These proofs may contain colour figures. Those figures may print black and white in the final printed book if a colour print product has not been planned. The colour figures will appear in colour in all electronic versions of this book.

AUTHOR QUERY FORM

ELSEVIER	**Book: Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry** **Chapter: 13435**	**Please e-mail your responses and any corrections to:** **E-mail: mrw-ifcc@elsevier.com**

Dear Author,

Any queries or remarks that have arisen during the processing of your manuscript are listed below and are highlighted by flags in the proof. (Q indicates author queries; ED indicates editor queries.) Please check your proof carefully and answer all Q queries. Mark all corrections and query answers at the appropriate place in the proof (e.g., by using on-screen annotation in the PDF file http://www.elsevier.com/book-authors/science-and-technology-book-publishing/overview-of-the-publishing-process) or compile them in a separate list, and tick off below to indicate that you have answered the query.
Please return your input as instructed by the project manager.

Location in Chapter	**Query / remark**	
Q:1, page 2	Please provide complete details for reference “Hausmann (1984)”.	☐
Q:2, page 8	Please provide complete details for references “Breit, 2001, Vassie, 1984, Swiss Road tunnel, 2016”.	☐
Q:3, page 1	Please check the sentence “In emerging countries…” for clarity.	☐
Q:4, page 1	“Per style, cross references to other articles are not allowed in text or as See Also. Kindly modify the sentence “The topic passivation…” here and similar instances elsewhere in this article.”	☐
Q:5, page 2	Per style, cross references to other articles are not allowed in text or as See Also. Kindly modify the sentence “A more detailed…” here and similar instances elsewhere in this article.	☐
Q:6, page 9	Please check whether the edits made in this sentence is okay.	☐
Q:7, page 9	Please provide the volume number and page range for the bibliography in Angst (2017).	☐
Q:8, page 4	Please provide better quality artwork for figure 5.	☐
Q:9, page 9	Please provide publisher name and location for Parrott (1987).	☐
Q:10, page 9	Please provide the volume number and page range for the bibliography in Segui et al. (2017).	☐
Q:11, page 9	Please provide the volume number and page range for the bibliography in Stefanoni et al. (2016).	☐
Q:12, page 9	Please provide the volume number and page range for the bibliography in Stefanoni et al. (2017).	☐

To protect the rights of the author(s) and publisher we inform you that this PDF is an uncorrected proof for internal business use only by the author(s), editor(s), reviewer(s), Elsevier and typesetter SPi. It is not allowed to publish this proof online or in print. This proof copy is the copyright property of the publisher and is confidential until formal publication.

These proofs may contain colour figures. Those figures may print black and white in the final printed book if a colour print product has not been planned. The colour figures will appear in colour in all electronic versions of this book.

a0010 Corrosion of Steel in Concrete: New Challenges

B Elsener, ETH Zurich, Zurich, Switzerland; Università degli Studi di Cagliari, Cagliari, Italy
UM Angst, ETH Zurich, Zurich, Switzerland

© 2017 Elsevier Inc. All rights reserved.

ELSEVIER FIRST PROOF

s0010 Introduction

p0010 Reinforced concrete is the most used construction material worldwide, especially for civil infrastructures such as bridges, tunnels, marine structures, water distribution, and sewer systems, and so on. These engineering structures are important for economy and everyday lives. Despite the proven durability of reinforced concrete, many structures are aging and start to show signs of degradation due to the corrosion of the reinforcing steel when chloride ions from seawater or deicing salts or carbonation destroy the protective passive film on the steel. The required repair work negatively affects the environment due to consumption of materials and energy. Additionally, corrosion of the infrastructures leads to very high costs estimated in the order of 1.5% of the gross domestic product annually. The cost of corrosion of reinforced concrete infrastructure in the United States is calculated to about 50×10^9 dollars per year.

p0015 In industrialized countries, the major part of infrastructure has been built in the years from 1960 to 1980, thus, they have reached or are reaching a critical age where major maintenance work has to be performed. The continuous aging of these existing assets will lead to an increased need of repair as reported by Polder et al., for the Netherlands, it has been estimated that structures needing repair will increase in the next 20 years by a factor of 2–4, and over the next 40 years by a factor of 3–6.

p0020 In emerging countries, the civil engineering infrastructure is expanded and built today and tomorrow, the main challenge is that these new structures have to be designed and constructed durable. As has been discussed at the *international RILEM workshop on present and future durability challenges for reinforced concrete structures*, held in Zurich, Switzerland, in 2012, building new structures and maintaining existing ones, operates “in the context of an ever-increasing need to reduce the overall environmental impact of this infrastructure while selecting practical and cost-effective solutions. More specifically, this will mean to combine long service life and low environmental footprint of the materials used.” Q3

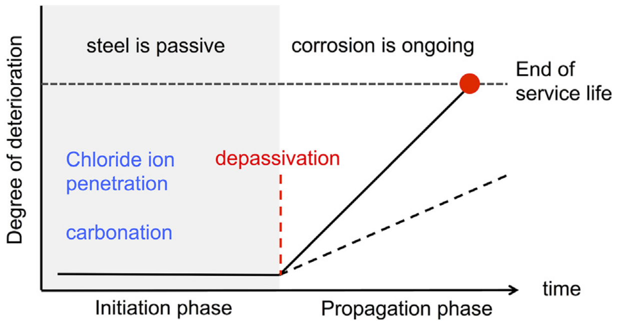
p0025 The main problem of the cement industry is the intrinsic emission of CO_2 when producing clinker. As a consequence, clinker is increasingly being replaced with supplementary cementitious materials (SCM) and new cement blends are brought on the market. These new blended cements (see the following sections), however, face problems due to carbonation.

s0015 Fundamentals

p0030 Reinforcing steel in concrete is protected by a thin oxide film. This so-called passive film grows spontaneously in alkaline environments, such as the pore solution in concrete that has a $pH > 12.5$, due to the reaction of cement clinker with the mixing water. The corrosion rate in the passive state is lower than 0.1 μm/year, thus practically negligible. The topic passivation of steel and stainless steel is presented in more detail in a separate chapter of this encyclopedia (Elsener and Rossi). The famous “Tuuti diagram” (Fig. 1) shows the evolution of degradation of reinforced concrete over time: at the beginning, no degradation occurs. When the initiation time t_{init} is reached, the passive film is destroyed (the steel is depassivated) and corrosion of the reinforcement can start in presence of oxygen and water; this is called the propagation state. The requirements given in the codes of practice, a high cover Q4

To protect the rights of the author(s) and publisher we inform you that this PDF is an uncorrected proof for internal business use only by the author(s), editor(s), reviewer(s), Elsevier and typesetter SPi. It is not allowed to publish this proof online or in print. This proof copy is the copyright property of the publisher and is confidential until formal publication.

