Steel corrosion in concrete – Achilles' heel for sustainable concrete?

Journal Article

Author(s):
Angst, Ueli

Contents lists available at ScienceDirect

Cement and Concrete Research

Steel corrosion in concrete – Achilles' heel for sustainable concrete?

Ueli M. Angst

ETH Zurich, Institute for Building Materials (IfB), CH-8093 Zurich, Switzerland

ABSTRACT

The reduction of greenhouse gas emissions from concrete production leads to decreased alkalinity of the concrete. This is generally perceived as a durability problem, because the prevailing doctrine assumes that reduced alkalinity leads to corrosion of the reinforcing steel. It is exactly this paradigm that presents a barrier preventing the potential of low-emission concretes from being fully exploited. Practical experience, however, shows that the loss of alkalinity does not necessarily lead to significant steel corrosion. This knowledge presents an opportunity for a new paradigm that allows controlling corrosion while tolerating reduced alkalinity. However, this change can hardly be successfully achieved on the basis of empirical experience. Instead, science-based models are needed to predict the corrosion performance of new concretes. This contribution showcases advances related to the fundamental understanding of steel corrosion and coupled processes occurring in the cementitious matrix. Opportunities for integrating these findings in next-generation corrosion models are discussed.

1. Introduction

Achilles, the legendary hero of the Greek myths, was known for his extraordinary strength and endurance, being invulnerable except for his heel. Similarly, reinforced concrete is known for its high strength and generally very good durability. Corrosion of the reinforcing steel, however, is the by far most common cause for degradation [1], which may lead to catastrophic failures. Thus, one may consider steel corrosion being Achilles' heel for concrete. In the coming decades, this potential weakness of reinforced concrete will increasingly demand attention in science and engineering, namely because of the modifications that concrete will continue to undergo in response of the cement and concrete industry to global warming. These modifications lead to the loss of an important protection layer against corrosion – the high alkalinity of traditional concrete. For concrete structures to be sustainable, not only the environmental footprint of the materials used for construction are relevant, but also the long-term durability over the anticipated service life.

Climate change, without doubt a major global challenge, is driven by the emission of greenhouse gases (GHG), including carbon dioxide (CO_2). It is well known that the cement industry causes significant CO_2 emissions, with concrete production accounting for up to 8 % of total global anthropogenic CO_2 emissions [2]. The primary source of CO_2 emissions from the cement industry is the decomposition of calcium carbonate (limestone) that takes place during the production of the cement clinker at high temperature in a kiln [3]. The use of alternative or supplementary cementitious materials (ACMs, SCMs), together with other measures such as the implementation of energy-efficient production processes, can reduce GHG emissions from the cement industry [3,4]. This is illustrated in Fig. 1 that shows a compilation of literature data where the global warming potential (GWP) of different concretes was calculated [5–8]. The concretes shown in this figure were produced from binary and ternary binders including fly ash, limestone, calcined clay, and ground granulated blast slag in range of different combinations. The figure clearly shows the reduction in GWP with increasing clinker substitution, irrespective of the type of SCM.

In addition to clinker substitution, carbon sequestration technologies can also play a role in reducing the environmental footprint of cement and concrete. Such carbon sequestration technologies include the reaction of concrete with environmental CO_2, the so-called carbonation process later addressed in more detail in this contribution, which is a process that naturally occurs over the life of a concrete structure. Reducing GHG emissions from concrete productions is important, not only because of the significant emissions caused today, but also considering the increasing demand for construction materials over the coming years, driven by factors such as population growth, urbanization, and economic development. In this context, the cement industry's climate target, namely to deliver carbon-neutral cement by the year 2050 in order achieve the UN Sustainable Development Goals [9], appears ambitious.

The goal is particularly ambitious when considering that the current paradigm in engineering presents a barrier against fully exploiting the
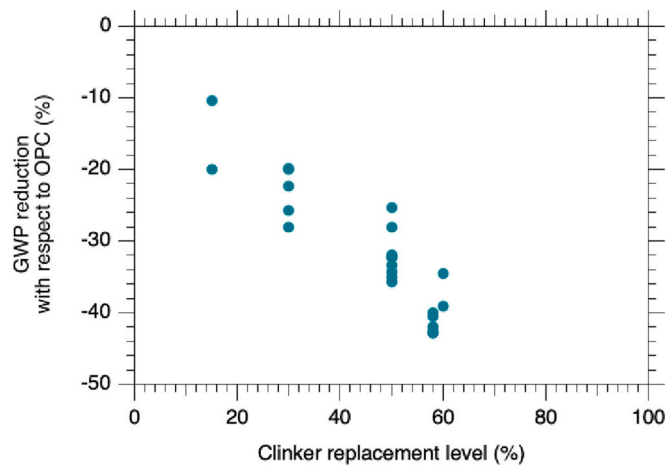
Fig. 1. Reduction of global warming potential (GWP) of concrete mixes with various degrees of clinker replacements with respect to reference concrete produced from ordinary Portland cement (OPC).
Data compiled from the literature [5–8].

potential of alternative cementitious materials (ACMs). This is because ACMs lead to decreased alkalinity of the pore solution within concrete. This reduced alkalinity is generally perceived as a durability problem, especially with respect to corrosion of reinforcing steel in concrete. This perception raises a goal conflict, also known as "the carbonation dilemma". Section 2 briefly discusses this goal conflict, considering traditional and recent development in the field of cementitious binders with reduced GHG emissions. Section 3 reviews scientific progress made related to the corrosion of steel in concrete, with a particular focus on research needs. Scientific progress is needed to implement engineering approaches that allow controlling corrosion while tolerating reduced alkalinity.

2. The carbonation dilemma

2.1. Laws of nature cannot be overruled

In the context of concrete, the term "carbonation" describes the multi-step process in which CO_2 gas enters into the concrete (transport), where it dissolves in the alkaline electrolyte held in the concrete pores,

yielding bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions, which react with different cementitious phases [10,11]. Generally, the bicarbonate and carbonate ions react with calcium ions present in the concrete to form thermodynamically stable calcium carbonate.

Calcium ions originate from various calcium-containing cementitious phases. In particular, cement pastes produced from clinker-containing binders contain calcium hydroxide ($Ca(OH)_2$), which is a phase buffering the pH in the electrolyte in the concrete around 12.6. In this case, calcium hydroxide reacts with ingressing CO_2. Once the pH buffering effect of calcium hydroxide is exhausted or kinetically hindered, the pH of the pore liquid decreases. The carbonation process and its effect on the pH can be visualized for instance with the help of thermodynamic modelling [12,13] or by means of pH monitoring with embedded sensors [14,15]. Examples are shown in Fig. 2. These data illustrate the stepwise decrease of pH associated with the carbonation of different phases. In zone I, the pH remains around 12.5 as long as Ca(OH)$_2$ is present. The pH then decreases to a lower level along with the decalcification of C-S-H, reaching an equilibrium in the zone II. Decomposition of further phases (monocarboaluminate, ettringite) lead to a fully carbonated system with even lower pH [13]. Fig. 2b additionally shows that the pH may initially be higher than 12.5, which is generally ascribed to the presence of hydroxyl ions balanced by sodium and potassium ions. The initial pH decrease apparent in Fig. 2b can be explained by carbonation of these additional alkalis.

