partial immersion conditions [6,9,10,52,53]. For instance, a field survey in Finland found out that corrosion related damage only occurred in the location with low cover depth and high moisture variation, such as the sidewall of the balcony.

Figure 3b provides a schematic illustration of concrete with steel bars placed at different depths, along with an example of a possible moisture distribution in concrete (Figure 3a) and the corresponding instantaneous corrosion rates (Figure 3c). This illustrates that the distribution of moisture in concrete can directly influence the corrosion rate of rebar. It should be noted, however, that the literature data shown in Figure 3c were obtained at the moisture equilibrium state. A recent study further visualized the dynamic interaction between water at the SCI and steel corrosion utilizing neutron imaging to observe the real-time moisture ingress into carbonated mortar and simultaneously monitor electrochemical corrosion of an embedded steel wire [10]. When the waterfront reached the steel surface, the steel potential sharply dropped to more negative values, indicating that active corrosion occurred. The measured corrosion rate after water ingress was about 200 times higher than that before the measurement. The rapid transition from negligible to appreciable corrosion rate implies that the dynamic moisture conditions at the steel surface are undoubtedly the primary factor governing steel corrosion in carbonated concrete.

2.3 Chloride ingress in concrete

The rate of chloride-induced corrosion is influenced by moisture in concrete because all rate-limiting steps are strongly related to the moisture state in concrete [56], including chloride ingress, oxygen reduction, and concrete resistivity [57].

2.3.1 Effect of moisture on chloride ingress in concrete

Transport of chloride ions through the concrete cover to the reinforcement requires a certain S in the pore system. Several studies of ion transport by diffusion at varying moisture levels have been performed with different techniques [58–62]. It has been frequently reported that the diffusion coefficient of chloride D_{Cl} increases with the equilibrated RH and the internal S [59,63–66].

Different forms of chlorides and transport mechanisms can be related to the moisture state and moisture transport in concrete. Advection of chloride ions is possible where ions are moving with the bulk water. For instance, when concrete is exposed to water with chlorides after the self-desiccation process, in which the pore system is partly empty, and the pore water activity reduces to 85-90 %, the initial chloride ingress occurs simultaneously with water penetration [67]. Measurements of chloride accumulation during transport of salt water at non-saturated conditions confirmed increases in both moisture and chloride profiles [6,68]. In addition, chloride binding is influenced by the moisture variations in concrete. When the concrete surface is wetted by pure water, such as long periods of rain, concrete may lose free chlorides due to leaching [69], but the chemically bound or physically adsorbed chlorides may remain in a certain fraction.

When concrete is alternately exposed to wetting by salt water or pure water and drying, such as in the “splash zone” or tidal zone of structures exposed to sea water above the water table or structures exposed to de-icing salts, chloride transport is extremely complicated. The chloride transport mechanism, combining diffusion and advection, is decisively influenced by the moisture conditions and moisture transport. Experimental results showed that such cyclic drying and wetting conditions can accelerate the ingress of oxygen and aggressive ions dissolved in water and thus facilitate corrosion reactions at both anode and cathode [70]. However, such cases are especially difficult to analyse because it is not easy to analytically describe the boundary

