Corrosion rate of steel in carbonated concrete – new test setup and first results

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Abstract

The major concern of building industry is sustainability of reinforced concrete structures – thus using cements with low CO_2 emissions that allow producing structures with long-term durability. Clinker substitution of up to 65% is nowadays allowed according to European and Swiss standards, but the use of these new blended cements is limited due to the higher carbonation rate and the resulting uncertainty regarding carbonation-induced corrosion of the reinforcement. In literature only few data on the corrosion rate of steel in carbonated concrete are available, originating mainly from studies with ordinary Portland cement. In order to reach sustainability of concrete structures made with new blended cements, corrosion rate data are needed, because the so called "corrosion propagation stage" might be a significant part of the total service life. An innovative test setup consisting in small and thin mortar samples with a size of 80 x 80 x 6 mm is presented that allows fast carbonation and equilibration to changing environmental conditions. Five steel wires, counter electrode and reference electrode are embedded in the samples and corrosion rate of steel in carbonated samples can be studied by electrochemical methods at any relative humidity in a short time. The first results show that new binders could be more susceptible to corrosion in certain exposure conditions. Up to 20 μm/year were measured in wet conditions whereas below 80% the corrosion rate has been found negligible.

Keywords

Steel corrosion, carbonated concrete, relative humidity, corrosion rate, supplementary cementitious materials (SCM)

Riassunto

La principale preoccupazione dell'industria edile è la sostenibilità delle strutture in calcestruzzo – cioè utilizzando cementi a bassa emissione di CO_2 costruendo strutture durevoli. Mentre la sostituzione del clinker fino al 65% è permesso dagli standard europei, l'utilizzo di questi nuovi cementi miscelati è ancora limitato a causa della maggiore velocità di carbonatazione e della conseguente incertezza sulla corrosione delle armature. Nella letteratura sono disponibili solo pochi dati sul tasso di corrosione dell'acciaio in calcestruzzo carbonatato, derivanti principalmente da studi condotti in cemento Portland. Al fine di raggiungere la sostenibilità delle strutture realizzate con nuovi cementi miscelati, sono necessari dati riguardanti la velocità di corrosione, perché la fase di propagazione della corrosione potrebbe rappresentare una parte rilevante della vita utile delle strutture. E stato sviluppato un test innovativo che si basa su campioni di malta sottili e di piccole dimensioni (80 x 80 x 6 mm); ciò consente sia una carbonatazione veloce sia il raggiungimento di condizioni di equilibrio in diverse condizioni ambientali. Cinque fili d'acciaio, il contro elettrodo e l'elettrodo di riferimento sono incorporati nei campioni e la velocità di corrosione dell'acciaio in campioni carbonatati può essere misurata con tecniche elettrochimiche a ogni umidità relativa in breve tempo. I primi risultati mostrano che i nuovi leganti potrebbero essere più suscettibili alla corrosione in determinate condizioni di esposizione. Sono state misurate velocità di corrosione pari a 20 μm / anno in condizioni bagnate mentre al di sotto dell' 80% umidità relativa la velocità di corrosione è risultata trascurabile.

Parole Chiave

Corrosione, calcestruzzo carbonatato, umidità relativa, velocità di corrosione, nuovi cementi

Introduction

In the last years a lot of attention has been directed to environmental issues: global warming, ice melting and greenhouse gases are just few examples. In the 2015 United Nations Climate Change Conference that took place in Paris, where 197 nations agreed on the necessity of a global commitment, declaring the reduction "as soon as possible" of the CO_2 emissions in order to reach a "balance between anthropogenic emissions by sources and removals by sinks". According to *Trends in global CO_2 emissions: 2015 Report* [1] cement production accounts for roughly 8% of global CO_2 emissions, including endogenic emission by carbonate calcination and indirect emission by fuel consumption.

The cement industry made great efforts; a solution to reduce the environmental impact of cement production has been found in the reduction of the clinker content in modern binders. A study by the *Cement Sustainability Initiative* (CSI) [2] has shown that the share of blended cement has considerably increased in most countries, lowering the clinker fraction to between 60% and 80% and leading to emission reduction of about 20%. Even greater reduction of the clinker content will be possible in the future. Uncertainty about durability, especially carbonation-induced corrosion of the reinforcing steel, is the main factor limiting the practical use of these blended cements. The increased risk of carbonation is due to the inherent chemical properties of the blended systems, in particular the reduced pH buffering capacity due to the decreased calcium hydroxide content:

- Lower amount of calcium hydroxide formed during the hydration reaction [3], as consequence of a reduced amount of CaO with respect to Ordinary Portland Cement depending on the type and amount of substituents;
- Consumption of Portlandite [3, 4, 5] in presence of SiO_2-rich components by the pozzolanic reactions.

For these reasons the carbonation rate, viz. the penetration of the carbonation front in the concrete matrix, is faster in case of blended cements as documented in comprehensive reviews [6, 7] for slag (GGBS) and for fly ash concrete.