The carbonation process is a reactive transport process. Carbonation first occurs at the zone directly exposed to the atmosphere and then progressively occurs deeper within the concrete (Fig. 2b). The penetration of the carbonation front slows down with time as the diffusion of CO_2 into the concrete is becoming increasingly difficult with increasing diffusion length. Furthermore, the carbonation process becomes limited by the formation of calcite layers that may shield Ca(OH)$_2$ crystals from reacting with the ingressing bicarbonate and carbonate ions. The penetration of the carbonation front (x_c) is generally described empirically by square root of time (t) laws, that is, $x_c = k\sqrt{t}$, where k can be considered as the carbonation coefficient, depending on the pore structure, chemistry and phase assemblage of the concrete. For some exposure conditions, the exponent was found to deviate from 0.5 and thus from square root law [16], but for the reasons given above, the general trend, namely a deceleration of the penetration of the carbonation front with time, still applies.

Moreover, the basic fact that the pH is buffered for a certain period of time, depending on the phases present, holds true. In particular, the duration of buffering at pH 12.6 (zone I in Fig. 2) depends significantly
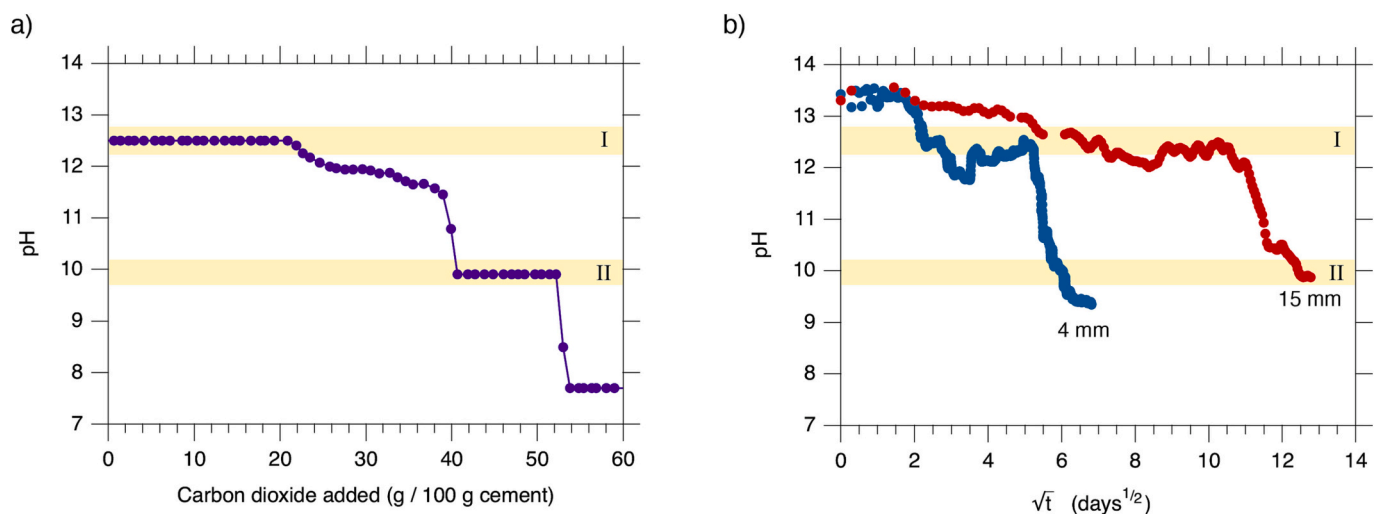
a)

b)

Fig. 2. a) pH of the electrolyte held in the pore system of a model cement paste, obtained from thermodynamic modelling (adapted from [13]), b) pH measured with sensors embedded at two different depths in Portland cement paste samples exposed to accelerated carbonation (adapted from [15]). See text for description of zones I and II.

on the quantity of Ca(OH)$_2$ present in the system. This relationship directly affects the rate at which carbonation occurs, which can be seen from measured carbonation coefficients k as a function of clinker replacement (Fig. 3). In this figure, carbonation coefficients k, determined from various methods (including accelerated and natural carbonation testing), were related to the carbonation coefficient for OPC determined under the same conditions. It can clearly be seen that with increasing level of clinker replacement, the carbonation coefficient increases. Thus, whenever Portland cement clinker is replaced with ACMs for the sake of reducing the GWP (Fig. 1), the inevitable consequence is a lower resistance against carbonation (Fig. 3).

If Figs. 1 and 3 are merged, the schematic relationship displayed in Fig. 4 is obtained. This fundamental relationship, dictated by nature, cannot be overruled. This is an important fact to recognize. In other words: Attempts to reduce the GWP of cement while maintaining a high carbonation resistance of the final concrete, are deemed to fail.

2.2. Goal conflict

Unfortunately, being faced with reduced carbonation resistance (Fig. 3) when reducing the GWP of concrete (Fig. 1) presents a ubiquitous dilemma in science and engineering. The reason for this is that a reduction in alkalinity is generally perceived as a durability problem, because the prevailing doctrine assumes that reduced alkalinity leads to corrosion of the embedded reinforcing steel. This doctrine is deeply rooted in text books, lectures, codes and design rules, standardized test methods, durability indicators, etc. [24–26]. Educational materials generally include the basic information that steel in alkaline environments is passive, and that passivity may get lost upon carbonation of the concrete. While this is correct, it does not necessarily mean that technically relevant steel corrosion occurs upon loss of passivity. In fact, a large number of cases have been documented where corrosion of steel in carbonated concrete was negligible [27].

Nevertheless, this underlying and highly conservative paradigm, namely that alkalinity lower than what can be found in uncarbonated, traditional Portland cement concrete leads to corrosion, dominates science and engineering. This paradigm widely serves as motivation for research proposals in the area of studying the carbonation behavior of cementitious materials.
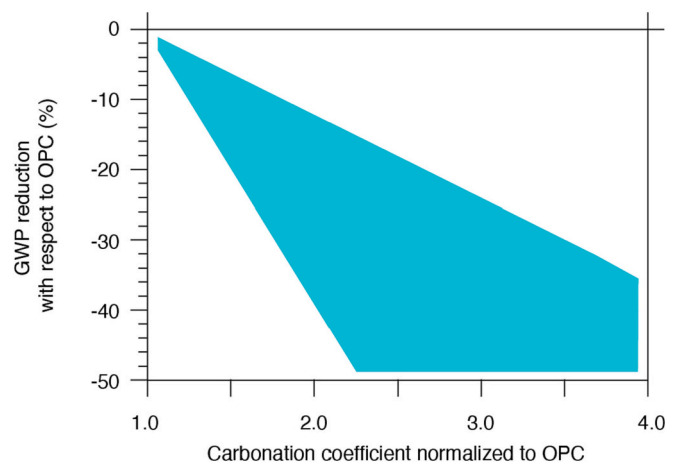
Fig. 4. Relationship between global warming potential (GWP) and carbonation coefficient, based on the information displayed in Figs. 1 and 3.