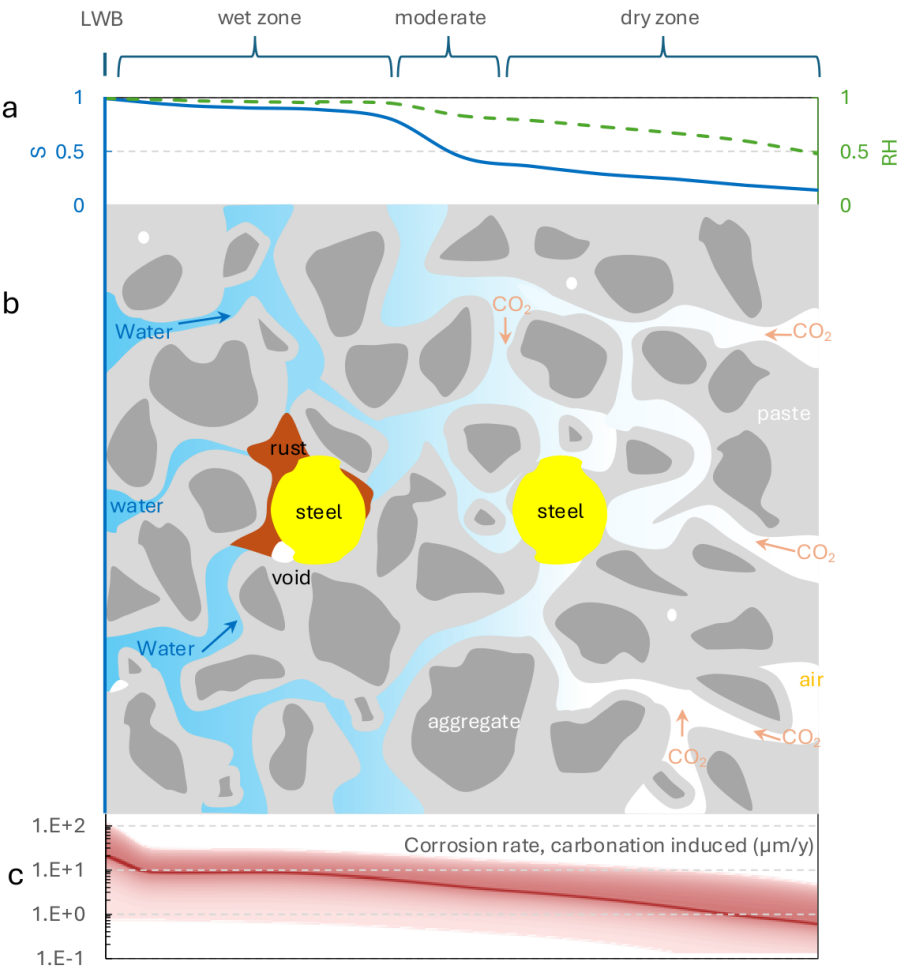

Figure 3. Illustration of the effect of water on steel corrosion in carbonated concrete: a) RH and water saturation S profiles with depth (sorption isotherm calculated based on measured data in [55]). We consider the case that a concrete block contacts liquid water on the left-hand side (LWB = liquid water boundary) and air on the right. Based on S, concrete is divided into dry, moderate, and wet zones; b) Two steel rebars in carbonated concrete. Only the rebar in the high-S region has visible corrosion, and more rust form in the pores with liquid water; c) steel corrosion rates varying with moisture condition if the steel rebar were placed at different depth. The measured corrosion rates were reported in [52], the red thick line represents the average corrosion rate, and the shaded zones stand for the range of measured data.

conditions at the concrete surface. The duration and frequency of the periods when the concrete is wet must be quantified.

Another scenario that moisture can significantly affect salt transport is known as "wick transport" in which a structure is exposed to salt water on one side and drying conditions on the other side. With drying creating the driving forces for water transport, ions can penetrate deeper into the pore system beyond the simple diffusion [71]. Therefore, the risk of steel corrosion under wick chloride transport is high.

2.3.2 Effect of moisture on chloride-induced steel corrosion

- Corrosion Initiation

A common concept to describe chloride-induced corrosion initiation is whether the chloride concentration at the steel surface exceeds a threshold, the so-called critical chloride content (C_{crit}), which was reported to vary with the moisture condition [72,73]. RILEM TC 262-SCI tried to quantify and to evaluate the effect of moisture on C_{crit} for corrosion initiation [16] based on measured data collected from the literature [74–76]. Although RH below 65 % may have limited practical significance for chloride-induced corrosion, the data demonstrate that moisture conditions significantly impact the range from RH 80 % to capillary saturation. Nevertheless, the fundamental role of moisture in chloride-induced corrosion initiation is complex and still needs further research.

