Beyond the chloride threshold concept for predicting corrosion of steel in concrete

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11 Abstract

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12 All existing models to forecast the corrosion performance of reinforced concrete structures exposed to chloride 13 environments are based on one common theoretical concept, namely a chloride threshold, as a sharply defined 14 trigger for corrosion, followed by a period of active corrosion. We critically review the resulting treatment of 15 corrosion initiation and propagation as two distinct, successive stages. We conclude that this concept presents a major barrier for developing reliable corrosion forecast models, and that a new approach is needed. In reality, 16 17 steel corrosion in concrete is a continuous process that is rarely separable into uncoupled, sequential phases. We 18 propose that the focus be placed on the quantification of the time- and space-variant corrosion rate from the 19 moment steel is placed in concrete until it reaches the end of the service life. To achieve this, a multi-scale and 20 multi-disciplinary approach is required to combine the scientific and practical contributions from material science, 21 corrosion science, cement/concrete research, and structural engineering.

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Introduction 22

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23 Concrete is the most widely manufactured material in the world by mass, and is responsible for about 6-10% of 24 the total anthropogenic greenhouse gases¹. The use of reinforced concrete will increase substantially in the coming 25 decades in order to satisfy the demands for the renewal and expansion of our built environment², thereby 26 dramatically intensifying the burden on the environment¹. Although modern, low-emission cementitious materials 27 offer opportunities to mitigate the increase in greenhouse gas emissions¹, long-term durability of reinforced 28 concrete structures remains key to achieving a sustainable infrastructure (Figure 1a). In the context of the 29 worldwide need to save natural and financial resources, it is more important than ever to extend the service life of 30 ageing structures while assuring their safety². To this end, combined service life predictions and life cycle analyses 31 (LCA) play an important role in assessing the total environmental impact of novel materials and in tackling the 32 challenge of ageing infrastructure^{3, 4}. In the absence of long-term experience with new low-emission cementitious 33 materials, service life predictions and LCA would benefit from integrating science-based models to describe the 34 exposure-dependent degradation and ageing of the materials. Such science-based models are also needed by 35 owners of reinforced concrete structures and engineers who design and manage them, to know when, and to what 36 extent, their structures will be deteriorating.

37 Among the various degradation mechanisms of reinforced concrete structures, chloride-induced corrosion of the 38 embedded steel is by far the most common and costly one⁵. The corrosion-related damage can lead to any 39 combination of different engineering limit states including reduction of steel cross section, loss of bond between 40 steel and concrete, and concrete cover cracking/delamination from expansive corrosion products, all of which 41 threaten the safety and serviceability of structures. Predictive models are needed to provide information on the 42 time and probability to reach a given engineering limit state⁶⁻⁸.



Fig. 1: Elements of the established approach of forecasting the life of a reinforced concrete structure. a, life cycle of a structure, showing the steps that most consume natural and financial resources and impact the environment through greenhouse gas emissions. b, schematic illustration of the traditional two-stage service life model to predict the operational life of a structure, c, conceptual approach at the basis of current models to forecast onset of corrosion, relying on corrosion threshold (CT). d, variability in CT reported in the literature over time (based on Refs. 20-22). e, variability from applying one CT test method to 88 samples taken from engineering structures and 27 samples made in the laboratory (based on here open access data base²⁵). In figures d and e, the width of the shaded areas indicates the normalized frequency of occurrence of the different values in the reviewed literature, and all data considered are for carbon steel in Portland cement concrete.

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43 Steel corrosion in concrete has been studied extensively in the past three decades. In the most recent decade alone, 44 over 5,000 scientific articles have been published on the subject9. Many journal publications, books, and 45 committee documents provide comprehensive reviews on the state-of-the-art and the latest progress made on the 46 topic¹⁰⁻²⁴. These reviews clearly indicate that the concept of the so-called "chloride threshold (CT)", also referred 47 to as "critical chloride content", is at the core of a vast number of these investigations, particularly those that focus on modeling chloride transport and chloride binding processes²⁵⁻³⁵, corrosion propagation^{10, 18, 23, 24, 36-41}, and 48 49 corrosion-induced damage42-51. Therefore, it is not the objective of this paper to provide another general review 50 on the subject. Instead, this paper critically focuses on the concept of a chloride threshold.

All current predictive models for chloride-induced corrosion of reinforced concrete structures rely on the notion of two distinct and successive stages, initiation and propagation (Figure 1b,c). The CT conceptually indicates the level of chloride in the concrete adjacent to the steel that initiates active corrosion, i.e., the start of the propagation stage, as opposed to negligibly slow iron dissolution that occurs when the steel is in passive state. As per Tuutti's⁵² definition, the initiation stage describes the period in which the aggressive chlorides penetrate the concrete cover, and the subsequent propagation stage is the period in which active corrosion occurs. The concept of CT is therefore closely tied to Tuutti's definition of service life.

58 While CT may originally have been hypothesized as a pragmatic engineering concept for the decoupled initiation-59 propagation modelling approach^{53, 54}, it has increasingly become a ubiquitously-accepted parameter that 50 dominates research and practice, with little attention to its scientific validity or practical applicability. Today, the 51 concept of CT is deeply rooted in both engineering and scientific communities, where it is generally considered 52 as "established wisdom" that is rarely questioned. It also serves as an *a priori* concept for research proposals, 53 publications, and international committee work.

It is the aim of this contribution to critically assess the decoupled initiation-propagation modelling approach and the CT concept which is needed for its implementation. We address the question of to what extent, and under which circumstances, the CT concept, as presently used, is an adequate tool for predictive modelling of chlorideinduced corrosion in structures under design or in-service. Alternative approaches to the formulation of the transition from passive to active corrosion behaviour are considered. It is proposed that an integration of the initiation and propagation stages of corrosion in predictive modelling is necessary, and research areas meriting intensified effort to accomplish this are identified.

71 Background and historical review of CT

72 The pH of the liquid contained in the pore system of concrete is typically above 12.5 and, more commonly, greater 73 than 13 due to the buffering effect of portlandite and the presence of alkali metal hydroxides^{55, 56}. It is well known that carbon steel in such an alkaline medium is passivated⁵⁷, and exhibits negligibly low corrosion rates, less than 74 75 0.1-1 µm/y (corresponding to a corrosion current density of ~0.01 - 0.1 µA/cm²)^{13,58}. In atmospherically exposed, 76 thus aerated, concrete structures, passivity is often associated with relatively noble electrochemical potentials of 77 the carbon steel, in the range of -100 to +200 mV vs. the saturated calomel electrode (SCE)^{13, 59}. The passive 78 behaviour of carbon steel in alkaline environments has enabled it to be used successfully as embedded 79 reinforcement in concrete, an ideal application that complemented the unprecedented advancements that humanity 80 experienced since the industrial revolution.

81 By the middle of the last century, it became evident, however, that loss of passivity with consequent active 82 corrosion did occur in many situations associated with the presence of chloride-containing salts (e.g., from seawater, de-icing chemicals, or chemical admixtures) 53, 54, 60. Early studies suggested that the chloride content 83 84 needs to exceed a threshold to initiate corrosion, although it was apparent that there is stochastic variability in this 85 threshold. For steel in an aqueous electrolyte, this threshold appeared to be around a chloride-to-hydroxyl ion ratio ([Cl⁻]/[OH⁻]) ranging from 0.5 to 1.0⁵³ but, in later reports, often simply cited as a value of 0.6. For steel embedded 86 87 in a cementitious matrix, the early studies suggested threshold chloride contents in concrete around 0.4% total chloride by cement mass^{54, 61}. The choice of expressing CT as a [Cl⁻]/[OH⁻], or as a chloride/cement mass (the 88 89 main source of OH-) ratio, effectively assumed that the onset of active corrosion in concrete could be viewed 90 primarily as the outcome of a competitive process between aggressive and inhibiting ions. Thus, such CT 91 expressions would be normalized indices that permitted treating a variety of cases - such as concretes with 92 different cement contents - via a single CT value.