International durability design codes [26,28] are generally conceived such that the carbonation depth does not reach the reinforcement during the planned service life (or only in a very late stage). The concept of avoiding corrosion damage consists of an interplay between ensuring sufficient reinforcement cover and ensuring sufficient resistance of the cover concrete against carbonation. As previously mentioned, this presents a goal conflict between ensuring durability (with the current paradigm) and reducing GHG emissions. Currently, the dominance of the paradigm that may be summarized as "carbonation = corrosion" leads to an unequal treatment of cements, with modern low-emission cements being disadvantaged compared to Portland cement.

This can be illustrated by various country-specific examples. In the national annexes of the European standards, for instance, which generally follow a prescriptive design approach, different countries impose stricter requirements for low-clinker binders compared to traditional systems. UK, Spain, and Portugal stipulate requirements for higher cover depth and/or lower w/b ratios for binders with lower clinker content than for traditional systems. Germany even excludes specific low-clinker binders DIN 1045-2. For performance-based design
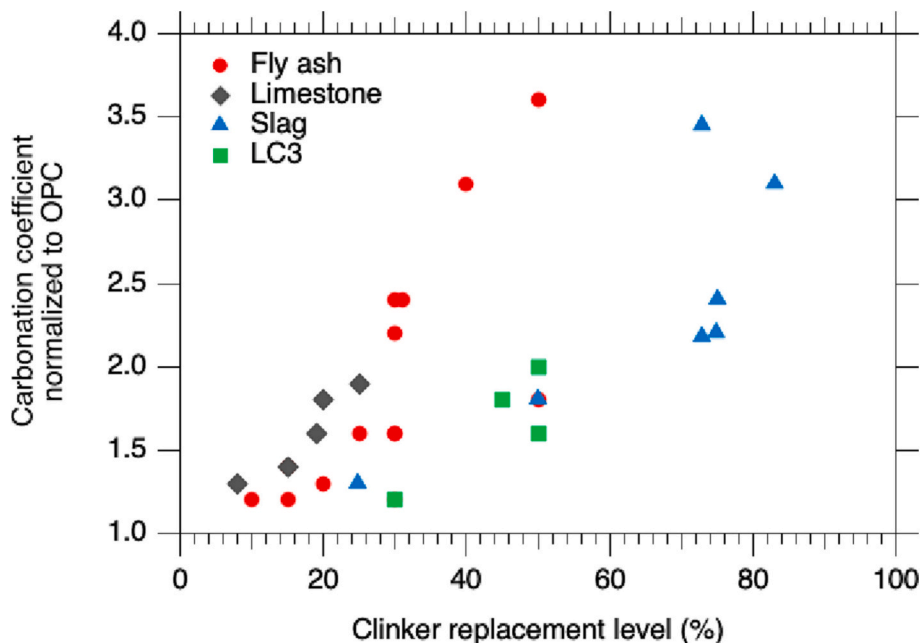
Fig. 3. b) Effect of clinker replacement on the resistance against carbonation. Data from [11,17–23]. OPC = ordinary Portland cement.

approaches, such as for instance in the Swiss standard, threshold values for the "carbonation resistance" (Annex I of the Swiss standard SIA 262/1) are defined, which are often difficult to satisfy with low-carbon binders. It is exactly the above-mentioned prevailing paradigm that here presents a barrier preventing the potential of low-emission cements and concretes from being fully exploited.

This goal conflict can only be overcome, if the current view of considering durability merely as a question of carbonation resistance, is expanded to towards an approach that also considers the stage in the service life of a structure after carbonation reaches the steel. For this, corrosion processes have to be considered.

3. Scientific progress to overcome the conflict of goals

3.1. The importance of studying corrosion – concrete's Achilles' heel

At high pH, steel is passive [29]. The alkalinity of traditional concrete thus is an important reason for protection steel against corrosion in concrete, and for reinforced concrete being a generally very durable construction material [30]. Thus, the loss of alkalinity means the loss of *one* layer of protection against corrosion. Nevertheless, it is well documented from practical experience that the reduction of alkalinity due to carbonation down to pH values shown in Fig. 2 does not necessarily lead to significant corrosion of the steel in concrete [27]. Empirical observations and anecdotal evidence [31] as well as scientific literature [32–38] suggested that the moisture of the concrete is a major influencing factor controlling corrosion in carbonated concrete. More specifically, various authors reported that carbonated reinforced concrete and mortar specimens conditioned at different moisture states showed increasing corrosion rates of the embedded steel with increasing moisture condition [32,35,38]. In a recent study [39], the penetration of capillary water uptake in a carbonated mortar sample was monitored by means of neutron radiography, while the corrosion state of an embedded steel electrode was simultaneously monitored with electrochemical techniques. The results confirmed that the instantaneous rate of corrosion of the (depassivated) steel dramatically rose from 0.16 um/y, which can be considered negligible, in the initially dry state to over 30 um/y exactly in the moment when the water front reached the steel. In summary, based on the state-of-the-art, the circumstance that carbonation alone does not lead to corrosion, but that a certain moisture content must be achieved, can be considered well-established. This knowledge, especially the "proof of concept" from the documented cases in practice [27], clearly presents an opportunity to escape the "carbonation dilemma". The author's vision is to establish a new engineering approach that tolerates reduced alkalinity (thus facilitating increasing levels of clinker substitution (Fig. 3)), while controlling corrosion.

However, this vision cannot be realized merely on the basis of qualitative relationships and empirical evidence. Instead, rigorous scientific understanding is needed to devise mechanism-based models to forecast the performance of low-emission-reinforced-concrete structures. The next sections review progress in this area, especially related to the fundamental understanding of steel corrosion and the coupled processes occurring in the cementitious matrix surrounding the steel.

3.2. Steel corrosion mechanism

A considerable portion of the scientific literature on steel corrosion in concrete has pursued a phenomenological approach. This means that authors attempted to establish relationships between different parameters – such as cement type, concrete mix proportions (w/b ratio), concrete moisture content, or exposure conditions – and a parameter reflecting the corrosion state or corrosion-related damage of the concrete. The latter parameters generally are steel weight loss measurements or electrochemical data, such as potential or corrosion rate measurements, or observations of when concrete surface cracking due to internal steel corrosion occurs. As is apparent from the literature [37]

the focus of many studies traditionally was on the effect of different ACMs on the corrosion rate, where often electrochemical techniques were used. Such studies, without doubt, provided valuable knowledge about various relationships and gave insight into the controlling factors. "Macroscopic" or "bulk" properties such as the concrete electrical resistivity [38,40–43], the concrete moisture content [32,43,44], the pore solution pH [42], or the concrete's oxygen permeability [45] have been hypothesized to play major roles (or negligible roles).