Factors that affect the rate of carbonation of concrete and thus lead to a shorter induction period for the onset of a corrosion process (Fig. 1) are thus well documented. It becomes obvious that also the propagation-stage of corrosion in carbonated concrete has to be taken into account in order to reach the required service life. Factors that influence the rate of corrosion of steel in concrete that has been depassivated as a consequence of carbonation are by far less investigated. Despite variables such as relative humidity or temperature are known to influence corrosion rates in carbonated concrete [8], the corrosion rate can not be predicted due to scarse laboratory data and field experience [9] and mechanistic understanding. Nevertheless, substitution of clinker up to 65% is now possible according to European and Swiss cement standards - but a widespread commercialization and use of such new binders is possible only after ensuring minimum service life requirements in order to reach durable structures and thus to meat the target sustainability of cement industry. This paper presents an innovative sample design for corrosion rate measurements of steel in carbonated concrete and first results obtained, in part presented at international conferences [10, 11, 12].

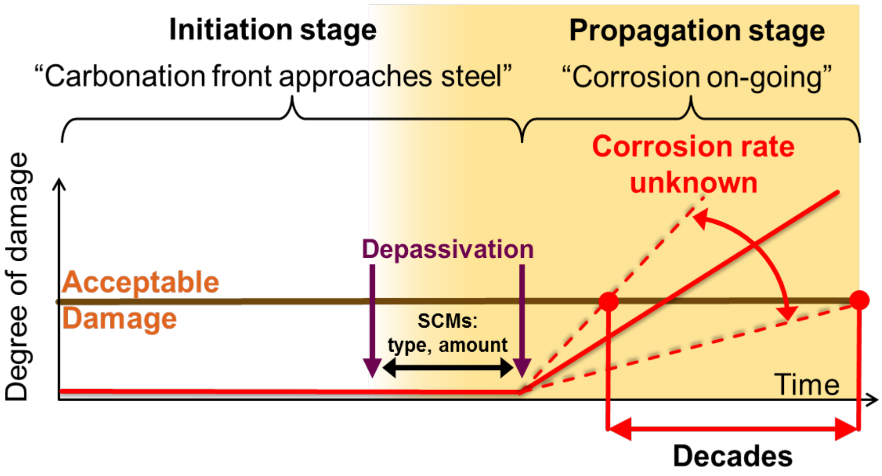

Figure 1: Schematic representation of the service life of a reinforced concrete structure (Tuutti diagram) showing the importance of the propagation-stage of corrosion in carbonated concrete.

Summary of literature results

Carbonation of 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. 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). The codes of practice since then give guidance for reinforced concrete (maximum w/c ratio, minimum cement content, minimum cover depth) made with Portland cement (CEM I) on how to avoid carbonation induced corrosion for structures with expected service life of 50 or 100 years. As the initiation time (Fig. 1) was long enough, the corrosion rate of steel in carbonated mortar or concrete (propagation phase) was no more of interest for service life considerations and only few papers studied this topic.

Today, the topic of corrosion of steel in carbonated concrete became of great interest again (Figure 2) for two reasons: first, many old structures have reached their service life and the carbonation front is approaching the reinforcement; second, in the new blended cements carbonation penetrates much faster and the propagation phase can become a significant part of the total service life (see introduction).

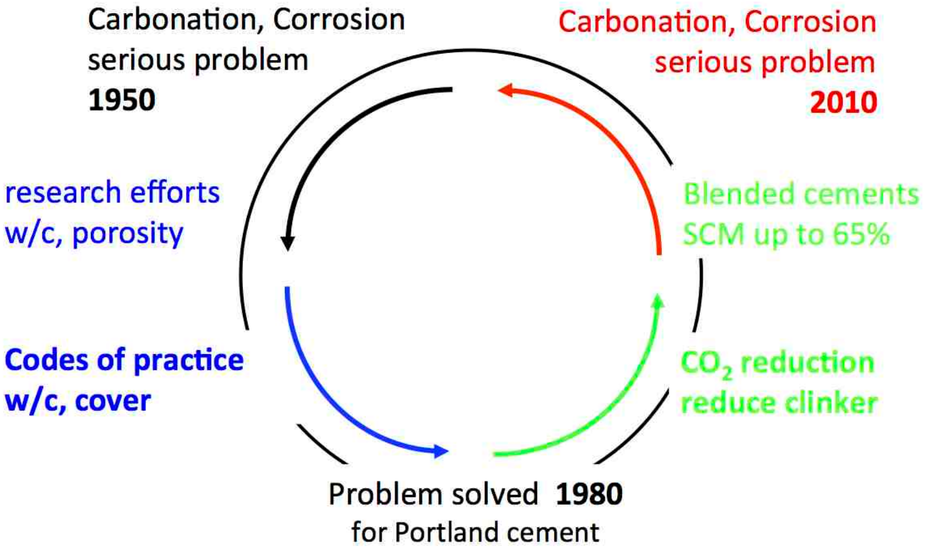

Figure 2: The “carbonation cycle” showing the evolution in time of the topic “corrosion of steel in carbonated concrete”