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CT variability as a fundamental problem of the CT concept 93

94 Despite that definitional normalization, the CT values reported in the literature for carbon steel reinforcement in concrete have shown great variability⁶²⁻⁶⁵, ranging over more than two orders of magnitude. Sources of variability 95 96 may be broadly divided into (i) physicochemical factors that exist in addition to the relative amount of chloride 97 and hydroxyl ions, (ii) choice of experimental methodology used to determine CT19, and (iii) inherent stochastic 98 processes in passivity breakdown and pitting corrosion progression phenomena²¹. These factors are addressed in 99 detail in the next section but suffice it to note here that when reinforcing steel is embedded in concrete, the 100 markedly increased degree of heterogeneity at the steel surface amplifies the stochastic behaviour^{20, 66}. It is, thus, 101 not surprising that, as the volume of research has increased with time, the range of reported values of CT as 102 defined above increased as well. For example, Figure 1d shows the reported range (i.e., scatter) of CT for plain 103 carbon reinforcing steel in a matrix made of Portland cement binder, which is the most traditional, and perhaps 104 the simplest, reinforced concrete system. In the 1970s the state-of-the-art knowledge suggested that active 105 corrosion would start above chloride contents ranging from 0.1 to 1.5 % total chloride by cement weight. By the 106 2000s the range had more than doubled. Recent work showed that CT variability could not be significantly reduced 107 by eliminating some of the variability related to experimental methodology, as is apparent from Figure 1e. These 108 data were collected⁶⁷ by rigorously applying one single test method to more than 100 samples of carbon steel in 109 Portland cement concrete from a group of structures. The results still spanned a range comparable to the range of 110 CT reported in the numerous different studies reviewed in⁶²⁻⁶⁴.

111 The variability in CT values, as they are defined and measured, poses a difficult obstacle to developing reliable 112 corrosion performance forecasts for existing, as well as newly designed, structures. One solution would be to view 113 CT as a conservative statistical limit. Choosing a reliability-targeted lower bound for CT based on the complete 114 state-of-the-art data shown in Figures 1d and e, however, could lead to the adoption of very low CT values that 115 are generally perceived as unrealistically conservative and in disagreement with anecdotal engineering experience. 116 Furthermore, overly conservative lower bounds inhibit sustainable design, because the conservative approach increases the consumption of resources, caused by the need for greater cover depths, cement contents in the 117 118 concrete, etc.

119 An alternative approach is to treat the problem stochastically, e.g., by means of probabilistic modeling⁶. However, 120 in such models, the large variability in CT (Figure 1d) translates into an even larger uncertainty in terms of 121 estimated service life⁶⁸. Facing this problem, a procedural – somewhat arbitrary – approach has been to narrow the reported range of CT in the literature by excluding selected published CT values. An example is the *fib* model 122 123 code for service life design⁶ in which CT is based only on one single (laboratory) study⁶⁹. It is difficult to justify 124 why exactly this study is the one to be applied in engineering practice while the majority of the body of knowledge 125 is excluded. If attempts were made to apply rigorous criteria in excluding literature studies, one would inevitably face the conflict of either excluding too much of the literature data (thus making it difficult to justify the harsh 126 127 selection process) or leaving a scatter of CT data that is still too high for practical engineering purposes.

128 Thus, the CT body of knowledge accumulated over the last decades (Figure 1d,e) and applied without 129 qualification offers a poor basis for accurate engineering forecasts. The variability apparent from Figures 1d and 130 e hardly allows for an improvement of engineering practice other than, for example, in the comparative 131 examination of the effect of design alternatives. The usefulness of performing further studies measuring CT as a 132 function of different material combinations must then be severely questioned.

Factors influencing CT 133

134 The extensive research carried out over the last decades, has resulted in some of the factors influencing the 135 variability of CT being well understood, while others still need dedicated scientific studies. Mainstream research 136 was generally centered on investigating the effect of material properties of concrete and steel and has shown that 137 the alkalinity of the liquid phase in the concrete pore system^{53, 70}, in particular the local pH buffer capacity at the steel-concrete interface55, plays an important role. Another important feature related to the concrete is the range 138 of interfacial macroscopic voids such as entrapped air voids^{71, 72} or bleeding and settlement zones⁷³. Regarding 139 140 the contribution of the reinforcing steel to the CT variability, it is well documented that surface properties of the 141 steel, including the presence of pre-existing rust layers or mill scale, as well as differences in composition and 142 microstructure, have a significant influence74-79 because they affect the mechanism of chloride-induced corrosion 143 initiation⁸⁰. Numerous studies addressed the influence of concrete mix design, such as the cement type and content and the water/cement ratio^{69, 81, 82}. However, a critical assessment of the relative importance of different factors 144



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for chloride-induced corrosion initiation in concrete, concluded that these concrete-related features have a
 comparatively small effect²⁰. Instead, that review found that the most dominant parameters affecting initiation of
 corrosion, besides the metallurgy and surface conditions of the reinforcing steel, were the content and spatial
 distribution of moisture in interfacial voids in the concrete.

149 This understanding transfers the focus from considering CT as a function of material properties (steel, concrete) 150 towards the actual condition of reinforced concrete in a structure. Here, the moisture condition plays an important 151 role. For instance, changing the moisture condition from 90% relative humidity to capillary saturation was found to affect CT approximately by a factor of 10 (Figure 2a)83. Other studies have also highlighted the role of moisture 152 153 in corrosion of steel in concrete^{84, 85}. Further experimental support for the importance of the moisture state is seen 154 in the findings surrounding the role of interfacial voids in different moisture states. In concrete close to saturation, 155 it was generally found that corrosion tends to initiate adjacent to interfacial voids and that these voids decrease 156 CT^{71, 72, 86}. In concrete below saturation, on the other hand, interfacial voids were very rarely preferential locations 157 for corrosion initiation^{87, 88}. Another aspect related to the moisture condition was that wetting/drying exposure 158 was consistently found to create more favourable conditions for corrosion initiation and to decrease the CT compared to constant moisture states (Figure 2b)89-91 159

160 It should be noted that the effect of the moisture state is not necessarily due to a decrease in steel potential resulting 161 from O2 starvation at the steel-concrete interface. For instance, the steel potentials prior to corrosion initiation of the experiments shown in Figure 2b were very similar for both tested exposure conditions. The pore structure of 162 163 the concrete will only be completely saturated with water^{92, 93} under extreme long-term immersion. Thus, in the 164 absence of oxygen scavenging processes such as corrosion, sufficient oxygen will generally be present in 165 reinforced concrete prior to corrosion initiation to maintain relatively noble potentials of passive steel in many 166 situations relevant in practice, such as splash water zones in marine and road salt exposure. However, under some 167 conditions, such as long-term submersion, a decrease in oxygen concentration may shift the (passive) steel potential to more cathodic values¹³ with a corresponding increase in the CT^{94, 95} (Figure 2c). This phenomenon 168 169 can play an important role in both corrosion initiation and propagation due to mutual polarization of various zones 170 in the steel assembly94.

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171 In addition to the effects of material properties and exposure conditions reviewed above, CT has also been found 172 to depend on the size of the studied specimen (Figure 2d). This size effect, which contributes to the variability 173 associated with experimental method and stochastic nature of the depassivation process was already recognized 174 by Evans more than half a century ago⁹⁶. Later, the size effect was quantitatively studied for chloride-induced corrosion of carbon steel in alkaline solution⁹⁷ and in concrete⁸⁷. It was shown that with increasing specimen size 175 176 (e.g., rebar length) under test, both CT and its variability decrease. This can be explained by the circumstance that 177 chloride-induced corrosion initiation is a localized phenomenon98, occurring at the "weakest spot" within the 178 surface of an exposed metal sample. If experimental CT values are to be used in service life modelling, the size 179 of the specimens on which CT was determined needs to be considered, because results from small scale laboratory 180 tests are too optimistic. Another important consequence of the size effect is that the usually small dimensions of 181 laboratory samples require high numbers of replicate samples to ensure reasonable reproducibility⁸⁷. In common 182 laboratory testing, this requirement is however rarely satisfied, which may partially explain the large scatter in the 183 literature