These proofs may contain colour figures. Those figures may print black and white in the final printed book if a colour print product has not been planned. The colour figures will appear in colour in all electronic versions of this book.



f0010 **Fig. 1** Schematic representation of the service life or reinforced concrete structure ("Tuutti diagram") showing the initiation phase, depassivation of steel, and corrosion propagation phase.

depth, good quality concrete, and long curing, intend to reach a long-service life of reinforced concrete, thus to preserve the passive state as long as possible by avoiding or at least retarding the ingress of aggressive agents such as chloride ions or CO_2.

s0020 Chloride-Induced Corrosion

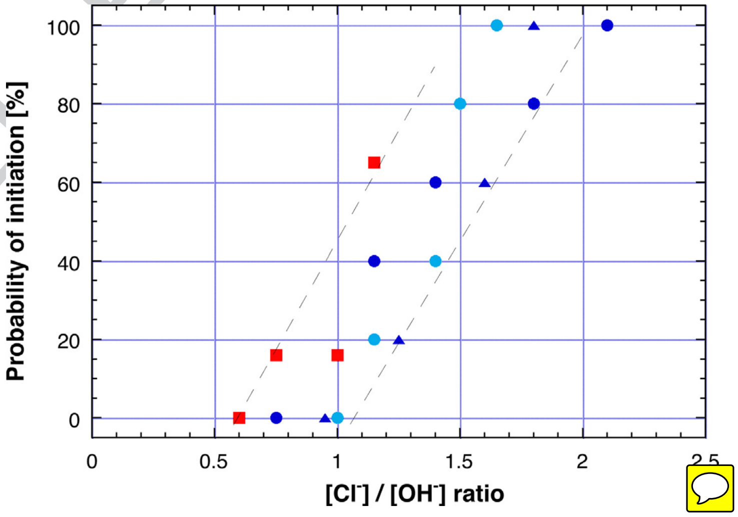
p0035 Depassivation of the reinforcing steel occurs when a sufficiently high chloride ion concentration is present on the steel surface. The chloride ion concentration necessary to depassivate the steel surface (the so-called "critical chloride content, C_{crit}") is an important topic of research for a long time. As has been reported in a review paper of the authors, C_{crit} is far from being a constant value but depends on the environmental conditions, the alkalinity of concrete and the reinforcing steel thus it cannot be expected to be a "universal" value as it is sometimes assumed in civil engineering practice. In an early work of Hausmann, the stochastic nature of pitting corrosion has been documented (Fig. 2) and a first concept to take into consideration both chloride content and type of cement was proposed in defining a critical (average) ratio of $Cl^-/OH^- = 0.6$. Today, more than 40 years later, there is still a lack of scientific basis to rationalize the huge variation in C_{crit}. A first attempt has been made to describe and if possible to quantify the different influencing factors at the steel–concrete interface in a publication of a RILEM technical committee TC 262-SCI. A more detailed discussion of this topic follows in the chapter "Critical chloride content." Q5

s0025 Corrosion-Induced by Carbonation

p0040 Depassivation of the reinforcing steel also occurs when the alkaline environment of the concrete has been neutralized by carbonation, the reaction of carbon dioxide from the atmosphere with the alkaline components of concrete:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$

p0045 This reaction occurs only in the presence of water, because the CO_2 has to dissolve in water, forming carbonic acid that then neutralizes the alkaline components. The carbonation rate of concrete is governed by its porosity (easy access of CO_2), the CO_2



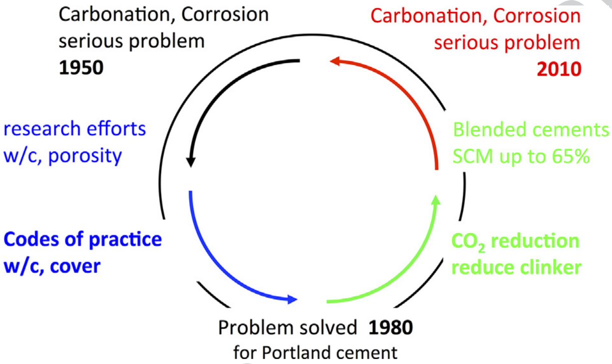
f0015 **Fig. 2** Probability of corrosion initiation as a function of the chloride/hydroxide ratio. Data according to Hausmann (1984) in sat. $Ca(OH)_2$. Data in synthetic pore solution pH 13.2–13.5. Q1

ELSEVIER FIRST PROOF

To protect the rights of the author(s) and publisher we inform you that this PDF is an uncorrected proof for internal business use only by the author(s), editor(s), reviewer(s), Elsevier and typesetter SPi. It is not allowed to publish this proof online or in print. This proof copy is the copyright property of the publisher and is confidential until formal publication.

These proofs may contain colour figures. Those figures may print black and white in the final printed book if a colour print product has not been planned. The colour figures will appear in colour in all electronic versions of this book.

f0020 **Fig. 3** Test of the carbonation depth with phenolphthalein spray on freshly split concrete sample. *Purple*: concrete still alkaline, colorless: concrete carbonated.



f0025 **Fig. 4** “Carbonation cycle” showing the evolution of research and standards regarding carbonation of concrete.