In recent years, scientific techniques became available that allowed tackling the problem from a more fundamental perspective. Relevant examples of advances in such areas will be discussed below. This will be done using a framework that illustrates the complexity and multidisciplinary nature of the processes occurring at the steel-concrete interface (SCI), which ultimately lead to what is known as "corrosion". Fig. 5 shows a schematic illustration of the SCI (generally assumed to be of the order of 10-100 micrometers) and the relevant processes within the SCI and in the adjacent porous bulk matrix. Release of ferrous ions in the electrochemical iron dissolution step (a) is inherently coupled to reactive mass-transfer in the electrolyte, present within the porous cementitious medium. This reactive mass-transfer includes the transport of species (diffusion, advection, migration, (b)) as well as chemical and electrochemical reactions (c) and potentially physical interaction (d) with the cementitious phases. Finally, moisture transport and retention in the cementitious pore system (e) is an important process, as this governs the amount and location of electrolyte present, that is, the phase in which the processes mentioned above can occur.

3.2.1. Electrochemical iron dissolution

While electrochemical theory and corrosion kinetics have been well established for decades for metals in bulk electrolytes, the situation of steel in a porous medium requires additional considerations. A concept has recently been proposed [35,36], taking into account the influences related to the presence of the porous medium on the electrochemical iron dissolution kinetics. The key idea is that the presence of the porous medium has a twofold influence. First, it controls the area fraction of the metal which can potentially be "electrochemically active". Portions of the metal surface in contact with solid phases (shielded) or in contact with gas phase (in unsaturated concrete) are considered to not significantly take part in the electrochemical processes. Instead, all relevant metal dissolution occurs at the "electrochemically active area" fraction. This fraction depends on both the pore size distribution of the solid matrix and the moisture condition [35]. Second, the pore structure and moisture condition affect the reactive mass transfer (see next section) in the solid matrix. The extent to which these reactive transport processes are feasible, in combination with the rate of iron ions release, impacts the ferrous ion concentration at the metal surface [46]. This concentration in turn controls the kinetics of the anodic iron dissolution reaction [35,36]. Thus, to fundamentally understand corrosion of steel in carbonated concrete, the reactive mass-transfer processes need to be considered in detail.

3.2.2. Reactive mass-transfer

As mentioned above, reactive mass-transfer includes the diffusion, migration, and possibly advection of species and considers (electro-) chemical reactions as well as physical interaction with the cementitious phases. While the governing transport processes – diffusion and migration – have been well covered in the literature [47,48], taking into account the "reaction part" of reactive mass-transfer still presents a challenge. Various authors have presented numerical implementations of coupled transport and chemical reaction modelling schemes [49–52]. However, several aspects have not been fully covered so far. This will be briefly discussed below.

First of all, generally thermodynamic equilibria are assumed to establish simultaneously to the transport process [49–52]. However, since the transport processes are in kinetic competition with the reactions, reaction processes may in reality not fully develop, while this is
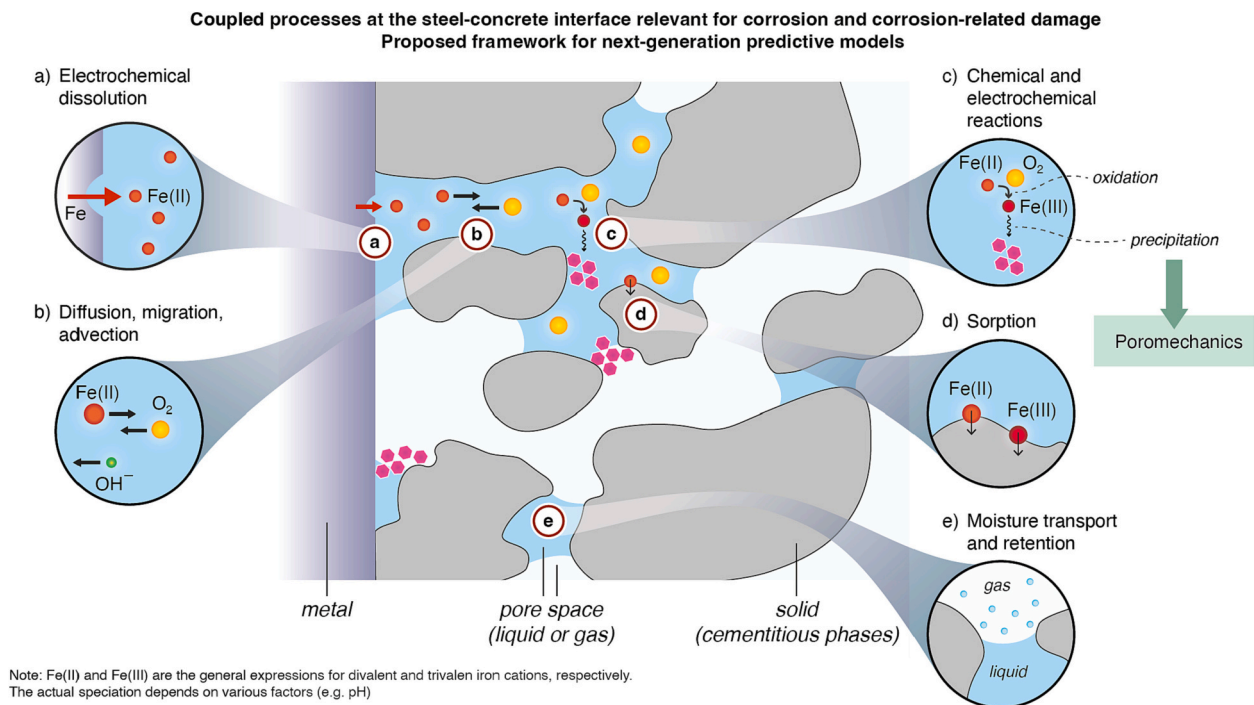
Fig. 5. Schematic illustration of the fundamental processes occurring at the steel-concrete interface (SCI), ultimately relevant for corrosion and corrosion-related damage of the concrete.

assumed to happen within a time step of the operator splitting approaches generally implemented in numerical simulations. This aspect is of particular relevance when considering reactive transport of iron species, where considerable complexity arises. As described by Furcas et al. [53], the ferrous species can potentially undergo a wide range of reactions, including the oxidation to ferric species and different hydration reactions, potentially leading to the precipitation of solid phases, which, later on, may undergo transformations over long time scales until the thermodynamically stable phase is finally reached. While data on the thermodynamics, that is, solubility and speciation, of iron in aqueous solutions representative for cementitious systems is available (and has recently been compiled in [54]), less is known about the kinetics of various of these reactions. Mundra et al. recently shed light on the oxidation kinetics of ferrous to ferric species in cementitious environments [55, 56], but further research is needed to provide the data needed to consider these reactions adequately in reactive mass-transfer modelling.