184 Therefore, all the influencing factors affecting CT - material properties, exposure conditions (moisture, 185 temperature), potential, and structural aspects (size) - must be considered when applying CT to engineering 186 practice. Furthermore, it is important to consider the structural consequences of localized corrosion, depending on the location of corrosion within structural members and possible interferences with other damage⁹⁹. Another 187 188 key challenge in translating laboratory data to structures is related to the complexity of the steel-concrete interface (SCI) and the many local characteristics and heterogeneities present⁶⁶. Due to this complexity, it is virtually 189 190 impossible, in laboratory made samples, to create conditions at the SCI that are representative for a given structure. 191 An important part of the problem is also that the SCI can differ significantly, not only between different structures. 192 but between different locations within a structure, depending on the age, the conditions during casting, 193 workmanship, etc.⁶⁶. At the same time, the SCI includes some of the most important influencing factors for CT, 194 such as the steel surface condition or macroscopic concrete voids. Bearing this in mind, it is difficult to justify 195 applying CT to conditions that are different from those under which CT was determined. This limited applicability 196 has severe consequences when attempting to transfer previous understanding from practical experience or



Fig. 2 Influencing factors on CT. a,b, effect of moisture conditions. c, effect of steel potential. d, effect of exposed metal area (size effect). e, effect of criterion for CT illustrated by the fact that the transition from passive steel to active corrosion is a process characterized by depassivation-repassivation events over time during which the chloride concentration at the steel surface increases, until stable localized corrosion is possible. Data replotted from different literature sources, namely for fig. a from Pettersson⁴¹, fig. b from Boschmann⁴⁹, fig. c from Sagüés⁵², fig. d from Angst⁴⁵; fig. e is unpublished data from U.M. Angst.

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197 laboratory CT to accurate engineering forecasting questions. For instance, the foregoing arguments seriously 198 challenge attempts to devise test methods¹⁰⁰⁻¹⁰² from which tables could be produced listing CT for different 199 cement types, w/c ratios, steel grades, etc., regardless of the conditions at the SCI and in a structure. Such task 200 may prove to be fruitless.

201 The above describes the inherent shortcomings in establishing meaningful CT values. In the following, 202 corresponding concerns in other aspects of the traditional corrosion initiation-propagation modelling approach are 203 addressed.

The transition from passivity to stable active corrosion 204

205 The transition from a passive state to active chloride-induced corrosion is a complex process, and it is well 206 established that this is not an instantaneous and uniform event, but rather a process that occurs over an extended period and at different times for different locations^{103, 104}. Unstable, microscopically small corrosion pits form 207 208 even at low chloride concentrations; however, these pits can repassivate. This well-known repassivation phenomenon of localized corrosion^{105, 106} can be explained, among other reasons, by mass transport of different 209 210 ions towards the anodic site and the related competition between Cl⁻ and OH⁻ (and other anions) at the anodic 211 surface^{107, 108}. With further increase in chloride concentration, repassivation becomes more difficult until at some 212 point, stable, active corrosion is possible. Figure 2e shows an example observed in a reinforced concrete specimen 213 exposed in sodium chloride solution. Repeated repassivation events occurred until finally stable corrosion was 214 observed. It should be noted that considerable time (and related increase in chlorides at the surface) was needed 215 for the transition. It is important to recognize that the early unstable pitting and frequent repassivation phenomena 216 of the sort shown in Figure 2e are not related to temporary drying of the concrete. Even under constantly high 217 moisture conditions, repassivation can occur. The moisture and temperature conditions in structures are generally 218 variable over time, which are additional causes for interrupted corrosion propagation. Note that localized pits that 219 repassivate rapidly do not usually generate any harm to a concrete structure. For damage to occur, stable active 220 corrosion must usually develop and occur over an extended time period.

221 In the absence of a clear definition for corrosion initiation, different researchers are likely to interpret the CT value 222 from experiments, such as those shown in Figure 2e, differently. In the absence of a definition, even when a 223 standardized testing procedure is developed, it is not likely that CT values that are consistent among different 224 studies can be obtained. A corrosion initiation definition should ideally relate to a measurable parameter and be 225 straightforward to interpret. Since the size of local anode areas cannot be monitored directly, experiments 226 generally involve the monitoring of an electrochemical parameter during chloride exposure. CT is usually 227 determined when the monitored parameter reaches a pre-defined threshold indicating depassivation. However, the 228 transition from passivity to stable pitting occurs over a wide range of chloride concentrations and an indeterminate 229 steel surface area. It is then clear that taking, for instance, the first drop in potential as the indicator will not likely 230 relate it to the chloride concentration at which stable corrosion occurs. Therefore, criteria have been proposed to 231 ensure that the obtained CT relates better to practice by taking into account the repassivation phenomenon, that 232 is, by requiring the potential to stay at a more negative level for a certain minimum time period¹⁰⁰.

233 Improved approaches to forecasting corrosion of steel in concrete

234 The concept of CT, resulting in a separation of the service life into two distinct and successive stages (Figure 1), 235 caused most of the research to be focused on the corrosion initiation stage. This led to significant advances, 236 primarily in measuring and modelling chloride ingress³² and chloride binding in concrete³⁵. Additionally, 237 substantial efforts in search of CT were made over the last decades, with, as has been shown, very questionable 238 success. It appears, however, that the concept of CT has rarely been critically reassessed. In recent years, 239 atomistic/molecular modeling techniques have been used to study passivity and chloride-induced depassivation 240 of iron in alkaline electrolytes to develop fundamental understanding on how chlorides interact with passive film at the molecular level in idealized systems¹⁰⁹⁻¹¹⁴. Although these techniques have the potential to help future 241 242 development of new corrosion inhibitors and corrosion-resistant steels, they are not very useful or practical in 243 improving forecasts of safety and sustainability of reinforced concrete structures experiencing corrosion. Machine 244 learning is a field that has received increased attention from researchers studying steel corrosion in concrete and 245 has been shown to be a promising approach for predicting damage in reinforced concrete structures experiencing corrosion^{51, 115, 116}. Some studies even have used machine learning to predict CT or corrosion initiation in concrete 246 247 structures^{117, 118}. However, these machine learning approaches rely on existing collected data on CT that are still



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248 subject to the challenges associated with the CT concept and cannot address the big questions that are described 249 in this paper. In light of these obstacles, we suggest that the focus be shifted towards approaches that embrace the 250 importance of additional aspects of forecasting safety and sustainability of concrete structures experiencing 251 reinforcement corrosion. This proposed paradigm shift starts with the recognition that initiation and stabilization 252 of active localized corrosion is a process that may occur over significant time, and that after this, periods with 253 higher and lower, sometimes even negligible corrosion rates may occur. This would necessitate the elimination 254 of the clear distinction between initiation and propagation stages. Instead, steel corrosion in concrete would be 255 considered as a continuous process. Figure 3 summarizes these different aspects by showing schematic plots for 256 both the instantaneous corrosion rate and the accumulated damage over time.

257 It is important to consider that steel experiences significant fluctuations in corrosion rate over time because of the 258 changes in the environmental conditions (e.g., temperature, moisture, chloride exposure) and associated 259 fluctuations in the local microclimate within the concrete. The corrosion rates also vary spatially, i.e., the corrosion 260 rates along the reinforcement surface can show significant variability, particularly in locations of concrete flaws, 261 such as pre-existing cracks. The chloride ingress there will be more rapid and the transition to stable active 262 corrosion may be more abrupt. In some cases, the corrosion rate may decrease after time as the cracks become 263 filled with corrosion products or may heal due to further cement hydration. However, even in sound concrete, some locations remain passive (negligible corrosion rate), while others may exhibit comparatively high corrosion 264 265 rates in the same time period, for example at intersections of, or bends or welds in, bars. The corrosion behaviour 266 of those different locations are coupled through the mechanism of macro-cell corrosion, which is governed by a 267 number of factors including the supply of aggressive agents (chloride) to the anodic sites, the availability of 268 oxygen at the cathodic sites, the geometry of the corroding system, and the electrical resistivity of the concrete⁹⁴. 269 Due to changes in external environmental conditions, corrosion may cease and dormant phases may occur during 270 the life of a structure. Depending on seasonal variations, such dormant phases may repeatedly occur, e.g., during 271 dry periods. During periods of high corrosion rates, significant steel sectional area may be lost, and significant 272 amounts of ferrous ions may be released into the pore solution adjacent to the steel surface. These species will 273 influence the subsequent dissolution rates and will be subjected to reactive transport processes, and may at some 274 point precipitate in the concrete pore system. The precipitation of corrosion products may first lead to pore 275 clogging (affecting any further transport and corrosion processes), and later lead to macroscopic expansive 276 stresses that may give rise to concrete cracking. The cracks will allow a more rapid transport of species into 277 concrete; therefore, after the first signs of corrosion-induced cracking, decoupling initiation and propagation 278 stages of corrosion is not possible.