ELSEVIER PROOF

concentration in the atmosphere, the relative humidity (RH) (capillary pores are open), and the amount of alkaline components, mainly $Ca(OH)_2$, that have to be neutralized. The carbonation reaction of ordinary Portland cement is well-known and under ideal test conditions (65% RH) follows a $\sqrt{t}$ law due to the progressively hindered CO_2 diffusion.

p0050 Usually, the ingress of the carbonation front into concrete is followed by spraying a solution of the indicator phenolphthalein on a freshly split surface, areas that are still alkaline ($pH > 11$) show a pink color and areas that are already neutralized (carbonated) are colorless (Fig. 3). This indicator test gives a “yes/no” answer, but it does not allow the following pH changes in concrete during carbonation that might be important for durability. A new in situ pH sensor developed in our laboratory might give more insight.

p0055 Corrosion of steel in carbonated concrete was a major concern of research and practice in the years from 1950 to 1990 as shown in a review by Parrot in 1987. The research findings led to the requirement of dense concrete (lower w/c ratio), the control of concrete properties and to a marked increase in the cover depth (from 20 mm to 35 mm) in the codes of practice (Fig. 4). The European standard on concrete EN 206-1 published in the year 2000 classified the risk of carbonation-induced corrosion depending on the severity of the environment (XC1 to XC4). Since then, corrosion in carbonated mortar or concrete was no more of interest for service life considerations because the initiation time (see Fig. 1) was long enough. The main factor controlling the corrosion rate of steel in concrete is the exposure conditions of the structure; in relatively dry concrete (up to 80% of RH), the corrosion rate is lower than 1 μm/year and thus not considered critical for structural safety and durability. Higher values were found at humidity >95% and in immersed conditions. Nowadays, the topic corrosion of steel in carbonated concrete became of great interest again (Fig. 4) for two reasons: (1) many structures have reached their service life and the carbonation front is approaching the reinforcement and (2) the propagation phase in the new blended cements can become a significant part of the total service life.

s0030 New Blended Cements

p0060 For decades, ordinary Portland cement has been the most used cement type (CEM I) to build our infrastructure made of reinforced concrete. It has very good performance, based on the high alkalinity of the concrete pore solution that protects the reinforcing steel

To protect the rights of the author(s) and publisher we inform you that this PDF is an uncorrected proof for internal business use only by the author(s), editor(s), reviewer(s), Elsevier and typesetter SPi. It is not allowed to publish this proof online or in print. This proof copy is the copyright property of the publisher and is confidential until formal publication.

These proofs may contain colour figures. Those figures may print black and white in the final printed book if a colour print product has not been planned. The colour figures will appear in colour in all electronic versions of this book.

by the formation of a passive film, is documented by experience of more than half a century. The disadvantage is the environmental footprint, that is, the production of Portland cement requires huge amount of energy and the process to produce clinker releases CO_2, summing up cement industry is responsible for about 7% of the manmade CO_2.

p0065 The cement industry already has made great efforts in changing from fuel to waste incineration. However, for a substantial CO_2 reduction, the amount of clinker content in the cements has to be reduced and substituted with SCMs such as limestone, fly ash (FA), geopolymers, and so on. This substitution is ongoing and reflected in the decreasing amount of Portland cement and the increase of blended cements used for concrete construction. In the future, blended cements with decreasing clinker contents and an increasing variety in terms of SCMs will be used. As a result, the pore solution chemistry in concrete is becoming increasingly variable. The hydroxide (OH^-) concentration in the pore solution of systems with SCMs is typically about a factor of 10 lower than in Portland cement systems. Additionally, also the pH buffer capacity is generally depressed as a result of the reduction (or elimination) of the calcium hydroxide reserve, which is considered one of the main reasons for the corrosion inhibiting nature of Portland cement systems. Whereas, it is clear that the different pore solution chemistry of concrete made with blended cements will affect the corrosion protection of the reinforcing steel, precise information on how this will influence the service life of structures (Fig. 1) are not (yet) available.

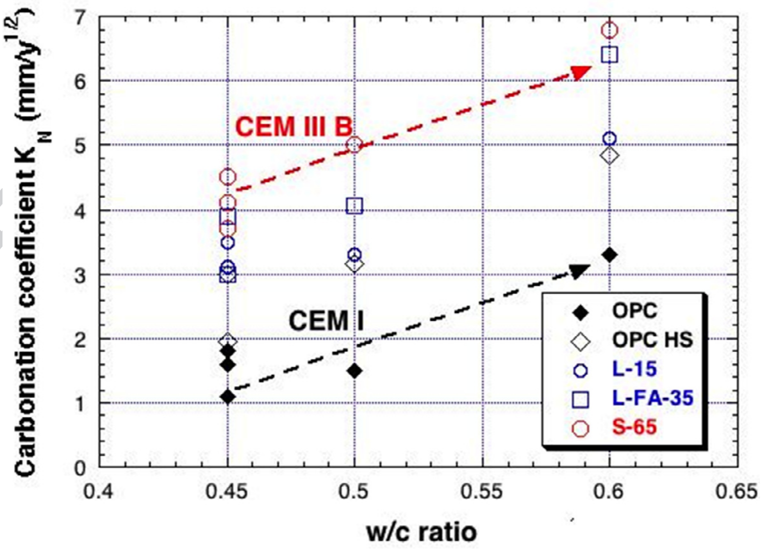
s0035 Carbonation Rate

p0070 The carbonation process is described in the section "Fundamentals" earlier referring to the data from ordinary Portland cement. The carbonation rate of blended cements such as binders containing ground granulated blast-furnace slag and FA has been extensively studied in literature. In general, a decrease in carbonation resistance was found with increasing clinker replacement. In a recent work of Leemann et al., in which different mix designs and exposure conditions were compared, it was found that the carbonation resistance is directly linked to the buffer capacity of the cement paste, more precisely expressed as the ratio between the water added during production and the amount of reactive CaO in the binder (if cement contains e.g., limestone powder, the amount of CaO in the limestone has to be subtracted as it is not reactive). This novel parameter $w/CaO_{reactive}$ allows characterizing and predicting the carbonation resistance of new blended cements by a material parameter (Fig. 5). The carbonation rate of blended cements has been found to be a factor of 2–4 higher than for Portland cements due to lower alkali reserve of $Ca(OH)_2$. This correlation found in laboratory experiments is becoming worse when samples are exposed to unsheltered conditions in outdoors.

p0075 *Two challenges arise*: First, the carbonation mechanisms of OPC and blended cements have to be studied in more detail. Second, for service life predictions of concrete structures with new, blended cements with fast carbonation rate, implementation of the so-called "corrosion propagation stage" is needed because it might become a significant part of the total service life. Both aspects will be discussed in the following sections.

s0040 Measuring Carbonation In Situ

p0080 Knowledge of the carbonation mechanism of cementitious materials might be considerably improved with new nondestructive in situ pH sensors. Such a sensor was developed and tested in our laboratory. It is based on iridium oxide and allows continuous monitoring of the pH of the pore solution during carbonation, providing a more detailed insight into the carbonation reaction.