Finally, it should be mentioned that iron species can interact with cementitious phases. Recent work has provided insight in to the sorption of Fe(II) [57] and Fe(III) [58] into calcium silicate hydrates. From these studies, it became apparent that sorption effects are not negligible and should thus be taken into account.

3.2.3. Moisture in concrete

As mentioned above, the presence of moisture at the SCI is among the most important parameters for controlling corrosion of steel in carbonated concrete. Therefore, reliable methods and models to measure and predict the amount as well as the distribution of water in concrete are absolutely indispensable for ensuring the durability of reinforced concrete, especially for the cases in which the level of alkalinity is lower than in traditional Portland cement based. Despite the critical role of moisture in concrete, however, research has paid only moderate attention to this area in recent decades.

The relationship between moisture and concrete is complex and still not fully understood, because of i) the fact that cementitious phases are not inert towards water, ii) the complex pore structure of concrete, and iii) the numerous interrelated mechanisms playing a role, including

diffusion, capillary transport, adsorption/desorption, evaporation and condensation. Especially for long-term predictions, the anomalous nature [59] of water transport in concrete presents a major challenge. This particular aspect has received increasing attention over the last years, also thanks to the rise of investigative techniques such as Nuclear Magnetic Resonance (NMR) techniques [60–66]. Such studies have revealed changes in pore size distribution of cementitious phases upon wetting and drying [63–66], vividly described as "collapse of C—S—H interlayer pore spaces" during drying a "expansion of C—S—H gel" during contact with water in Ref. [64]. Other characterization techniques, including XRD, TG-DTA and water vapor sorption isotherms, led so similar observations [67]. Such changes in pore structure, however, do not occur instantaneously, but have been reported to show an exponential decay type of behavior [65,66], likely slow with respect to the capillary transport of water. This feature has recently been implemented in moisture transport modelling for concrete [68,69], which appeared as a promising approach to enhance the predictive power of the models. Other aspects, hypothesized to contribute to the anomalous moisture transport properties of cementitious materials, have also been integrated in numerical models. For instance, the complex pore structure of cementitious media, with features ranging from the nm to the mm scale, may play a role, namely that the transport in different ranges of pore sizes may happen on different time scales. Accordingly, the introduction of concepts such dual porosity [70] or dual permeability [69] has revealed a potential for the improvement of moisture transport models.

Finally, different authors have drawn the attention to the importance of the moisture exposure conditions for the prediction of moisture in concrete, and illustrated the significance of knowledge of the moisture exposure conditions, e.g. time-resolved heterological information [71], or the boundary conditions implemented in a numerical model [72].

3.2.4. Microstructural characterization at the SCI

As has been discussed above, the microstructure, especially the pore structure, of the cementitious matrix surrounding the steel is highly relevant for various aspects related to the steel corrosion process. These aspects include the quantification of the amount of electrolyte being

available at the SCI and mass transport processes. A recent RILEM technical committee report presented a review of experimental techniques to study the micro- and pore structure at the SCI [73]. Techniques that have increasingly been used for the characterization of the microstructure at the SCI are X-ray computed micro- (and to a lesser extent nano-) tomography [74–77]. More recently, neutron has been explored as a complementary imaging modality, for combined X-ray and neutron imaging techniques [78,79]. Such studies, gave insight into microstructural features (pores, voids), but also the distribution of corrosion products in the cementitious matrix. Another promising technique that has recently been applied to obtain information on the SCI the pore scale is focused ion beam - scanning electron microscopy (fib-sem) [73].

3.3. Next generation models for corrosion of steel in carbonated concrete

In engineering, what ultimately matters is whether or not corrosion of steel in carbonated concrete leads to appreciable and relevant damage at the level of the structure. Thus, to assess to what extent related possible limit states (cracking of the concrete cover, loss of bond steel-concrete, loss of steel sectional area) may be exceeded within the design service life, reliable models to forecast these processes are needed. In recognition of this, numerous models have been proposed to predict concrete cover cracking resulting from internal corrosion. A literature review [80] about such models, however, revealed the limited predictive power, which can be traced back to the general empirical nature of such models.

For reliable and generic predictive models to describe the corrosion-related processes that lead to damage at the level of a structure, all the aspects described in Section 3.2 need to be considered. Such fundamental and mechanism-based models, implementing the processes shown in Fig. 4, would allow describing the rate at which corrosion occurs as well as the precipitation of corrosion products within the pore space. Finally, such models need to be coupled with mechanical models to forecast the cracking of the concrete due to precipitation of corrosion products in the pore system. An example of a recent concept in this regard was presented in [81], where a poro-mechanical, multi-scale approach has been implemented, considering aspects such as release of ferrous ions at the steel, ion transport, chemical and electrochemical reactions (including kinetic laws for the Fe(II) to Fe(III) oxidation), poro-mechanical aspects taking into account the wide range of pore sizes encountered in concrete, and cracking of the concrete. It is believed that such approaches will form the basis for next generation models to forecast the corrosion performance of carbonated reinforced concrete.

4. Conclusions and research needs

A review of literature data on both the global warming potential (GWP) and the carbonation coefficient of various types of concrete confirmed what is expected from theoretical considerations: The most efficient approach to reduce the GWP of concrete, that is, the replacement of the clinker with alternative cementitious materials, inevitably reduces the resistance against carbonation.

The related loss of alkalinity means the removal of a protection layer that effectively guards against the corrosion of steel in concrete. While this increases the risk for corrosion, both practical experience and scientific knowledge show that it is still possible to keep corrosion in check. This knowledge presents an opportunity, perhaps the only one, to escape from the "carbonation dilemma".

To achieve this, substantial progress is needed in terms of the scientific understanding of all the coupled processes relevant for corrosion and corrosion-related damage. A framework considering the relevant processes has been outlined in this contribution, which may lay the ground for developing next-generation models to forecast the corrosion performance. Areas where particular efforts are needed include:

- reliable methods and models to measure and predict the amount as well as the distribution of water in concrete.
- quantitative data and fundamental understanding about the competitive, coupled chemical, electrochemical, and physical processes for iron species in environments representative for (carbonated) cementitious systems; relevant aspects include iron speciation, phase transformations, chemical reactions, electrochemical reactions, and sorption by cementitious phases.
- information on the microstructure, pore structure, and phase assemblage at the steel-concrete interface in carbonated cementitious systems.