279 To take into account all these influences, quantitative, scientific models for localized corrosion are needed that 280 consider the electrochemistry of the steel/porous medium system as well as reactive mass transport, corrosion 281 product precipitation and concrete cracking as well as porosity changes related to these phenomena. Although 282 significant advances have been made in the modelling of steel corrosion (i.e., prediction of corrosion rates) in sound concrete^{36, 37, 119, 120}, there are limited research efforts to systematically incorporate the simultaneous and 283 284 coupled processes of transport of aggressive species, moisture, and temperature variations in concrete structures, 285 the progression of reinforcement corrosion rates, and deterioration of the concrete. We see major opportunities 286 for scientific advances in combining measurements and modelling of these aspects with recent developments in 287 invasive and non-invasive imaging techniques to characterize the pore structure at the SCI.

288 To reliably quantify corrosion rates for conditions relevant for practice, the time-variable exposure should be 289 considered, as this, together with moisture transport and moisture retention of the concrete cover zone, determines 290 the time periods during which significant active corrosion is possible (Figure 3). Local and time-dependent 291 exposure conditions in terms of concrete surface wetting (e.g., splash water, rain), relative humidity, temperature, 292 chloride loading, etc. and material properties such as pH and electrical resistivity are needed for the quantification 293 of corrosion rates¹²¹. For many geographic regions in the world, high quality meteorological data are available to 294 describe the exposure conditions. To link these "macroscopic" exposure data to the in-situ microclimate for 295 specific situations, e.g., road splash water on a bridge barrier wall, advantage should be taken of state-of-the-art 296 monitoring systems, possibly supported by machine learning algorithms. Such sensor systems^{122, 123} allow 297 monitoring in-situ the ingress of moisture, chlorides, and pH evolution. Collecting temporospatial variations of 298 such microclimatic data within a structure and relating it to macroscopic meteorological exposure data would 299 open new perspectives for better exposure condition modelling and, thus, pave the way towards more reliable 300 modelling of the performance of reinforced concrete structures in their exposure environments.



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Fig. 3: Illustration of monitored or predicted corrosion rate and related damage accumulation over time. Depending on the exposure climate and concrete properties, local microclimate at the steel-concrete interface can be different at different locations in the structure (examples A, B, C; Fig. a: d). As a result, the corrosion evolution – comprising periods of passivity, active corrosion, and dormant phases – will be different (Fig. e-g). Note that the different corroling sites and their electrochemical behavior are coupled through possible mutual polarization (depending on various factors, such as concrete electrical resistivity distribution). Note that the type of damage at the structural level may differ (e.g., steel sectional loss (Fig. h) or concrete cracking (Fig. II) depending on various parameters such as the pore structure and mechanical properties of the cementitious matrix, iron solubility and speciation in the given local pore liquid chemistry (pH, chlorides, oxygen, etc.). Precipitation of corrosion products in the concrete pore system can lead to pore clogging and concrete cracking which both affect the mass transport behavior.

312 Additionally, empirical data of the temporal variations of corrosion rates of steel in concrete should be collected 313 and correlated to the micro- and macroclimatic conditions as mentioned above. It must be recognized, however, 314 that state-of-the-art measurement techniques for the instantaneous corrosion rate of reinforced concrete lack the accuracy to provide reliable data124-127. A particular problem is that present electrochemical corrosion rate 315 316 measurement techniques provide data averaged over the measurement area and are unable to focus on the local 317 corrosion rates. It is clear that future endeavours must focus on improving corrosion rate prediction models and 318 corrosion rate sensing devices that can accurately work in real structures, to make significant advancements in 319 service life prediction of reinforced concrete.

320 Concluding remarks

On the basis of the above discussion, one could ask: is it time to abandon the concept of a CT with its associated, sharply defined, separation between initiation and propagation stages? As is clear from this review, the answer to that question is not straightforward. Concerning scientific research, now is definitely the time to shift the focus from CT to questions on the mechanisms and factors controlling the entire service life of a structure. After more than half a century of searching for a CT, and with the current limited usefulness of the concept in engineering, there are clearly research areas that are more promising in terms of achieving understanding and knowledge that, finally, would allow substantially enhanced predictions of the life of concrete structures.



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First, the mechanism of the transition from passive to stable active localized corrosion of steel in the complex porous medium (concrete) must be fully established. The onset of active corrosion of steel in concrete is a phenomenon with complexity clearly beyond published pitting and depassivation theories, which are generally developed for the case of a well-defined metal electrode immersed in a homogeneous liquid electrolyte^{128, 129}. We advocate the research community to consider the heterogeneity of the steel, the concrete and the steel-concrete interface more specifically in attempts to study the transition from passive steel to stable localized corrosion of steel in concrete. An example discussed in this review would be the role of interfacial concrete voids, especially the effect of their moisture state and the chemical environment within the voids in the process of corrosion onset. This can only be addressed by combining new advanced material characterization techniques¹³⁰ with holistic theory considering the interdependencies between physical, chemical, and electrochemical principles.

Second, to ensure that corrosion predictions are relevant and useful for the engineering community, there is
a need to spend more effort on the quantification of corrosion *rate*, in particular the temporospatial variability
of corrosion rates in a structure. We see opportunities in methods for the in-situ measurement of corrosion
rate as well as in modeling, as outlined below:

- Reliably measuring the corrosion rate of localized corrosion in concrete structures can be achieved by combining refined electrochemical measurements with numerical models¹³¹⁻¹³⁶, taking advantage of the progress in computational power and mechanistic understanding made over the last decades. In addition to non-destructive techniques for on-site measurements, the potential benefit from monitoring techniques, particularly their ability to create large amounts of time- and space-resolved data, is huge. This further creates opportunities in relating time-variable exposure conditions (e.g., based on meteorological data available for many regions in the world) to the temporospatial microclimates in the concrete (e.g. based on embedded sensors) and to couple these microclimatic variations to corrosion rates. Such approaches involving large data-sets from structures, combined with data science methods, will enhance the understanding of corrosion behaviour of steel in concrete under actual exposure conditions.

Scientific models for localized corrosion and related structural deterioration should integrate the electrochemistry of the steel in the cementitious porous matrix and link it to the various relevant transport processes (moisture, heat, ionic species, gases) and related phenomena, namely chemical reactions such as corrosion product precipitation, and their physical consequences (concrete cracking, porosity changes). Additional opportunities for scientific advances in this regard lie in combining modelling and experiment, especially data on the temporospatial microclimate mentioned in the previous point and microstructural characterization of the SCI with recent developments in invasive and non-invasive imaging techniques.

These scientific developments will take time to allow for a breakthrough in forecasting corrosion of steel in concrete. Thus, it is yet too early to advocate abandoning the CT concept for engineering purposes, especially in cases where only comparative evaluation of alternatives is sought. However, research must evolve to include how to translate CT to conditions in practice, beyond just expanding the database of CT measurements. That translation to practice concerns aspects related to the moisture and temperature conditions during testing vs. actual exposure conditions of a structure, aspects related to the complex features of the steel-concrete interface (including concrete flaws, particularly macro- and micro-cracks), as well as addressing the conceptual questions raised by the size effect.

In summary, to make progress in all the above-listed research priorities, a multi-scale and multi-disciplinary approach is needed to combine the scientific and practical contributions from material science, corrosion science, cement/concrete research, and structural engineering. This would present an opportunity to, at least partially, evolve away from the commonly held view of the service life being separated in two district and successive phases, and to consider steel corrosion as a continuous process. Instead of the binary approach of "passive" and "active" steel, the corrosion rate will become a more prominent parameter, both in monitoring and predicting the service life. One major advantage of this approach is that it would reduce or even eliminate the reliance on CT, thus obviating many of the difficulties reviewed here.