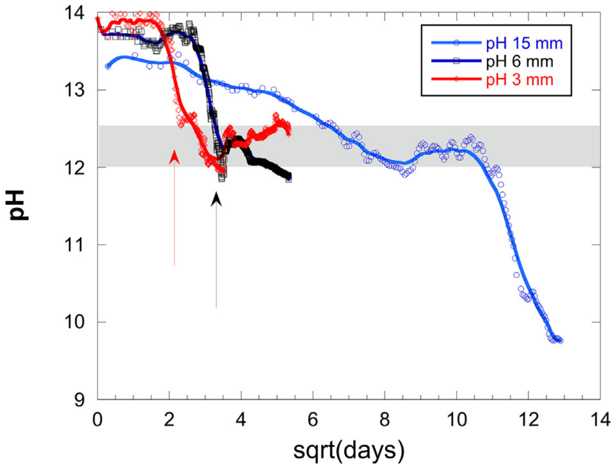


f0030 **Fig. 5** Velocity of carbonation propagation expressed as carbonation coefficient *K* for CEM I and different types of blended cements for *w/b* ratios from 0.45 to 0.6. Data from Leemann et al. Q8

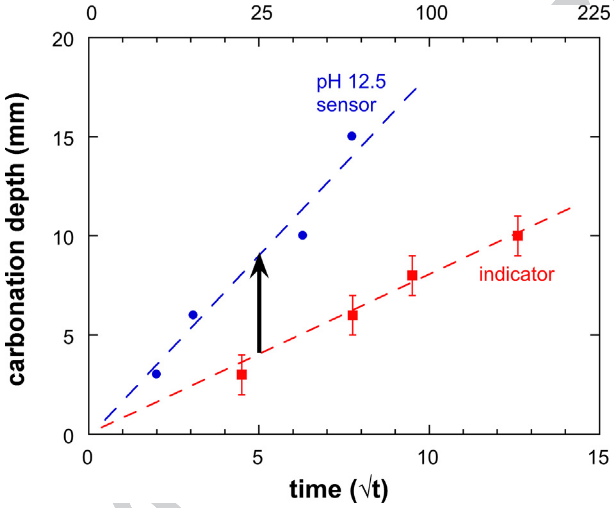
ELSEVIER FIRST PROOF

To protect the rights of the author(s) and publisher we inform you that this PDF is an uncorrected proof for internal business use only by the author(s), editor(s), reviewer(s), Elsevier and typesetter SPi. It is not allowed to publish this proof online or in print. This proof copy is the copyright property of the publisher and is confidential until formal publication.

These proofs may contain colour figures. Those figures may print black and white in the final printed book if a colour print product has not been planned. The colour figures will appear in colour in all electronic versions of this book.



f0035 **Fig. 6** Evolution of the pH of the pore solution with time measured in situ with the new pH sensor at 3, 6, and 15 mm cover depth during accelerated carbonation (4% CO_2, 65% RH).



f0040 **Fig. 7** Carbonation depth versus √time for pH 12.5 (in situ with the sensor) and full carbonation (indicator test with phenolphthalein).

ELSEVIER PROOF

It was found that carbonation is a two-step process (Fig. 6); in a first phase, the pH drops to about 12.5—this occurs relatively fast and can be interpreted as reaction of the dissolved alkaline components of the pore solution with CO_2. Afterwards, the pH remains almost constant at about 12.5, the duration of this phase depends on the amount of the solid alkaline reserve of Portlandite ($Ca(OH)_2$). In this phase, the alkaline reserve based on the solid $Ca(OH)_2$ is progressively dissolved, neutralized by CO_2 and calcium carbonate is formed. Finally, a rapid drop of the pH occurs when the residual pore solution of pH 12.5 is neutralized. The results obtained with the pH sensor clearly document that CO_2 penetrates in the open pore system far beyond the actual carbonation front as determined usually with the indicator test (Fig. 7).

p0085 On the one hand, the new in situ pH sensors can be used in the future to test the carbonation process of new, blended cements, in a more rapid and rational way than with indicator spray tests. More importantly, the results obtained with the sensors have consequences for the durability of reinforced concrete structures compared to complete carbonation (drop of pH to about 9), the front of pH 12.5 penetrates much more rapidly into concrete. A drop in pH from 13.5 to 12.5 means a reduction of the OH^- concentration by a factor of 10. Considering that depassivation of passive steel requires an average ratio of chloride ions to hydroxide ions, $Cl^-/OH^- = 0.6$, corrosion initiation on passive reinforcing steel at pH 12.5 would require 10 times less chloride ions than at pH 13.5. This has to be taken into account when studying the critical chloride content C_{crit} for corrosion initiation.

s0045 Corrosion Rate in Carbonated Concrete

p0090 More than 40 publications regarding corrosion of steel in carbonated concrete published in the last 50 years were analyzed in a recent review by the authors. It emerges that the main parameters that influence the corrosion rate of steel in carbonated mortar and concrete are the exposure conditions, the type of binder, and the water/binder ratio.

To protect the rights of the author(s) and publisher we inform you that this PDF is an uncorrected proof for internal business use only by the author(s), editor(s), reviewer(s), Elsevier and typesetter SPi. It is not allowed to publish this proof online or in print. This proof copy is the copyright property of the publisher and is confidential until formal publication.