- Corrosion rate in chloride-induced corrosion

The measured corrosion rate in chloride-induced corrosion is closely related to concrete's moisture condition. Tuutti [6] conducted pioneering research on the effect of RH on corrosion rate of steel in cement-based materials mixed with 5% $CaCl_2$. The extensive weight loss measurements were done to evaluate corrosion rate values after initiation. A

corrosion rate of approximately a few µm/year, independent of the initiating mechanism and cement type, was observed in concrete fully saturated with water. The corrosion rate showed strong moisture dependency with an increasing trend from 60% RH to 90–95% RH, and a sudden drop to water saturated condition due to the low oxygen availability under a long submerged condition. The effect of S on measured corrosion shows a similar trend to RH as reported in [7].

The amount of oxygen available as a reactant for cathodic reactions in an electrochemical corrosion cell is controlled by the amount of moisture in concrete [73,77]. It is generally seen that the oxygen diffusion coefficient decreases with S in concrete [78,79] (see Figure 4). However, the supply of oxygen to the cathodic steel surface is complex and involves many factors, including the cover depth, concrete porosity, and the geometrical arrangement of the reinforcing steel. Particularly in chloride-induced corrosion, because the cathodic area is usually significantly larger than the anodic area, the competition between the rates of consumption and resupply of oxygen at the cathodes is not straightforward to predict. While in small-scale laboratory samples, oxygen starvation may be achieved within days or weeks under certain conditions (especially high corrosion rates achieved by severe admixed chloride contents), the prediction is often more difficult in structures with realistic dimensions and with varying moisture conditions.

In addition, pore solution contaminated with chlorides serves as an electrolyte, thereby affecting the transfer of charges in the electrochemical corrosion cell between anodic and cathodic regions, which can be reflected by concrete resistivity [30]. The critical role of water on concrete resistivity is clear that concrete resistivity decreases with increasing S [7]. Therefore, when S is low, ion transport in concrete is limited, and the corrosion rate is low, even may be negligible.

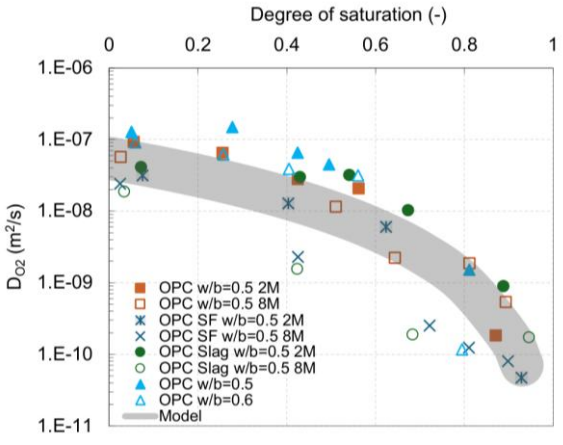

Figure 4. Effects of saturation degree on the oxygen diffusion coefficient, both measured [78,79] and modelled. The model for D_{O2} is $D_0 S_0{}^{a-1}(1-S)^{1+a}$, with $D_0 = 1\times10^{-7} m^2/s$, $S_0 = 0.3$, and $a = 1.5$.

3 Challenges in moisture determination methods

The complex, dynamic, and non-linear role of moisture in steel corrosion in reinforced concrete, coupled with its localized effects at the SCI, requires highly accurate and reliable determination methods. However, both current modeling and experimental approaches face significant challenges in capturing the accurate moisture state and the dynamic impact on durability. Accurate moisture determination is not only about quantifying water content but also about understanding its distribution, movement, and intricate interactions with the concrete matrix and aggressive agents.