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AIP Publishing 380 Finally, it should be mentioned that one of the challenges associated with the lack of progress made in forecasting 381 corrosion of steel in concrete, is that engineers are forced to be very conservative to ensure uncritical 382 concentrations of chloride at the steel level over the design life of a structure. This translates into unnecessarily 383 high consumption of materials and energy, hence, excessive greenhouse gas emissions and costs. Therefore, 384 uncritical adherence to the 2-stage model framework and the concept of CT risks compromising the urgent needs 385 to reduce the environmental impact of the construction sector, and is clearly not in alignment with ambitions such 386 as the "net zero target" of the Global Cement and Concrete Association¹³⁷, aiming at entirely decarbonizing the 387 cement and concrete industry within the next 30 years.

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405 Author contributions

The five authors were equally involved in developing the concepts, in editing the manuscript and in collecting
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408 Data availability statement

Most of the data analyzed in this study is accessible in publications according to the indicated references.
 Additional data that support the findings of this study are available from the corresponding author upon reasonable
 request.

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413 **References**

- 414 1. K.L. Scrivener, V.M. John, and E.M. Gartner, Eco-efficient cements: Potential economically viable solutions for a
- 415 low-CO2 cement-based materials industry. 2017, United Nations Environment Programme, Paris, France.

PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0076320

416	2.	C. Heathcote and I. Mulheirn, Global Infrastructure Outlook - Infrastructure investment needs, 50 countries, 7 sectors
417		to 2040. 2017, Global Infrastructure Hub.
418	3.	F. Collins and F. Blin, Ageing of Infrastructure - A Life-Cycle Approach. 1st ed. 2020: CRC Press.
419	4.	M.D. Lepech, M. Geiker, and H. Stang, Probabilistic design and management of environmentally sustainable repair
420		and rehabilitation of reinforced concrete structures. Cement & Concrete Composites, 2014. 47: p. 19-31.
421	5.	Development of an holistic approach to ensure the durability of new concrete construction, Research Report Project
422		38/13/21 (cc 1031). 1997, Crowthorne, UK: British Cement Association.
423	6.	Model code for service life design, fib bulletin No. 34. 2006, Lausanne: Fédération internationale du béton.
424	7.	Model code for concrete structures 2010, fédération internationale du béton. 2013, Berlin, Germany: Wilhelm Ernst
425		& Sohn.
426	8.	M.R. Geiker, A. Michel, H. Stang, and M.D. Lepech, Limit states for sustainable reinforced concrete structures.
427		Cement and Concrete Research, 2019. 122: p. 189-195.
428	9.	O.B. Isgor, U. Angst, M. Geiker, C. Halmen, C. Hansson, J. Pacheco, D. Tepke, D. Trejo, and P. Vaddey,
429		Recommended practice for reporting experimental data produced from studies on corrosion of steel in cementitious
430		systems. RILEM Technical Letters, 2019. 4: p. 22-32.
431	10.	M. Raupach, Models for the propagation phase of reinforcement corrosion - an overview. Materials and Corrosion-
432		Werkstoffe Und Korrosion, 2006. 57(8): p. 605-613.
433	11.	J.P. Broomfield, Corrosion of Steel in Concrete. 2007, New York: Taylor & Francis.
434	12.	M.B. Otieno, H.D. Beushausen, and M.G. Alexander, Modelling corrosion propagation in reinforced concrete
435		structures - A critical review. Cement & Concrete Composites, 2011. 33(2): p. 240-245.
436	13.	L. Bertolini, B. Elsener, P. Pedeferri, E. Redaelli, and R. Polder, Corrosion of Steel in Concrete: Prevention, Diagnosis,
437		Repair (2nd Edition). 2013, Weinheim: WILEY VCH.
438	14.	A. Poursaee, Corrosion of steel in concrete structures, in Corrosion of Steel in Concrete Structures, A. Poursaee,
439		Editor. 2016, Woodhead Publishing: Oxford. p. 19-33.
440	15.	A. Goyal, H.S. Pouya, E. Ganjian, and P. Claisse, A Review of Corrosion and Protection of Steel in Concrete. Arabian
441		Journal for Science and Engineering, 2018. 43(10): p. 5035-5055.
442	16.	U.M. Angst, Challenges and opportunities in corrosion of steel in concrete. Materials and Structures, 2018. 51(4).
443	17.	ACI-222, 222R-19: Protection of Metals in Concrete Against Corrosion. 2019, American Concrete Institute: Detroit,
444		MI, USA.
445	18.	C. Andrade, Propagation of reinforcement corrosion: principles, testing and modelling Materials and Structures, 2019.
446		53(1).
447	19.	A. James, E. Bazarchi, A.A. Chiniforush, P.P. Aghdam, M.R. Hosseini, A. Akbarnezhad, I. Martek, and F. Ghodoosi,
448		Rebar corrosion detection, protection, and rehabilitation of reinforced concrete structures in coastal environments: A
449		review. Construction and Building Materials, 2019. 224: p. 1026-1039.



PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0076320

450	20.	U.M. Angst, M.R. Geiker, M.C. Alonso, R. Polder, B. Elsener, O.B. Isgor, H. Wong, A. Michel, K. Hornbostel, C.
451		Gehlen, R. François, M. Sanchez, M. Criado, H. Sørensen, C. Hansson, R. Pillai, S. Mundra, J. Gulikers, M. Raupach,
452		J. Pacheco, and A. Sagüés, The effect of the steel-concrete interface on chloride-induced corrosion initiation in
453		concrete - a critical review by RILEM TC 262-SCI. Materials and Structures, 2019. 52: p. 88.
454	21.	M. Dixit and A.K. Gupta, A Review of Different Assessment Methods of Corrosion of Steel Reinforcement in Concrete.
455		Iranian Journal of Science and Technology-Transactions of Civil Engineering, 2021.
456	22.	W. Tahri, X. Hu, C.J. Shi, and Z.H. Zhang, Review on corrosion of steel reinforcement in alkali-activated concretes
457		in chloride-containing environments. Construction and Building Materials, 2021. 293.
458	23.	J. Saire-Yanez, C.L. Alexander, and A.A. Sagüés, The Corrosion Propagation Stage of Stainless Steel Reinforced
459		Concrete: A Review. Corosion, 2021. 77(8): p. 812-828.
460	24.	R.E. Melchers, Experience-Based Physico-Chemical Models for Long-Term Reinforcement Corrosion. Corrosion and
461		Materials Degradation, 2021. 1: p. 100-119.
462	25.	D.P. Bentz, P.E. Stutzman, and E.J. Garboczi, Experimental and simulation studies of the interfacial zone in concrete.
463		Cement and Concrete Research, 1992. 22(5): p. 891-902.
464	26.	L. Tang and LO. Nilsson, Chloride binding capacity and binding isotherms of OPC pastes and mortars. Cement and
465		Concrete Research, 1993. 23(2): p. 247-253.
466	27.	Y.T. Puyate, C.J. Lawrence, N.R. Buenfeld, and I.M. McLoughlin, Chloride transport models for wick action in
467		concrete at large Peclet number. Physics of Fluids, 1998. 10(3): p. 566-575.
468	28.	B. Martin-Perez, S.J. Pantazopoulou, and M.D.A. Thomas, Numerical solution of mass transport equations in concrete
469		structures. Computers & Structures, 2001. 79(13): p. 1251-1264.
470	29.	B. Reddy, G.K. Glass, P.J. Lim, and N.R. Buenfeld, On the corrosion risk presented by chloride bound in concrete.
471		Cement & Concrete Composites, 2002. 24(1): p. 1-5.
472	30.	E. Samson and J. Marchand, Modeling the transport of ions in unsaturated cement-based materials. Computers &
473		Structures, 2007. 85(23-24): p. 1740-1756.
474	31.	L.O. Nilsson, Models for chloride ingress into concrete - from Collepardi to today. International Journal of Modelling,
475		Identification and Control, 2009. 7(2): p. 129-134.
476	32.	L. Tang, L.O. Nilsson, and P.A.M. Basheer, Resistance of Concrete to Chloride Ingress: Testing and modelling. 2012,
477		Abingdon: Spon Press. 264.
478	33.	V.J. Azad, C. Li, C. Verba, J.H. Ideker, and O.B. Isgor, A COMSOL-GEMS interface for modeling coupled reactive-
479		transport geochemical processes. Computers & Geosciences, 2016. 92: p. 79-89.
480	34.	O.B. Isgor and W.J. Weiss, A nearly self-sufficient framework for modelling reactive-transport processes in concrete
481		(vol 52, 3, 2019). Materials and Structures, 2019. 52(6).
482	35.	K. De Weerdt, Chloride binding in concrete: recent investigations and recognised knowledge gaps: RILEM Robert
483		L'Hermite Medal Paper 2021. Materials and Structures, 2021. 54(6): p. 214.



PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0076320

484	36.	S.C. Kranc and A.A. Sagues, Detailed modeling of corrosion macrocells on steel reinforcing in concrete. Corrosion
485		Science, 2001. 43(7): p. 1355-1372.
486	37.	O.B. Isgor and A.G. Razaqpur, Modelling steel corrosion in concrete structures. Materials and Structures, 2006. 39(3):
487		p. 291-302.
488	38.	S. Jäggi, H. Böhni, and B. Elsener, Macrocell corrosion of steel in concrete - experiments and numerical modelling,
489		in Corrosion of reinforcement in concrete - mechanisms, monitoring, inhibitors and rehabiliation techniques, M.
490		Raupach, et al., Editors. 2007, Woodhead Publishing Limited / CRC Press: Cambridge. p. 75-88.
491	39.	J. Warkus and M. Raupach, Numerical modelling of macrocells occurring during corrosion of steel in concrete.
492		Materials and Corrosion, 2008. 59(2): p. 122-130.
493	40.	R. François, I. Khan, N.A. Vu, H. Mercado, and A. Castel, Study of the impact of localised cracks on the corrosion
494		mechanism. European Journal of Environmental and Civil Engineering, 2012. 16(3-4): p. 392-401.
495	41.	M. Stefanoni, U.M. Angst, and B. Elsener, Kinetics of electrochemical dissolution of metals in porous media. Nature
496		Materials, 2019. 18(9): p. 942-+.
497	42.	C. Andrade, C. Alonso, and F. Molina, Cover cracking as a function of bar corrosion: Part I - Experimental test.
498		Materials and Structures, 1993. 26(8): p. 453-464.
499	43.	J.G. Cabrera, Deterioration of concrete due to reinforcement steel corrosion. Cement & Concrete Composites, 1996.
500		18(1): p. 47-59.
501	44.	C. Alonso, C. Andrade, J. Rodriguez, and J.M. Diez, Factors controlling cracking of concrete affected by
502		reinforcement corrosion. Materials and Structures, 1998. 31(211): p. 435-441.
503	45.	A.A. Torres-Acosta and A.A. Sagüés, Concrete cracking by localized steel corrosion - Geometric effects. ACI
504		Materials Journal, 2004. 101(6): p. 501-507.
505	46.	C.Q. Li, R.E. Melchers, and J.J. Zheng, Analytical model for corrosion-induced crack width in reinforced concrete
506		structures. Aci Structural Journal, 2006. 103(4): p. 479-487.
507	47.	U. Angst, B. Elsener, A. Jamali, and B. Adey, Concrete cover cracking owing to reinforcement corrosion - theoretical
508		considerations and practical experience. Materials and Corrosion, 2012. 63(12): p. 1069-1077.
509	48.	J. Ozbolt, F. Orsanic, G. Balabanic, and M. Kuster, Modeling damage in concrete caused by corrosion of
510		reinforcement: coupled 3D FE model. International Journal of Fracture, 2012. 178(1-2): p. 233-244.
511	49.	A. Jamali, U. Angst, B. Adey, and B. Elsener, Modeling of corrosion-induced concrete cover cracking: A critical
512		analysis. Construction and Building Materials, 2013. 42: p. 225-237.
513	50.	E.M. Guneyisi, K. Mermerdas, E. Guneyisi, and M. Gesoglu, Numerical modeling of time to corrosion induced cover
514		cracking in reinforced concrete using soft-computing based methods. Materials and Structures, 2015. 48(6): p. 1739-
515		1756.

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This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset. PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0076320

516	51.	S. Okazaki, C. Okuma, M. Kurumatani, H. Yoshida, and M. Matsushima, Predicting the Width of Corrosion-Induced
517		Cracks in Reinforced Concrete Using a Damage Model Based on Fracture Mechanics. Applied Sciences-Basel, 2020.
518		10(15).
519	52.	K. Tuutti, Service Life of Structures with Regard to Corrosion of Embedded Steel. Journal of the American Concrete
520		Institute, 1980. 77(5): p. 380-381.
521	53.	D.A. Hausmann, Steel corrosion in concrete. How does it occur? Materials Protection, 1967. 6: p. 19-23.
522	54.	K.W.J. Treadaway, R.N. Cox, and B.L. Brown, Durability of corrosion resisting steels in concrete. Proc. Instn Civ.
523		Engrs., 1989. Part 1, 86: p. 305-331.
524	55.	C.L. Page, Mechanism of corrosion protection in reinforced concrete marine structures. Nature, 1975. 258: p. 514-
525		515.
526	56.	A. Bäumel, Die Auswirkung von Betonzusatzmitteln auf das Korrosionsverhalten von Stahl in Beton. Zement-Kalk-
527		Gips, 1959. 7: p. 294-305.
528	57.	M. Pourbaix, Atlas d'équilibres électrochimiques. 1963, Paris: Centre Belge d'Etude de la Corrosion CEBELCOR /
529		Gauthier-Villars & Cie.
530	58.	C. Andrade, C. Alonso, J. Gulikers, R. Polder, R. Cigna, Ø. Vennesland, M. Salta, A. Raharinaivo, and B. Elsener,
531		Recommendation of RILEM TC 154-EMC: "Test methods for on-site corrosion rate measurement of steel
532		reinforcement in concrete by means of the polarization resistance method". Materials and Structures, 2004. 37(273):
533		p. 623-643.
534	59.	B. Elsener, C. Andrade, J. Gulikers, R. Polder, and M. Raupach, Half-cell potential measurements - potential mapping
535		on reinforced concrete structures (RILEM TC 154-EMC recommendation). Materials and Structures, 2003. 36: p. 461-
536		471.
537	60.	R.F. Stratfull, The corrosion of steel in a reinforced concrete bridge. Corrosion, 1957. 13: p. 43-48.
538	61.	W. Richartz, Die Bindung von Chlorid bei der Zementerhärtung. Zement-Kalk-Gips, 1969. 10: p. 447-456.
539	62.	M.C. Alonso and M. Sanchez, Analysis of the variability of chloride threshold values in the literature. Materials and
540		Corrosion, 2009. 60(8): p. 631-637.
541	63.	U. Angst, B. Elsener, C.K. Larsen, and O. Vennesland, Critical chloride content in reinforced concrete - A review.
542		Cement and Concrete Research, 2009. 39(12): p. 1122-1138.
543	64.	G.K. Glass and N.R. Buenfeld, The presentation of the chloride threshold level for corrosion of steel in concrete.
544		Corrosion Science, 1997. 39: p. 1001-1013.
545	65.	Y. Cao, C. Gehlen, U. Angst, L. Wang, Z.D. Wang, and Y. Yao, Critical chloride content in reinforced concrete - An
546		updated review considering Chinese experience. Cement and Concrete Research, 2019. 117: p. 58-68.
547	66.	U.M. Angst, M.R. Geiker, A. Michel, C. Gehlen, H. Wong, O.B. Isgor, B. Elsener, C.M. Hansson, R. Francois, K.
548		Hornbostel, R. Polder, M.C. Alonso, M. Sanchez, M.J. Correia, M. Criado, A. Sagues, and N. Buenfeld, The steel-
549		concrete interface. Materials and Structures, 2017. 50(2): p. 143.