These proofs may contain colour figures. Those figures may print black and white in the final printed book if a colour print product has not been planned. The colour figures will appear in colour in all electronic versions of this book.

p0095 Atmospheric exposure conditions with varying RH (exposure class XC3) are frequently encountered inside buildings or in sheltered conditions outside and are thus of great practical relevance. As a general trend, the corrosion rate increases with higher RH in the environment; exposure to about 50% RH shows negligible corrosion rates, exposure to about 95% RH shows much higher values. The corrosion rate in 95%–100% RH corresponds to 5–20 μm/year loss of cross section, which is considered significant. In wet or partially immersed conditions (exposure class XC4), corrosion rates are even 2–4 times higher than in high RH environment. All the publications in the review of the present authors report consistently higher corrosion rates in exposure class XC4, suggesting that contact with water is the most aggressive condition in terms of carbonation-induced corrosion.

p0100 Regarding the influence of the binder type, generally higher corrosion rates can be observed in blended cements compared to pure OPC. This increase in corrosion rate with clinker substitution is very significant (more than by a factor 5) for partially or fully immersed conditions. In the humidity range from 95% to 65% RH, a modest increase in corrosion rate with clinker replacement is observed. At low RH (50%), the corrosion rate in all samples is very low (<1 μm/year) and the effect of clinker substitution is irrelevant.

s0050 Mechanism of Corrosion of Steel in Carbonated Concrete

p0105 Despite the valuable information summarized in the review on corrosion rate of steel in concrete, the mechanism of corrosion of steel in carbonated concrete is still not fully understood. Based on the quite universal correlation showing that the corrosion rate decreases with increasing concrete resistivity, a mechanism based on ohmic control has generally been assumed. However, as corrosion of steel in carbonated concrete develops as uniform corrosion, where anodic and cathodic partial reactions occur very close by, ohmic control from a theoretical standpoint is not expected to play a significant role. In addition, the exponential dependence of the corrosion rate on the open circuit potential indicates anodic control of the corrosion reaction and is in contradiction to ohmic control. Thus, further systematic research is needed.

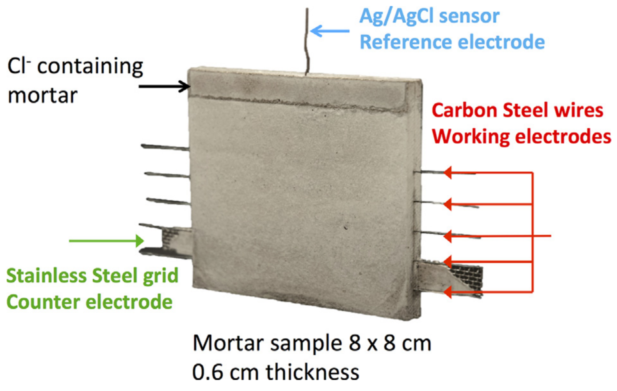
p0110 Data on corrosion of steel in carbonated concrete made with new blended cements are greatly missing. With the traditional approach of using relatively large reinforced concrete samples, the experiments are time consuming because (1) it takes a long time until the concrete is carbonated down to the steel and (2) equilibration to different exposure conditions (e.g., RH) takes long time due to the slow drying out of concrete.

p0115 A new, small, and light-weight setup has been developed and tested in our laboratory. The setup consists of an 8 cm × 8 cm wide mortar sample of only 0.6 cm thickness (Fig. 8). The fine mortar mix (sand of 1 mm) can be prepared with any cement and with *w*/*b* ratio from 0.4 to 0.6. In this sample, four steel wires, a platinum counter electrode, and an Ag/AgCl reference electrode are embedded, which allow all kinds of electrochemical measurements such as open circuit potential, linear polarization resistance, electrochemical impedance, and so on. Full carbonation of these thin samples took place between 2 and 3 weeks in a carbonation chamber (4% CO_2 and 65% RH), which is significantly shorter than in experiments using common sample dimensions. The samples were then exposed to different relative humidities (50%, 80%, 95%, and 99%) or ponded with water (wetting and drying).

p0120 The corrosion rate of steel in carbonated concrete—both in CEM I (OPC) and CEM II (CEM II/B-M (T-LL) 42.5 blended cement with limestone and burnt oil shell)—was found negligible at RH of 50% and 80% but increased markedly with higher RH (Fig. 9). The maximum was reached at 99% RH with 0.15 and 0.27 $\mu A/cm^2$ in CEM I and CEM II, respectively. The corrosion rate in the blended cement studied was about two times higher than in CEM I. The loss of about 3 μm/year in a cross-section is too high for long-term durability. When liquid water reaches the steel (exposure conditions XC4), the corrosion rate increased up to 20 μm/year.

p0125 Additional experiments have shown that the cathodic oxygen reduction reaction is always much higher than the corrosion rate—thus oxygen availability can be ruled out as rate controlling step. Ohmic resistance and corrosion rate were found to be proportional also in these studies, it was, however, concluded that this has to be considered as a purely empirical relationship. This can be explained by the fact that both the water content at the steel surface and in the pore system are interrelated.

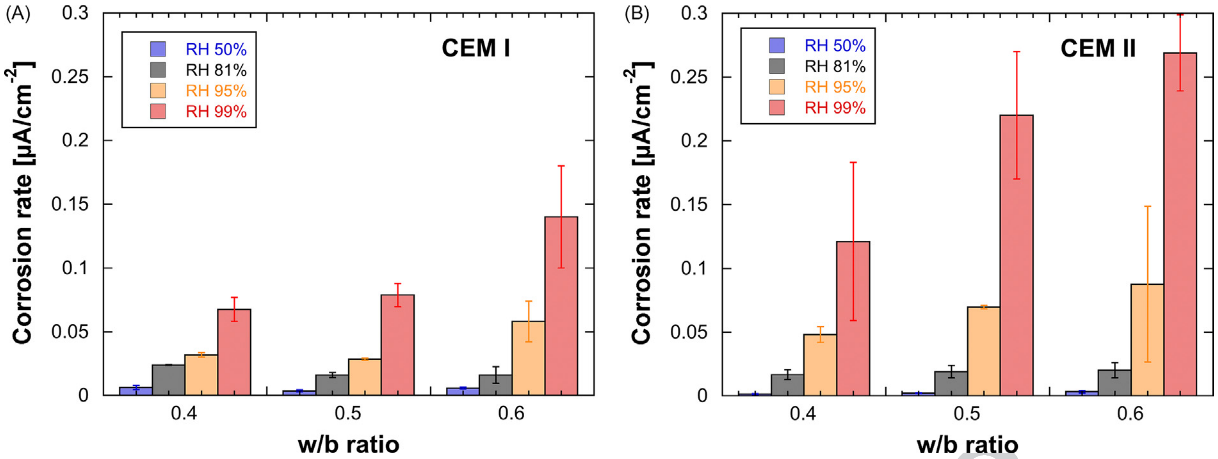
ELSEVIER FIRST PROOF



f0045 **Fig. 8** Photograph of the new setup to measure open circuit potential, corrosion rate, resistivity, and oxygen diffusion on steel in carbonated mortar.