3.1 Modeling methods

3.1.1 Moisture transport in bulk concrete

Conventionally, moisture transport in cementitious materials is simulated by Fick's law of diffusion, Darcy's law, or Richards' equation, including the original models and their variants, which were generally applied by assuming the homogeneous material microstructure and/or a rigid solid skeleton [80–83]. Even though these models are widely used for engineering practices and scientific research, they are frequently found to be insufficient for certain experimental observations, such as the anomalous moisture transport [84–89]. The commonly accepted reasons for anomalous moisture transport are changes in the material's microstructure due to water uptake [63,90] or drying [91–93], air dissipation during water absorption [10,94,95], and different moisture transport mechanisms in the complex pore network [96,97]. Based on these considerations, modified conventional models that can capture the anomalies of moisture transport are proposed, such as the fraction/fractal models [98,99], dual-porosity/permeability models [96], time-dependent permeability models [87,100,101], and models based on the pore size distribution [102]. However, these models largely simplify the causes of anomalous moisture transport and are typically used to simulate 1D (or rarely 2D) moisture transport, in which the complex, heterogeneous pore structure cannot be fully considered. These simplifications provide an easy way to implement the models for engineering practices, but for scientific research that needs to fundamentally understand the deterioration process at the microscopic level, these models are not comprehensive enough. Therefore, from the scientific research perspective, advanced models with multiple phases (liquid water, air, water vapor, and adsorbed water), multiple scales (from nm to m), and multiple interactions (with solids and ions) are needed [103–106].

Additionally, moisture transport models should be calibrated and validated before being used to predict moisture state and moisture distribution. Depending on the model's complexity, the ways of calibration and validation are different. Conventionally, the parameters in a model are either directly measured such as sorption isotherms and water permeability or indirectly determined by other types of measured data. For instance, moisture transport coefficients (e.g., water permeability, moisture diffusivity) can be inversely calculated

by fitting the simulation results with the measured mass changes of a sample, such as mass loss during drying and mass gain during wetting (high RH) or water absorption (in contact with liquid water) [101,105,107–109]. However, the overall mass changes do not reflect the actual dynamic moisture distribution in the material. A complementary validation dataset such as moisture content profiles/distribution was suggested [83,97,110]. Nevertheless, most moisture transport models are typically calibrated or validated by only one type of data, either mass changes or moisture content (or S) profiles. Models that can be calibrated and validated by different types of data are expected to show a high robustness in predicting moisture content and moisture distribution. For advanced models, moisture measurements at the microscopic scale are required, but the available experimental techniques may not be sufficient for this purpose if the simulations are performed with sub-micron domains (with a resolution of around 100 nm or even lower). Thus, the alternative methods for model calibration and validation may be needed, such as simulation upscaling, using the mimic pore network for moisture transport measurements.

3.1.2 Moisture at the SCI

The SCI is a three-dimensional transition zone with distinct microstructural, chemical, and transport characteristics [18,111,112]. Despite the availability of sophisticated modeling techniques, their application to the SCI remains limited due to the difficulty of representing its complex and dynamic nature, which significantly differs from bulk concrete. A major challenge is to accurately capture the highly localized changes in material properties within this narrow region, which contains multiple interacting materials and shows pronounced multiscale heterogeneity. These features pose significant challenges for numerical simulations, as conventional macroscale models struggle to incorporate such spatial variability and the evolving nature of the materials involved, directly affecting transport processes at the SCI.

Therefore, to simulate moisture transport at the SCI, its microstructure needs to be simplified for conventional moisture models, such as by the homogenization method [10]. However, the practical aspects of parameterization and validation face difficulties. To be accurate, such models require reliable input data on the moisture transport properties of SCI, which is directly affected by the various constituents involved, including bulk concrete, steel, and corrosion products that may form during steel corrosion.

A comprehensive description of moisture transport at the SCI thus requires linking moisture transport in the bulk concrete with that occurring in the localized and microstructurally distinct interfacial region. While conventional macroscopic models can adequately simulate moisture transport in bulk concrete - providing boundary conditions for more detailed analyses at the SCI, additional insights may be gained by combining microscopic modeling with high-resolution imaging techniques.