Progress in these areas will allow devising the tools needed in engineering (test methods, models, etc.) and facilitate a paradigm change towards a paradigm that resolves the current goal conflict faced when attempting to simultaneously ensure durability and environmental-friendliness. This paradigm change will not only enable broader adoption of low-emission binders, resulting in more eco-friendly and long-term sustainable construction practices, but also create opportunities to activate the carbon sequestration potential of existing concrete structures and concrete demolition waste. Future carbon capture strategies may include innovative approaches such as bio-inspired processes to enhance carbon-storage in cementitious media, e.g. the enzymatic approach presented at ICCC 2023 by Chen et al. [82].

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ueli Angst reports financial support was provided by European Research Council.

Data availability

Data will be made available on request.

Acknowledgements

References

[1] Development of an holistic approach to ensure the durability of new concrete construction, Research Report Project 38/13/21 (cc 1031), British Cement Association, Crowthorne, UK, 1997.

[2] S.A. Miller, A. Horvath, P.J.M. Monteiro, Readily implementable techniques can cut annual CO2 emissions from the production of concrete by over 20%, Environ. Res. Lett. 11 (2016).

[3] K.L. Scrivener, V.M. John, E.M. Gartner, Eco-efficient Cements: Potential Economically Viable Solutions for a Low-CO2 Cement-based Materials Industry, United Nations Environment Programme, Paris, France, 2017.

[4] G. Habert, S.A. Miller, V.M. John, J.L. Provis, A. Favier, A. Horvath, K.L. Scrivener, Environmental impacts and decarbonization strategies in the cement and concrete industries, Nat. Rev. Earth Environ. 1 (2020) 559–573.

[5] M. Haist, K. Bergmeister, M. Curbach, P. Forman, G. Gaganelis, J. Gerlach, P. Mark, J. Moffatt, C. Müller, H.S. Müller, J. Reiners, C. Scope, M. Tietze, K. Voit, VII: Nachhaltig konstruiere und bauen mit Beton, in: K. Bergmeister, F. Fingerloos, J.-D. Wörner (Eds.), Beton-Kalender, Ernst & Sohn, Berlin, Germany, 2022, p. 421.

[6] R. Gettu, A. Patel, V. Rathi, S. Prakasan, A.S. Basavaraj, S. Palaniappan, S. Maity, Influence of supplementary cementitious materials on the sustainability parameters of cements and concretes in the Indian context, Mater. Struct. 52 (2019).

[7] R. Kurda, J.D. Silvestre, J. de Brito, Life cycle assessment of concrete made with high volume of recycled concrete aggregates and fly ash, Resour. Conserv. Recycl. 139 (2018) 407–417.

[8] K. Ram, D. Londono-Zuluaga, M. Serdar, K. Scrivener, The effect of cement reduction and substitution on the mechanical and durability properties of concrete, in: M.G. Alexander, H. Beushausen, F. Dehn, J. Ndawula, P. Moyo (Eds.) International Conference on Concrete Repair, Rehabilitation and Retrofitting

(ICCRRR 2022) MATEC Web of Conferences, Cape Town, South Africa, 2022, p. 02008.

[9] Global Cement and Concrete Association. https://gccassociation.org/concretefuture/.

[10] L.J. Parrott, A review of carbonation in reinforced concrete, Cement and Concrete Association, UK, 1987.

[11] S. von Greve-Dierfeld, B. Lothenbach, A. Vollpracht, B. Wu, B. Huet, C. Andrade, C. Medina, C. Thiel, E. Gruyaert, H. Vanoutrive, I.F.S.d. Bosque, I. Ignjatovic, J. Elsen, J.L. Provis, K. Scrivener, K.-C. Thienel, K. Sideris, M. Zajac, N. Alderete, Ö. Cizer, P.V.d. Heede, R.D. Hooton, S. Kamali-Bernard, S.A. Bernal, Z. Zhao, Z. Shi, N.D. Belie, Understanding the carbonation of concrete with supplementary cementitious materials – a critical review by RILEM TC 281-CCC, Mater. Struct. 53 (2020) 136.

[12] Z.G. Shi, B. Lothenbach, M.R. Geiker, J. Kaufmann, A. Leemann, S. Ferreiro, J. Skibsted, Experimental studies and thermodynamic modeling of the carbonation of Portland cement, metakaolin and limestone mortars, Cem. Concr. Res. 88 (2016) 60–72.

[13] T. Matschei, F.P. Glasser, Interactions between Portland cement and carbon dioxide, in: Proceedings of the ICCC Conference, 2007.

[14] Y. Femenias, U. Angst, B. Elsener, Monitoring pH in corrosion engineering by means of thermally-produced iridium oxide electrodes, Mater. Corros. 69 (2017) 76–88.

[15] Y.S. Femenias, U. Angst, B. Elsener, PH-monitoring in mortar with thermally-oxidized iridium electrodes, RILEM Techn. Lett. 2 (2017) 59–66.

[16] F. Hunkeler, S.v. Greve-Dierfeld, Karbonatisierung von Beton und Korrosionsgeschwindigkeit der Bewehrung im karbonatisierten Beton, in: ASTRA/VSS Report no. 696, Berne, Switzerland, 2019.

[17] E. Rozière, A. Loukili, F. Cussigh, A performance based approach for durability of concrete exposed to carbonation, Constr. Build. Mater. 23 (2009) 190–199.

[18] A. Younsi, P. Turcry, E. Rozière, A. Aït-Mokhtar, A. Loukili, Performance-based design and carbonation of concrete with high fly ash content, Cem. Concr. Compos. 33 (2011) 993–1000.

[19] P. Zhang, Q. Li, Effect of fly ash on durability of high performance concrete composites, Res. J. Appl. Sci. Eng. Technol. 1 (2013) 7–12.

[20] R. Gettu, M. Santhanam, R.G. Pillai, Y. Dhandapani, S. T., S. Rengaraju, F.S. M., S. Prakasan, S. Rathnarajan, A.S. Basavaraj, Recent research on limestone calcined clay cement (LC3) at Iit Madras, in: Conference in Honor of Centennial of Laboratory of Construction Materials and 60th Birthday of Prof. Karen Scrivener, Ecole Polytechnique Federale de Lausanne, Switzerland, Lausanne, Switzerland, 2018.

[21] M.S.H. Khan, Q.D. Nguyen, A. Castel, Carbonation of limestone calcined clay cement concrete, in: F. Martirena, A. Favier, K. Scrivener (Eds.), Calcined Clays for Sustainable Concrete, Springer, 2018, pp. 238–243.

[22] A. Leemann, H. Pahlke, R. Loser, F. Winnefeld, Carbonation resistance of mortar produced with alternative cements, Mater. Struct. 51 (2018).

[23] S. Steiner, T. Proske, F. Winnefeld, B. Lothenbach, Effect of limestone fillers on CO2 and water vapour diffusion in carbonated concrete, Cement 8 (2022), 100027.

[24] L. Bertolini, B. Elsener, P. Pedeferri, E. Redaelli, R. Polder, Corrosion of Steel in Concrete: Prevention, Diagnosis, Repair, 2nd edition, WILEY VCH, Weinheim, 2013.