To protect the rights of the author(s) and publisher we inform you that this PDF is an uncorrected proof for internal business use only by the author(s), editor(s), reviewer(s), Elsevier and typesetter SPi. It is not allowed to publish this proof online or in print. This proof copy is the copyright property of the publisher and is confidential until formal publication.

These proofs may contain colour figures. Those figures may print black and white in the final printed book if a colour print product has not been planned. The colour figures will appear in colour in all electronic versions of this book.



f0050 **Fig. 9** Corrosion rate of steel in carbonated concrete for (A) CEM I (ordinary Portland cement) and (B) CEM II/B-M (T-LL) 42.5 at different relative humidities and *w/b* ratios.

s0055 Critical Chloride Content

p0130 As shown in the section "Fundamentals," the critical chloride content C_{crit} necessary to depassivate the reinforcing steel in alkaline concrete has received a lot of interest in literature. The literature results scatter over two orders of magnitude and offer a poor basis for service life modeling. The influence of both chloride ions and pH of the pore solution was broadly taken into account by expressing the ratio of them. From the conceptual idea to link the critical chloride content to the critical (average) ratio of $Cl^-/OH^- = 0.6$, it would be expected that C_{crit} should vary systematically for different cement types, steel grades, and so on, but it was found that other effects, generally summarized as "local defects" were not systematically related to the materials under test, play a major role in corrosion initiation. RILEM technical committee 262-SCI has published a review and made a first attempt how to describe the different influencing "defects" at the steel concrete interface such as air voids, bleed water zone, the presence of mill-scale, and so on.

s0060 A New Way to Determine C_{crit}

p0135 One of the main disadvantages identified in the context of the complex steel concrete interface is the fact that most of the tests to determine C_{crit} are performed on relatively young reinforced concrete samples prepared in the laboratory. The possible positive effects of aging of the concrete and the passive film as well as the possible negative effects of a less homogeneous steel concrete interface on C_{crit} are not taken into account, so both the absolute values of C_{crit} and its statistical distribution determined on laboratory samples might not be representative for old reinforced concrete structures. For service life prediction of new and existing structures, this might lead to a very conservative approach.

p0140 Recognizing this, a new test method was recently suggested by the authors to measure the statistical distribution of C_{crit} in samples taken from structures. Based on half-cell potential condition assessment, areas with noncorroding reinforcement are determined and 10–15 concrete cores of diameter 150 mm, containing a segment of reinforcing steel, were drilled from this about 2 m^2 small area. C_{crit} was subsequently determined in the laboratory. The results from a more than 40 years old road tunnel ceiling showed a probability distribution of C_{crit} (Fig. 10). Compared to statistical distribution of C_{crit} from laboratory experiments, both average and standard deviation of the field tests were higher and in good agreement with other early data from bridge decks.

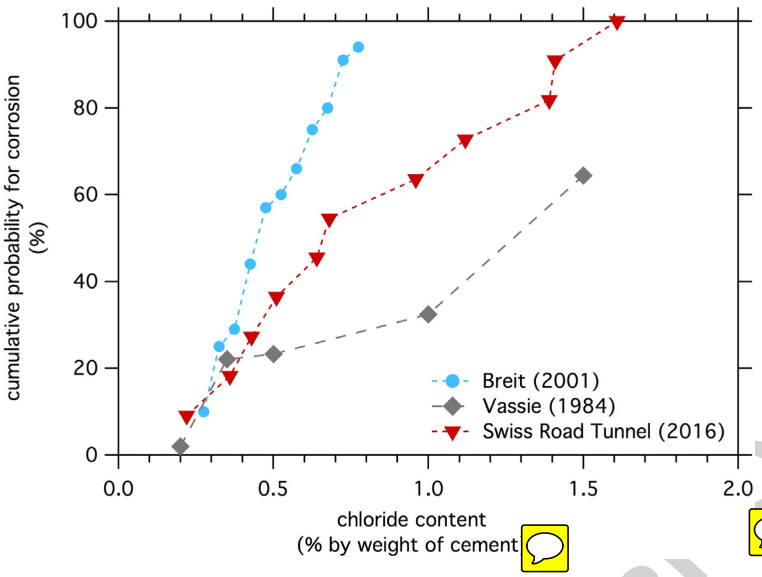
s0065 Influence of Specimen Size

p0145 Based on the concept that local "defects" are initiation sites for the onset of chloride-induced corrosion (see section "Fundamentals"), the experimentally documented fact that localized corrosion both on stainless steel in neutral solutions and on black steel in alkaline solutions is a function of the specimen size, can be explained by the increasing probability of the presence of preferable initiation sites (defects) with increasing specimen size. This has been shown recently also for steel in concrete by experiments performed by the authors. Based on the experimentally determined distribution of C_{crit} on small samples, the distribution of C_{crit} on large samples could be predicted by applying the weakest link theory. This mathematical approach permits transforming C_{crit} values determined on a series of small specimens to larger specimen size and finally to engineering structures. This "size effect" of the corrosion initiation raises the question of the correct sample size to determine the chloride threshold value C_{crit} and the question of extrapolating small laboratory scale results to large dimensions of real structures. Further research is needed to deliver the scientific basis that allows to implement this in engineering practice.

ELSEVIER FIRST PRO

To protect the rights of the author(s) and publisher we inform you that this PDF is an uncorrected proof for internal business use only by the author(s), editor(s), reviewer(s), Elsevier and typesetter SPi. It is not allowed to publish this proof online or in print. This proof copy is the copyright property of the publisher and is confidential until formal publication.

These proofs may contain colour figures. Those figures may print black and white in the final printed book if a colour print product has not been planned. The colour figures will appear in colour in all electronic versions of this book.