Promising tools, such as the lattice Boltzmann methods [113] and the pore scale models with computational fluid dynamics [22], can utilize image-based 3D microstructures (e.g., derived from X-ray micro-computed tomography (μCT) [95,114] or FIB-SEM techniques [115]) for direct simulations. Nevertheless, resolving the moisture transport dynamics within the submicron pores to capture localized SCI effects requires high-fidelity microstructural characterization, advanced numerical methods alongside fine spatial and temporal discretization, and the use of supercomputers. So far, the implementations of these models for this purpose are limited. Additionally, particle-based simulations, i.e. molecular dynamics simulations, can precisely reveal molecular interactions; however, the size of the computational domain is very small, much smaller than 1 μm [116].

3.2 Experimental methods

3.2.1 Moisture distribution in bulk concrete

Characterization of transport properties is needed to calibrate and validate the prediction models (as discussed in Section 3.1.1). Conventional models require knowledge of the overall amount of moisture and its state, with both being related to each other by a sorption isotherm, which can be experimentally obtained by the saturated salt solution method or a dynamic vapor sorption analyzer [117–119]. Mass changes of a sample during water absorption or drying are commonly measured by the gravimetric method, which involves weighing samples under a certain exposure condition, providing the overall water content and thereby allowing for the computation of the water ingress rate. Additionally, moisture measurement methods include quantifying moisture distribution within samples, which can be measured by radiographic methods including gamma-ray attenuation [120], X-ray attenuation [121], neutron radiography [10,122–124], and electromagnetic radiation methods, such as nuclear magnetic resonance (NMR) [125,126]. Electrical resistivity and capacitance methods measure the conductance of concrete, which correlates with its moisture content [57].

To calibrate and validate the advanced models at the microscopic scale, such as to reveal microstructural changes due to moisture transport and the redistribution of trapped air, microscopic techniques with a submicron 2D or 3D spatial resolution are required. The challenge is obvious: such a technique to observe the dynamic moisture transport and microstructural changes is hard for cementitious materials. The radiographic methods such as μCT, may provide a resolution of a few hundreds of nm, but require very small samples and the accuracy is not verified because of the low X-ray attenuation of water and low water content in cementitious materials. In heterogeneous cementitious materials, the beam hardening may occur at the interface between two dissimilar objects with different densities and attenuation coefficients, so leads to artifacts. Therefore, most of moisture in the gel and small capillary pores (<100 nm) is hard to be directly resolved by radiographic methods [127].

3.2.2 Moisture at the steel concrete interface

The distinction in the microstructure and moisture properties between the SCI and bulk concrete implies that macroscopic moisture measurements of bulk concrete, or even surface-level observations (e.g., via SEM), may not accurately represent the localized and unique conditions at the SCI. Due to the small scale, conventional methods for bulk concrete can easily overlook moisture transport at the SCI. One of the key microstructural features of the SCI is a broad range of pore sizes from nm in hydration products to hundreds of μm of the large pores and voids, which requires multiple techniques to quantify moisture distributions at the SCI. The most promising techniques are radiographic methods which can provide a reasonable resolution to cover the large pores at the SCI. A recent study demonstrated the potential application of μCT for detecting the presence and distribution of liquid solution within interfacial macrovoids at the SCI [128]. One challenge of μCT is the beam hardening problem which leads to the loss of a few pixels close to the steel surface, in which the distribution of solids and moisture cannot be resolved [15,128,129]. After corrosion initiation, corrosion products further increase the complexity of the microstructure and moisture transport at the SCI.