[25] J.P. Broomfield, Corrosion of Steel in Concrete, Chapman & Hall, 1997.

[26] Model code for service life design, fib bulletin No. 34, Fédération internationale du béton, Lausanne, 2006.

[27] U. Angst, F. Moro, M. Geiker, S. Kessler, H. Beushausen, C. Andrade, J. Lahdensivu, A. Köliö, K.-i. Imamoto, S. von Greve-Dierfeld, M. Serdar, Corrosion of steel in carbonated concrete: mechanisms, practical experience, and research priorities - a critical review by RILEM TC 281-CCC, RILEM Techn. Lett., 5 (2020) 85–100.

[28] European Standard EN 206:2013 + A2:2021, in: E.C.f. Standardization (Ed.), Concrete - Specification, Performance, Production and Conformity, European Committee for Standardization, 2021.

[29] M. Pourbaix, Atlas d'équilibres électrochimiques, Centre Belge d'Etude de la Corrosion CEBELCOR/Gauthier-Villars & Cie, Paris, 1963.

[30] C.L. Page, Mechanism of corrosion protection in reinforced concrete marine structures, Nature 258 (1975) 514–515.

[31] M. Hamada, Neutralization (carbonation) of concrete and corrosion of reinforcing steel, in: 5th Int. Symp. on Cement Chemistry, The Cement Association of Japan, Tokyo, 1968, pp. 343–369.

[32] J.A. Gonzalez, S. Algaba, C. Andrade, Corrosion of reinforcing bars in carbonated concrete, Br. Corros. J. 15 (1980) 135–139.

[33] G.K. Glass, C.L. Page, N.R. Short, Factors affecting the corrosion rate of steel in carbonated mortars, Corros. Sci. 32 (1991) 1283–1294.

[34] R.K. Dhir, M.R. Jones, M.J. Mccarthy, Pulverized-fuel ash concrete - carbonation-induced reinforcement corrosion rates, Proc. Inst. Civil Eng. Struct. Build. 94 (1992) 335–342.

[35] M. Stefanoni, U.M. Angst, B. Elsener, Electrochemistry and capillary condensation theory reveal the mechanism of corrosion in dense porous media, Sci. Rep. 8 (2018) 7407.

[36] M. Stefanoni, U.M. Angst, B. Elsener, Kinetics of electrochemical dissolution of metals in porous media, Nat. Mater. 18 (2019) 942.

[37] M. Stefanoni, U. Angst, B. Elsener, Corrosion rate of carbon steel in carbonated concrete - A critical review, Cem. Concr. Res. 103 (2018) 35–48.

[38] C. Alonso, C. Andrade, J.A. González, Relation between resistivity and corrosion rate of reinforcements in carbonated mortar made with several cement types, Cem. Concr. Res. 8 (1988) 687–698.

[39] Z. Zhang, P. Trtik, F. Ren, T. Schmid, C.H. Dreimol, U. Angst, Dynamic effect of water penetration on steel corrosion in carbonated mortar: A neutron imaging, electrochemical, and modeling study, CEMENT 9 (2022), 100043.

[40] K. Hornbostel, C.K. Larsen, M.R. Geiker, Relationship between concrete resistivity and corrosion rate - a literature review, Cem. Concr. Compos. 39 (2013) 60–72.

[41] J. Gulikers, Theoretical considerations on the supposed linear relationship between concrete resistivity and corrosion rate of steel reinforcement, Mater. Corros. 56 (2005) 393–403.

[42] J.A. Gonzalez, C. Alonso, C. Andrade, Corrosion rate of reinforcements during accelerated carbonation of mortar made with different types of cement, in: A.P. Crane (Ed.), Corrosion of Reinforcement in Concrete Construction, Soc. of Chemical Industry, 1983.

[43] F. Lollini, E. Redaelli, Corrosion rate of carbon steel in carbonated concrete made with different supplementary cementitious materials, Corros. Eng. Sci. Technol. 56 (2021) 473–482.

[44] C. Andrade, R. Buják, Effects of some mineral additions to Portland cement on reinforcement corrosion, Cem. Concr. Res. 53 (2013) 59–67.

[45] B. Huet, V. L'hostis, G. Santarini, D. Feron, H. Idrissi, Steel corrosion in concrete: determinist modeling of cathodic reaction as saturation a function of water degree, Corros. Sci. 49 (2007) 1918–1932.

[46] M. Stefanoni, Z. Zhang, U. Angst, B. Elsener, The kinetic competition between transport and oxidation of ferrous ions governs precipitation of corrosion products in carbonated concrete, RILEM Techn. Lett. 3 (2018) 8–16.

[47] E. Samson, J. Marchand, Modeling the transport of ions in unsaturated cement-based materials, Comput. Struct. 85 (2007) 1740–1756.

[48] E. Samson, J. Marchand, J.J. Beaudoin, Describing ion diffusion mechanisms in cement-based materials using the homogenization technique, Cem. Concr. Res. 29 (1999) 1341–1345.

[49] Y. Hosokawa, K. Yamada, B. Johannesson, L.O. Nilsson, Development of a multi-species mass transport model for concrete with account to thermodynamic phase equilibriums, Mater. Struct. 44 (2011) 1577–1592.

[50] O.B. Isgor, W.J. Weiss, A nearly self-sufficient framework for modelling reactive-transport processes in concrete, Mater. Struct. 52 (2019).

[51] M.M. Jensen, B. Johannesson, M.R. Geiker, Framework for reactive mass transport: phase change modeling of concrete by a coupled mass transport and chemical equilibrium model, Comput. Mater. Sci. 92 (2014) 213–223.

[52] B. Johannesson, K. Yamada, L.O. Nilsson, Y. Hosokawa, Multi-species ionic diffusion in concrete with account to interaction between ions in the pore solution and the cement hydrates, Mater. Struct. 40 (2007) 651–665.

[53] F.E. Furcas, B. Lothenbach, O.B. Isgor, S. Mundra, Z. Zhang, U. Angst, Thermodynamic and kinetic considerations of corrosion product formation in cementitious media, in: H. Beushausen, J. Ndawula, M.G. Alexander, F. Dehn, P. Moyo (Eds.)6th International Conference on Concrete Repair, Rehabilitation and Retrofitting (ICCRRR 2022), MATEC Web of Conferences, Cape Town, South Africa, 2022.

[54] F.E. Furcas, B. Lothenbach, O.B. Isgor, S. Mundra, Z.D. Zhang, U.M. Angst, Solubility and speciation of iron in cementitious systems, Cem. Concr. Res. 151 (2022).

[55] S. Mundra, D. Kunz, J. Tits, E. Wieland, U. Angst, Stability of Fe2+ in cementitious media, in: H. Beushausen, J. Ndawula, M.G. Alexander, F. Dehn, P. Moyo (Eds.), 6th International Conference on Concrete Repair, Rehabilitation and Retrofitting (ICCRRR 2022), MATEC Web of Conferences, Cape Town, South Africa, 2022.