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550	67.	C. Boschmann Käthler, U.M. Angst, A.M. Aguilar, and B. Elsener, A systematic data collection on chloride-induced
551		steel corrosion in concrete to improve service life modelling and towards understanding corrosion initiation.
552		Corrosion Science, 2019. 157: p. 331-336.
553	68.	J. Gulikers, Considerations on the reliability of service life predictions using a probabilistic approach. Journal de
554		Physique IV, 2006. 136: p. 233-241.
555	69.	W. Breit, Kritischer korrosionsauslösender Chloridgehalt – Neuere Untersuchungsergebnisse (Teil 2). Beton, 1998.
556		8(511).
557	70.	V.K. Gouda, Corrosion and corrosion inhibition of reinforcing steel. I. Immersed in alkaline solutions. British
558		Corrosion Journal, 1970. 5: p. 198-203.
559	71.	B. Reddy, Influence of the steel-concrete interface on the chloride threshold level. 2001, Imperial College, London.
560	72.	N.R. Buenfeld, G.K. Glass, B. Reddy, and R.F. Viles, Process for the protection of reinforcement in reinforced
561		concrete, U.S. Patent 6,685,822 B2. 2004.
562	73.	T.A. Soylev and R. François, Quality of steel-concrete interface and corrosion of reinforcing steel. Cement and
563		Concrete Research, 2003. 33(9): p. 1407-1415.
564	74.	L.T. Mammoliti, L.C. Brown, C.M. Hansson, and B.B. Hope, The influence of surface finish of reinforcing steel and
565		pH of the test solution on the chloride threshold concentration for corrosion initiation in synthetic pore solutions.
566		Cement and Concrete Research, 1996. 26(4): p. 545-550.
567	75.	L. Li and A.A. Sagues, Chloride corrosion threshold of reinforcing steel in alkaline solutions - Open-circuit immersion
568		tests. Corrosion, 2001. 57(1): p. 19-28.
569	76.	R.G. Pillai and D. Trejo, Surface condition effects on critical chloride threshold of steel reinforcement. Aci Materials
570		Journal, 2005. 102(2): p. 103-109.
571	77.	P. Ghods, O.B. Isgor, G.A. McRae, J. Li, and G.P. Gu, Microscopic investigation of mill scale and its proposed effect
572		on the variability of chloride-induced depassivation of carbon steel rebar. Corrosion Science, 2011. 53: p. 946-954.
573	78.	M. Stefanoni, U. Angst, and B. Elsener, Local electrochemistry of reinforcement steel - Distribution of open circuit
574		and pitting potentials on steels with different surface condition. Corrosion Science, 2015. 98: p. 610-618.
575	79.	M. Manera, O. Vennesland, and L. Bertolini, Chloride threshold for rebar corrosion in concrete with addition of silica
576		fune. Corrosion Science, 2008. 50(2): p. 554-560.
577	80.	P. Ghods, O.B. Isgor, G.A. McRae, J. Li, and G.P. Gu, Microscopic investigation of mill scale and its proposed effect
578		on the variability of chloride-induced depassivation of carbon steel rebar. Corrosion Science, 2011. 53(3): p. 946-954.
579	81.	C.M. Hansson and B. Sørensen, The threshold concentration of chloride in concrete for the initiation of reinforcement
580		corrosion, in Corrosion rates of steel in concrete, N.S. Berke, V. Chaker, and D. Whiting, Editors. 1990, ASTM STP
581		1065. p. 3-16.
582	82.	R. Polder, Critical chloride content for reinforced concrete and its relationship to concrete resistivity. Materials and
583		Corrosion, 2009. 60(8): p. 623-630.



accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset

PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0076320

This is the author's peer reviewed,

584 83. K. Pettersson, Service life of concrete structures - in saline environment; CBI Report 3:96. 1996, CBI: Stockholm, 585 Sweden 586 84. J. Enevoldsen, C. Hansson, and B. Hope, The Influence of Internal Relative Humidity on the Rate of Corrosion of Steel 587 Embedded in Concrete and Mortar. Cement and Concrete Research, 1994. 24: p. 1373-1382. 588 X. Song, Q. Kong, and X. Liu, Experimental study on chloride threshold levels in OPC. China Civil Eng Journal, 2007. 85. 589 40(11): p. 59-63. G.K. Glass and B. Reddy, The influence of the steel concrete interface on the risk of chloride induced corrosion 590 86. 591 initiation, in Corrosion of Steel in Reinforced Concrete Structures, COST 521, Final Workshop, R. Weydert, Editor. 592 2002: Luxembourgh, 18-19 Febrary 2002. p. 227-232. 593 87. U.M. Angst and B. Elsener, The size effect in corrosion greatly influences the predicted life span of concrete 594 infrastructures. Science Advances, 2017. 3(8). 595 88. C. Boschmann Käthler, Chloride-induced reinforcement corrosion in concrete: the role of the steel-concrete interface 596 and implications for engineering. Doctoral thesis ETH Nr. 26213. 2019, ETH Zurich. 597 89. P. Sandberg, K. Pettersson, H.E. Sørensen, and H. Arup, Critical chloride concentrations for the onset of active 598 reinforcement corrosion, in Proc. RILEM Int. Workshop "Chloride penetration into concrete", 15-18 October 1995, 599 L.O. Nilsson and P. Ollivier, Editors. 1997, RILEM: St-Remy-Les-Chevreuses. p. 453-459. 600 90. P. Sandberg and H. Sørensen, Factors affecting the chloride thresholds for uncracked reinforced concrete exposed in 601 a marine environment. Part II: laboratory- and field exposure of corrosion cells. Corros Eng Sci Technol, 1999. 1(2): 602 p. 99–109. 603 C. Boschmann Käthler, S.L. Poulsen, H.E. Sørensen, and U.M. Angst, Investigations of accelerated methods for 91. 604 determination of chloride threshold values for reinforcement corrosion in concrete. Sustainable and Resilient 605 Infrastructure, 2021: p. 1-12. 606 92. R.H. Relling and E.J. Sellevold, In situ moisture state of coastal concrete bridges, in Proc. Int. Conf. on Concrete 607 Repair, Rehabilitation and Retrofitting, M.G. Alexander, et al., Editors. 2006, Taylor & Francis/Balkema, The 608 Netherlands: Cape Town, South Africa. p. p. 191. 609 G. Fagerlund, A service life model for internal frost damage in concrete. Report TVBM-3119. 2004, Lund institute of 93 610 Technology, Sweden. 611 94. A.A. Sagüés, A.N. Sánchez, K. Lau, and S.C. Kranc, Service Life Forecasting For Reinforced Concrete Incorporating 612 Potential-Dependent Chloride Threshold. Corrosion, 2014. 70: p. 942-957. 613 95. C. Alonso, M. Castellote, and C. Andrade, Chloride threshold dependence of pitting potential of reinforcements. 614 Electrochimica Acta, 2002. 47: p. 3469-3481. 615 96. U.R. Evans, The corrosion and oxidation of metals: Scientific principles and practical applications. 1960, London: 616 Edward Arnold Ltd.