3.3 Challenges in low-carbon cementitious materials

The development of a new generation of low-carbon concrete, including low-clinker mixes and CO_2-sequestering concrete through carbonation curing, advances rapidly [12,130–134]. For these low-carbon materials, the existing literature still employs the same moisture transport models and experimental techniques used for the conventional OPC materials (e.g., [135]). Nevertheless, it is well recognized that the chemical phases in low-carbon cementitious materials are different from the conventional OPC materials, with less CH and C-S-H but more calcium carbonates, C-A-S-H (calcium-aluminosilicate hydrate), A-S-H (aluminosilicate hydrate), or AFm phases. However, there is a lack of experimental data for the moisture interactions with these emerging materials. Some studies proposed that carbonation products are less sensitive to water than CH and C-S-H [89,136], while direct experimental evidence is still missing. This makes it challenging to propose and validate comprehensive models to describe the moisture state in these materials and their relation to corrosion, which requires further investigation.

4 Research opportunities

The above review and discussion imply that we need to deepen our understanding of modeling and experimental validation of moisture in bulk cementitious materials and at the SCI. Therefore, we identify the following four research opportunities.

1. The primary research opportunity is to identify appropriate models for different engineering and scientific applications. This opportunity focuses on systematically reviewing existing moisture transport mechanisms and prediction models for cement-based materials. Models need to be classified based on their applications, either for engineering practice or scientific research, as different applications require (or allow for) different levels of complexity. This opportunity simultaneously determines what experimental data is needed to calibrate and validate these models. This creates opportunities for researchers to develop standardized protocols for model evaluation and to identify gaps in currently available experimental data.
2. Building on the needs of the above-identified data, the second opportunity addresses the practical challenges of obtaining moisture transport data for model calibration and validation through both laboratory and field observations. The research opportunity here centers on reviewing and comparing newly developed experimental techniques and measurement methodologies, with emphasis on assessing their practicality and applicability for real-world engineering contexts. This encompasses evaluating innovations in measurement technology and establishing best practices for data collection.
3. The third opportunity targets a specialized research area examining anomalous (non-conventional) moisture-related behaviors in cementitious materials. The key research opportunities include identifying the primary causes and developing or evaluating simulation models to predict these behaviors. Most significantly, this opportunity needs to address a critical knowledge gap by investigating how anomalous moisture transport mechanisms ultimately affect the long-term durability and performance of concrete structures.
4. The last opportunity targets an emerging research frontier by examining moisture transport at the SCI. This involves synthesizing existing knowledge about microstructure, chemical composition, and transport properties at this critical interface, while identifying and addressing substantial knowledge gaps in moisture measurement and simulation methods at the SCI. Given that moisture transport at the SCI is a relatively new and underexplored area, significant research opportunities exist for developing new experimental and modelling approaches, particularly at the microscopic level, and understanding how this transport influences concrete durability.

Acknowledgement

Z. Zhang and U. Angst are part of the SPEED2ZERO Joint Initiative, which received support from the ETH-Board under the Joint Initiatives scheme. Z. Zhang and L. Malenica disclose the support from Swiss National Science Foundation Project funding (10003479). C. Zhou acknowledges the financial supports from the National Natural Science foundation of China (No. 52478243). N. Alderete would like to thank the Research Foundation-Flanders (FWO-Vlaanderen) for the financial support (1247225N). L. Huang appreciates the financial support from VR international PF project (NO. 2024-

00569). Q. Xiong would like to thank the LETS GROUP for financial support. T. Chidiac received financial support from Alexander von Humboldt-Stiftung.

Authorship statement (CRediT)

Z. Zhang & C. Zhou: Conceptualization; Investigation; Coordination; Visualization; Writing - Original Draft. **Q. You and L. Malenica:** Investigation; Visualization; Writing - Original Draft: Section 2.1. **Z. Zhang, T. Chidiac**, and **U. Angst**: Section 2.2. **Z. Zhao, B. Guo, L. Huang** and **L.O. Nilsson**: Section 2.3. **Q. Xiong** and **C. Strangfeld**: Section 3.1. **N. Alderete** and **L. Huang:** Section 3.2. **All authors**:Writing – Review & Editing.

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