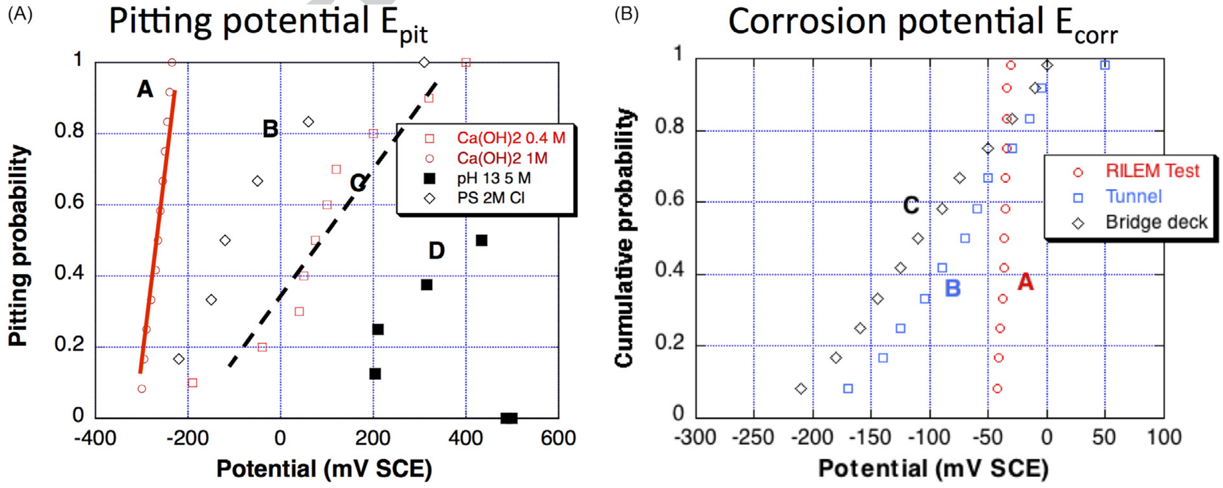
f0055 **Fig. 10** Cumulative probability for chloride-induced corrosion comparing laboratory tests (Breit, 2001) and field tests (Vassie, 1984; Swiss Road tunnel, 2016). Q2

ELSEVIER FIRST PROOF

s0070 Electrochemical Aspects

p0150 From an electrochemical point of view, depassivation due to chlorides occurs when the pitting potential, E_{pit}, is lower than the corrosion potential, E_{corr}, of the passive steel. With increasing chloride concentration in the pore solution, E_{pit} is shifted to more negative potentials. On the other hand, more corrosion resistant reinforcing steels (e.g., stainless steels) show much higher (more positive) pitting potentials. The corrosion potential, E_{corr}, of the passive steel depends on the pH of the pore solution and on the time of passivation, thus aging of the passive film. Both parameters, E_{pit} and E_{corr}, are however not constant values but are statistically distributed around a mean value (Fig. 11). In an aggressive situation (curve A: pH 12.5, 1 M Cl^-), the pitting potential measured on 10 samples is low and nearly constant, in a mild condition (curve C: pH 12.5 with 0.4 M Cl^-) the pitting potential is about 300 mV more positive but strongly distributed. The same is found for the corrosion potential when comparing laboratory and field results (Fig. 12B): in laboratory conditions E_{corr} is quite constant, on structures (only noncorroding areas were selected), the corrosion potential is much more distributed due to different pH and oxygen availability at the reinforcement.

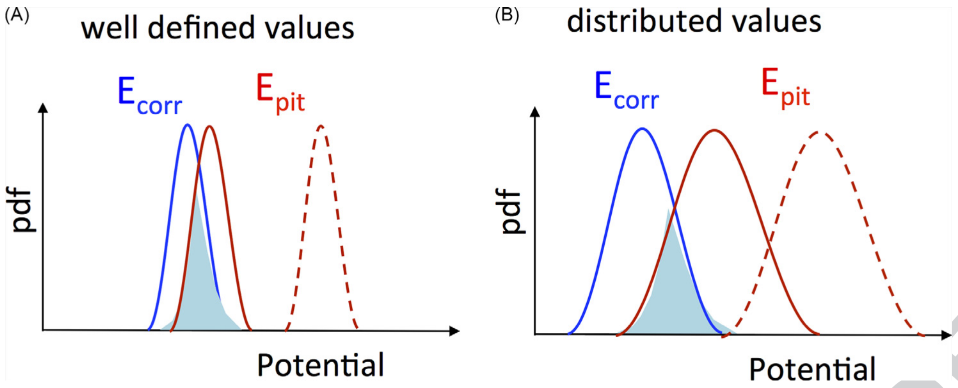
p0155 In consequence, the condition for depassivation usually given as $E_{pit} < E_{corr}$ is no more a "yes–no" answer, but depassivation of the steel in a given exposure condition will occur with a certain probability (Fig. 12). It still holds that the probability of depassivation is higher with lower E_{pit} (thus higher chloride ion concentration) and with more positive E_{corr} (thus with decreasing pH of the pore solution)—the more important result, however, is that for the same probability of depassivation (shaded area in Fig. 12) in the case of a narrow distribution (Fig. 12A), the mean values of E_{pit} and E_{corr} have to be very close, in the case of a broad



f0060 **Fig. 11** Statistical distribution of (A) the pitting potential E_{pit} for different exposure conditions and (B) the corrosion potential E_{corr} for laboratory samples (RILEM test) and RC structures (tunnel, bridge deck).

To protect the rights of the author(s) and publisher we inform you that this PDF is an uncorrected proof for internal business use only by the author(s), editor(s), reviewer(s), Elsevier and typesetter SPi. It is not allowed to publish this proof online or in print. This proof copy is the copyright property of the publisher and is confidential until formal publication.

These proofs may contain colour figures. Those figures may print black and white in the final printed book if a colour print product has not been planned. The colour figures will appear in colour in all electronic versions of this book.



f0065 **Fig. 12** Schematic representation of the pitting probability (shaded area) for (A) E_{corr} and E_{pit} have a narrow distribution and (B) E_{corr} and E_{pit} have a broad distribution (*y* axis is probability density function).

distribution (Fig. 12B) pitting can occur also when the mean value of E_{pit} is much more positive than the mean value of E_{corr}. This explains the stochastic nature of pitting corrosion and early results regarding initiation of chloride-induced corrosion (Fig. 2). A model to fully describe and predict the critical chloride content does not yet exist.

s0075 Conclusions

p0160 This article focuses on the present and future challenges in the field of durability of reinforced concrete structures as explained in recent studies with new insights. The following conclusions can be drawn: Q6

p0165 The massive use of blended cements with increasingly lower clinker content makes carbonation-induced corrosion, a serious durability issue. Due to the much higher carbonation rates of blended cements, the required service life of reinforced concrete structures can be reached only when including at least a part of the propagation stage, thus corrosion rate of steel in carbonated concrete has to be revisited.