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AIP Publishing

617	97.	L. Li and A.A. Sagüés, Chloride corrosion threshold of reinforcing steel in alkaline solutions - Effect of specimen size.
618		Corrosion, 2004. 60(2): p. 195-202.
619	98.	C. Chalhoub, R. Francois, and M. Carcasses, Determination of chloride threshold initiating corrosion: A new set-up
620		taking the localized aspect of corrosion into account. Cement and Concrete Research, 2019. 124.
621	99.	M.M. Kioumarsi, M.A.N. Hendriks, J. Kohler, and M.R. Geiker, The effect of interference of corrosion pits on the
622		failure probability of a reinforced concrete beam. Engineering Structures, 2016. 114: p. 113-121.
623	100.	L. Tang, J.M. Frederiksen, U.M. Angst, R. Polder, M.C. Alonso, B. Elsener, R.D. Hooton, and J. Pacheco, Experiences
624		from RILEM TC 235-CTC in recommending a test method for chloride threshold values in concrete. RILEM Technical
625		Letters, 2018. 3: p. 25-31.
626	101.	P.V. Nygaard and M.R. Geiker, A method for measuring the chloride threshold level required to initiate reinforcement
627		corrosion in concrete. Materials and Structures, 2005. 38: p. 489-494.
628	102.	European Committee for Iron and Steel Standardization, ECISS/TC 104/WG 3 N E178: Corrosion Resistant
629		Reinforcing Steels (WI EC104031), (draft version 2014).
630	103.	COST 521: Final report "Corrosion of steel in reinforced concrete structures", R. Cigna, et al., Editors. 2003:
631		Luxembourg.
632	104.	U. Angst, B. Elsener, C.K. Larsen, and Ø. Vennesland, Chloride induced reinforcement corrosion: electrochemical
633		monitoring of initiation stage and chloride threshold values. Corrosion Science, 2011. 53: p. 1451-1464.
634	105.	G.S. Frankel, Pitting corrosion of metals - A review of the critical factors. Journal of the Electrochemical Society,
635		1998. 145(6): p. 2186-2198.
636	106.	P.C. Pistorius and G.T. Burstein, Metastable pitting corrosion of stainless steel and the transition to stability.
637		Philosophical Transactions: Physical Sciences and Engineering, 1992. 341: p. 531-559.
638	107.	P. Ghods, O.B. Isgor, and G. McRae. Electrochemical studies on the corrosion initiation of black steel rebar in
639		concrete. in Proceedings, Annual Conference - Canadian Society for Civil Engineering. 2010.
640	108.	A. Pourbaix, Localized corrosion: behaviour and protection mechanisms, in Corrosion Chemistry within Pits, Crevices
641		and Cracks, A. Turnbull, Editor. 1984, National Physical Laboratory: Teddington, Middlesex. p. 1-15.
642	109.	H. DorMohammadi, Q. Pang, L. Arnadottir, and O.B. Isgor, Atomistic simulation of initial stages of iron corrosion in
643		pure water using reactive molecular dynamics. Computational Materials Science, 2018. 145: p. 126-133.
644	110.	H. DorMohammadi, Q. Pang, P. Murkute, L. Arnadottir, and O.B. Isgor, Investigation of iron passivity in highly
645		alkaline media using reactive-force field molecular dynamics. Corrosion Science, 2019. 157: p. 31-40.
646	111.	H. DorMohammadi, Q. Pang, P. Murkute, L. Arnadottir, and O.B. Isgor, Investigation of chloride-induced
647		depassivation of iron in alkaline media by reactive force field molecular dynamics. Npj Materials Degradation, 2019.
648		3(1).
649	112.	Q. Pang, H. DorMohammadi, O.B. Isgor, and L. Arnadottir, The effect of surface vacancies on the interactions of Cl
650		with a alpha-Fe2O3 (0001) surface and the role of Cl in depassivation. Corrosion Science, 2019. 154: p. 61-69.

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651	113.	Q. Pang, H. DorMohammadi, O.B. Isgor, and L. Arnadottir, Thermodynamic feasibility of the four-stage chloride-
652		induced depassivation mechanism of iron. Npj Materials Degradation, 2020. 4(1).
653	114.	Q. Pang, H. Dormohammadi, O.B. Isgor, and L. Arnadottir, The Effect of Surface Defects on Chloride-Induced
654		Depassivation of Iron-A Density Functional Theory Study. Corrosion, 2020. 76(7): p. 690-697.
655	115.	B. Fu and D.C. Feng, A machine learning-based time-dependent shear strength model for corroded reinforced concrete
656		beams. Journal of Building Engineering, 2021. 36.
657	116.	M.Y. Zhang, M. Akiyama, M. Shintani, J.Y. Xin, and D.M. Frangopol, Probabilistic estimation of flexural loading
658		capacity of existing RC structures based on observational corrosion-induced crack width distribution using machine
659		learning. Structural Safety, 2021. 91.
660	117.	B.A. Salami, S.M. Rahman, T.A. Oyehan, M. Maslehuddin, and S.U. Al Dulaijan, Ensemble machine learning model
661		for corrosion initiation time estimation of embedded steel reinforced self-compacting concrete. Measurement, 2020.
662		165.
663	118.	Y.K. Zhu, D.D. Macdonald, J. Qiu, and M. Urquidi-Macdonald, Corrosion of rebar in concrete. Part III: Artificial
664		Neural Network analysis of chloride threshold data. Corrosion Science, 2021. 185.
665	119.	S.C. Kranc and A.A. Sagues, Computation of Reinforcing Steel Corrosion Distribution in Concrete Marine Bridge
666		Substructures. Corrosion, 1994. 50(1): p. 50-61.
667	120.	A. Michel, H. Stang, M. Lepech, and M. Geiker, Multi-physics and multi-scale deterioration modelling of reinforced
668		concrete. Key Engineering Materials, 2016. 665: p. 13-16.
669	121.	M. Flint, A. Michel, S.L. Billington, and M.R. Geiker, Influence of temporal resolution and processing of exposure
670		data on modeling of chloride ingress and reinforcement corrosion in concrete. Materials and Structures, 2014. 47(4):
671		p. 729-748.
672	122.	M. Raupach and P. Schiessl, Monitoring system for the penetration of chlorides, carbonation and the corrosion risk
673		for the reinforcement. Construction and Building Materials, 1997. 11(4): p. 207-214.
674	123.	M.F. Montemor, J.H. Alves, A.M. Simoes, J.C.S. Fernandes, Z. Lourenco, A.J.S. Costa, A.J. Appleton, and M.G.S.
675		Ferreira, Multiprobe chloride sensor for in situ monitoring of reinforced concrete structures. Cement & Concrete
676		Composites, 2006. 28(3): p. 233-236.
677	124.	S. Feliu, J.A. Gonzalez, and C. Andrade, Effect of Current Distribution on Corrosion Rate Measurements in
678		Reinforced-Concrete. Corrosion, 1995. 51(1): p. 79-86.
679	125.	O.K. Gepraegs and C.M. Hansson, A Comparative Evaluation of Three Commercial Instruments for Field
680		Measurements of Reinforcing Steel Corrosion Rates. Journal of ASTM International 2005. 8(2).
681	126.	A. Poursaee and C.M. Hansson, Galvanostatic pulse technique with the current confinement guard ring: The
682		laboratory and finite element analysis. Corrosion Science, 2008. 50(10): p. 2739-2746.
683	127.	P.V. Nygaard, M.R. Geiker, and B. Elsener, Corrosion rate of steel in concrete: evaluation of confinement techniques
684		for on-site corrosion rate measurements. Materials and Structures, 2009. 42(8): p. 1059-1076.





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685	128.	H. DorMohammadi, Q. Pang, P. Murkute, L. Árnadóttir, and O.B. Isgor, Investigation of chloride-induced
686		depassivation of iron in alkaline media by reactive force field molecular dynamics. npj Materials Degradation, 2019.
687		3(1): p. 19.
688	129.	Q. Pang, H. DorMohammadi, O.B. Isgor, and L. Árnadóttir, The effect of surface vacancies on the interactions of Cl
689		with a α-Fe2O3 (0001) surface and the role of Cl in depassivation. Corrosion Science, 2019. 154: p. 61-69.
690	130.	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.
691		Gulikers, Y. Zhao, M. Criado, M. Raupach, H. Sørensen, R. François, S. Mundra, M. Rasol, and R. Polder, Methods
692		for characterising the steel-concrete interface to enhance understanding of reinforcement corrosion: a critical review
693		by RILEM TC 262-SCI. (submitted to Materials and Structures).
694	131.	M. Ridha, K. Amaya, and S. Aoki, Multistep genetic algorithm for detecting corrosion of reinforcing steels in concrete.
695		Corrosion, 2001. 57(9): p. 794-801.
696	132.	S.C. Kranc and A.A. Sagües, A numerical method for the recovery of local potentials and currents due to corrosion of
697		steel in concrete. Journal of ASTM International, 2005. 3: p. 1-11.
698	133.	P. Ghods, O.B. Isgor, and M. Pour-Ghaz, A practical method for calculating the corrosion rate of uniformly
699		depassivated reinforcing bars in concrete. Materials and Corrosion-Werkstoffe Und Korrosion, 2007. 58(4): p. 265-
700		272.
701	134.	P. Marinier and O.B. Isgor. Model-Assisted Non-destructive Monitoring of Reinforcement Corrosion in Concrete
702		Structures. 2013. Dordrecht: Springer Netherlands.
703	135.	M.C. Van Ede, C.J. Earls, A. Fichtner, and U. Angst, Electrochemical tomography as a nondestructive technique to
704		study localized corrosion of metals. Npj Materials Degradation, 2021. 5(1).
705	136.	R. Adriman, I.B. Ibrahim, S. Huzni, S. Fonna, and A.K. Ariffin, Improving half-cell potential survey through
706		computational inverse analysis for quantitative corrosion profiling. Case Studies in Construction Materials, 2022. 16.
707	137.	Global Cement and Concrete Association. "2050 Net Zero Roadmap" (https://gccassociation.org/concretefuture/).
708		2020.



a Life cycle of a reinforced concrete structure