[56] S. Mundra, J. Tits, E. Wieland, U.M. Angst, Aerobic and anaerobic oxidation of ferrous ions in near-neutral solutions, Chemosphere 335 (2023), 138955, https://doi.org/10.1016/j.chemosphere.2023.138955.

[57] A. Mancini, E. Wieland, G. Geng, B. Lothenbach, B. Wehrli, R. Dähn, Fe(II) interaction with cement phases: method development, wet chemical studies and X-ray absorption spectroscopy, J. Colloid Interface Sci. 588 (2021) 692–704.

[58] A. Mancini, E. Wieland, G. Geng, R. Dähn, J. Skibsted, B. Wehrli, B. Lothenbach, Fe(III) uptake by calcium silicate hydrates, Appl. Geochem. 113 (2020), 104460.

[59] C. Hall, Anomalous diffusion in unsaturated flow: fact or fiction? Cem. Concr. Res. 37 (2007) 378–385.

[60] H. Justnes, I. Meland, J.O. Bjoergum, J. Krane, T. Skjetne, Nuclear magnetic resonance (NMR) —a powerful tool in cement and concrete research, Adv. Cem. Res. 3 (1990) 105–110.

[61] P.J. McDonald, V. Rodin, A. Valori, Characterisation of intra- and inter-C—S—H gel pore water in white cement based on an analysis of NMR signal amplitudes as a function of water content, Cem. Concr. Res. 40 (2010) 1656–1663.

[62] N. Fischer, R. Haerdtl, P.J. McDonald, Observation of the redistribution of nanoscale water filled porosity in cement based materials during wetting, Cem. Concr. Res. 68 (2015) 148–155.

[63] C. Zhou, F. Ren, Z. Wang, W. Chen, W. Wang, Why permeability to water is anomalously lower than that to many other fluids for cement-based material? Cem. Concr. Res. 100 (2017) 373–384.

[64] C. Zhou, F. Ren, Q. Zeng, L. Xiao, W. Wang, Pore-size resolved water vapor adsorption kinetics of white cement mortars as viewed from proton NMR relaxation, Cem. Concr. Res. 105 (2018) 31–43.

[65] P.J. McDonald, O. Istok, M. Janota, A.M. Gajewicz-Jaromin, D.A. Faux, Sorption, anomalous water transport and dynamic porosity in cement paste: a spatially localised 1H NMR relaxation study and a proposed mechanism, Cem. Concr. Res. 133 (2020), 106045.

[66] M. Janota, O. Istok, D.A. Faux, P.J. McDonald, Factors influencing the time dependence of porosity relaxation in cement during sorption: experimental results from spatially resolved NMR, Cement 8 (2022), 100028.

[67] M. Segawa, A. Aili, I. Maruyama, Comparison of shrinkage and mass change of hardened cement paste under gradual drying and rapid drying, CEMENT 10 (2022), 100047.

[68] C. Hall, Capillary imbibition in cement-based materials with time-dependent permeability, Cem. Concr. Res. 124 (2019), 105835.

[69] Z. Zhang, U. Angst, Modeling anomalous moisture transport in cement-based materials with kinetic permeability, Int. J. Mol. Sci. 21 (2020) 837.

[70] Z. Zhang, M. Thiery, V. Baroghel-Bouny, An equation of drying kinetics for cementitious materials, Dry. Technol. 36 (2018) 1446–1459.

[71] L.-O. Nilsson, Predicting moisture in field concrete - decisive parameters, Cement 11 (2023), 100052.

[72] Z.D. Zhang, M. Thiery, V. Baroghel-Bouny, Numerical modelling of moisture transfers with hysteresis within cementitious materials: verification and investigation of the effects of repeated wetting-drying boundary conditions, Cem. Concr. Res. 68 (2015) 10–23.

[73] H.S. Wong, U.M. Angst, M.R. Geiker, O.B. Isgor, B. Elsener, A. Michel, M.C. Alonso, M.J. Correia, J. Pacheco, J. Gulikers, Y.X. Zhao, M. Criado, M. Raupach, H. Sorensen, R. Francois, S. Mundra, M. Rasol, R. Polder, Methods for characterising the steel-concrete interface to enhance understanding of reinforcement corrosion: a critical review by RILEM TC 262-SCI, Mater. Struct. 55 (2022).

[74] A. Michel, B.J. Pease, M.R. Geiker, H. Stang, J.F. Olesen, Monitoring reinforcement corrosion and corrosion-induced cracking using non-destructive x-ray attenuation measurements, Cem. Concr. Res. 41 (2011) 1085–1094.

[75] A. Cesen, T. Kosec, A. Legat, Characterization of steel corrosion in mortar by various electrochemical and physical techniques, Corros. Sci. 75 (2013) 47–57.

[76] B.Q. Dong, G.H. Fang, Y.Q. Liu, P. Dong, J.C. Zhang, F. Xing, S.X. Hong, Monitoring reinforcement corrosion and corrosion-induced cracking by X-ray microcomputed tomography method, Cem. Concr. Res. 100 (2017) 311–321.

[77] E. Rossi, R. Polder, O. Copuroglu, T. Nijland, B. Savija, The influence of defects at the steel/concrete interface for chloride-induced pitting corrosion of naturally-deteriorated 20-years-old specimens studied through X-ray computed tomography, Constr. Build. Mater. 235 (2020).

[78] C. Boschmann Käthler, Chloride-induced Reinforcement Corrosion in Concrete: The Role of the Steel-concrete Interface and Implications for Engineering, Doctoral thesis ETH Nr. 26213, ETH Zurich, 2019.

[79] S. Robuschi, A. Tengattini, J. Dijkstra, I. Fernandez, K. Lundgren, A closer look at corrosion of steel reinforcement bars in concrete using 3D neutron and X-ray computed tomography, Cem. Concr. Res. 144 (2021).

[80] A. Jamali, U. Angst, B. Adey, B. Elsener, Modeling of corrosion-induced concrete cover cracking: a critical analysis, Constr. Build. Mater. 42 (2013) 225–237.

[81] M. Pundir, D. Kammer, U. Angst, Corrosion-induced concrete cracking – a poro-mechanical, multi-scale approach, in: H. Beushausen, J. Ndawula, M.G. Alexander, F. Dehn, P. Moyo (Eds.), 6th International Conference on Concrete Repair, Rehabilitation and Retrofitting (ICCRRR 2022), MATEC Web of Conferences, Cape Town, South Africa, 2022.

[82] X. Chen, Z. Zhang, U. Angst, Enzymatic carbon sequestration in cementitious materials, the 16th international congress on the chemistry of cement 2023 (ICCC2023), Bangkok, Thailand, 2023.