p0170 Localized chloride-induced corrosion occurs on "weak spots" at the steel–concrete interface. It follows that with increasing sample size, the probability of such weak spots increases; indeed, it was found that the chloride threshold (critical chloride content, C_{crit}) to initiate corrosion decreases when larger samples are tested. As a consequence, using C_{crit} values determined on small samples in the laboratory for service life calculations, overestimations in the calculated service life might result.

p0175 Results from in situ pH measurements in cementitious materials show that CO_2 penetrates into the pore system fast and far beyond the carbonation front as determined with the indicator test and the pH decreases also in "noncarbonated" concrete. A decrease of one pH unit at the reinforcement level means that about 10 times less chloride ions are necessary to initiate localized corrosion, thus a slight decrease of the pH at the reinforcement might have significant effects on the durability.

Further Reading

Angst, U.; Elsener, B.; Larsen, C. K.; Vennesland, Ø. Critical Chloride Content in Reinforced Concrete—A review. *Cem. Concr. Res.* **2009**, *39*, 1122–1138.
Angst, U. M.; Hooton, R. D.; Marchand, J.; et al. Present and Future Durability Challenges for Reinforced Concrete Structures. *Mater. Corros.* **2012**, *63*, 1047–1051.
Angst, U. M.; Geiker, M. R.; Michel, A.; et al. The Steel–Concrete Interface. *Mater. Struct.* **2017**, *50*, 143, RILEM TC 262-SCI.
Angst, U. M.; Elsener, B. The Size Effect in Corrosion Greatly Influences the Predicted Life Span of Concrete Infrastructures. *Sci. Adv.* **2017**, 3. e1700751 published on-line 2nd august 2017. https://doi.org/10.1126/sciadv.1700751.
Angst, U. M. Challenges and Opportunities in Corrosion of Steel in Concrete. *Mater. Struct.* **2017**, accepted. Q7
Bertolini, L., Elsener, B., Redaelli, E., Pedeferri, P., Polder, R. (2013). *Corrosion of Steel in Concrete—Prevention, Diagnosis and Repair*, 2nd ed.; WileyWeinheim.
Elsener, B. Corrosion of Steel in Concrete. In *Corrosion and Environmental Degradation*; Schütze, M., Ed.; Materials Science and Technology; Wiley VCH: Weinheim, 2000; vol. 19.
Flatt, R. J.; Roussel, N.; Cheeseman, C. R. Concrete: An Eco Material That Needs to be Improved. *J. Eur. Ceram. Soc.* **2012**, *32*, 2787–2798.
Hausmann, D. A. Steel Corrosion in Concrete. How Does it Occur? *Mater. Prot.* **1967**, *6*, 19–23.
Leemann, A.; Nygaard, P.; Kaufmann, J.; Loser, R. Relation Between Carbonation Resistance, Mix Design and Exposure Condition of Mortar and Concrete. *Cem. Concr. Compos.* **2015**, *62*, 33–43.
Parrott, L. A review of carbonation in reinforced concrete. In *Cement and Concrete Association Report C/1-0987*, Cement and Concrete Association, 1987. Q9
Polder, R. B.; Peelen, W. H. A.; Courage, W. M. G. Non-Traditional Assessment and Maintenance Methods for Aging Concrete Structures—Technical and Non-Technical Issues. *Mater. Corros.* **2012**, *63*, 1147–1153.
Segui, Y.; Angst, U. M.; Elsener, B. pH-Monitoring in Mortar With Thermally Oxidized Iridium Electrodes. *RILEM Lett.* **2017**, submitted. Q10
Stefanoni, M.; Angst, U.; Elsener, B. Innovative Sample Design for Corrosion Rate Measurements in Carbonated Concrete. In *11th International Concrete Sustainability Conference (ICSC), 2016 May 15–18, Washington, DC*, 2016. Q11
Stefanoni, M.; Angst, U.; Elsener, B. Corrosion Rate of Carbon Steel in Carbonated Concrete—A Review. *Cem. Concr. Res.* **2017**, submitted. Q12

ELSEVIER FIRST PROOF

To protect the rights of the author(s) and publisher we inform you that this PDF is an uncorrected proof for internal business use only by the author(s), editor(s), reviewer(s), Elsevier and typesetter SPi. It is not allowed to publish this proof online or in print. This proof copy is the copyright property of the publisher and is confidential until formal publication.

These proofs may contain colour figures. Those figures may print black and white in the final printed book if a colour print product has not been planned. The colour figures will appear in colour in all electronic versions of this book.

IFCC: 13435

Non-Print Items

Abstract:

Reinforced concrete is the most used construction material worldwide, especially for civil infrastructures, with a long and proven track record regarding structural safety and durability. This technology faces new challenges that are as follows: (1) in industrialized countries, the aging stock of assets needs high maintenance and repair with very high costs and (2) in emerging countries, a great part of the infrastructure has to be built now as well as in the future in a durable way. For both situations, this means to combine long-service life and low environmental footprint of the materials used. To reduce the environmental impact of building industry, more and more blended cements with increasingly lower clinker content will be used—with possible negative effects on the durability. Civil engineering has to move forward from an empirical-based technology to a more science-driven way that allows understanding deterioration mechanisms and service life prediction. This article briefly presents the fundamentals of durability of RC structures. Focusing on the challenges "new blended cements," it is shown how the use of new sensors and measuring setups can contribute to the understanding of the carbonation mechanism and the corrosion rate of steel in carbonated concrete. Finally, some new aspects to the everlasting research challenge "critical chloride content" both from experimental and theoretical side are presented.

Keywords: Blended cements; Carbonation; Corrosion rate; Critical chloride content; Durability; Initiation of corrosion; In situ pH sensor; Pore solution; Reinforced concrete; Relative humidity; Service life prediction; Size effect on corrosion initiation

To protect the rights of the author(s) and publisher we inform you that this PDF is an uncorrected proof for internal business use only by the author(s), editor(s), reviewer(s), Elsevier and typesetter SPi. It is not allowed to publish this proof online or in print. This proof copy is the copyright property of the publisher and is confidential until formal publication.