More than 40 publications regarding corrosion of steel in carbonated concrete published in the last 50 years were analyzed in a recent review [9]. 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. Atmospheric exposure conditions with varying relative humidity (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 relative humidity in the environment: exposure to about 50% relative humidity (RH) show negligible corrosion rates, exposure to about 95% RH show much higher values. The corrosion rate in 95 – 100% RH correspond 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 to 4 times higher than in high relative humidity environment. All the publications in the review [9] 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.

New test setup

Test setup: Experiments to measure corrosion rate of steel in carbonated mortar have been found to be very time consuming due to the long time necessary for full carbonation of the sample and – once carbonated – to equilibrate with the environmental relative humidity [9]. To overcome this limitation, a new experimental set up has been designed. The new test setup consists of small (8 x 8 cm) and thin (0.6 cm) cement mortar samples instrumented with a reference electrode, 5 steel wire electrodes and a stainless steel grid counter electrode (Fig. 3).

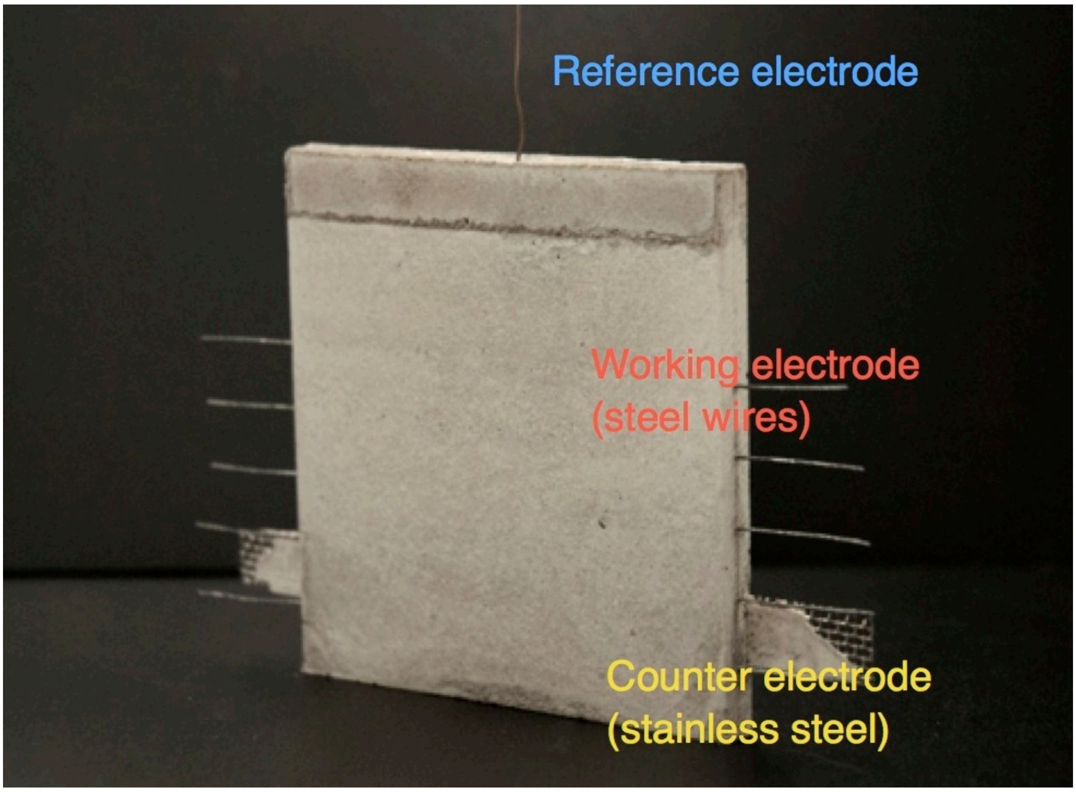

Figure 3: Picture of the mortar sample (8 x 8 x 0.6 mm) with embedded working, counter and reference electrode to perform electrochemical tests.

The thin sample allows rapid full carbonation (max 3 weeks in 4% CO_2) and rapid equilibration of environmental humidity (checked by the sample weight). The samples reached stable conditions after two weeks maximum (Fig. 4). The weight loss going from 95% RH to 65% RH was 0.5%, going from 95% RH to 45% the weight loss was 1.4% [10]. Parameters that can be measured are electrical resistivity of the mortar, corrosion potential and corrosion rate (LPR measurements) of the steel wires, oxygen diffusion and oxygen consumption rate. From these data the mechanism of steel corrosion in carbonated concrete made of different blended cements can be evaluated. The experimental setup is described in more detail in reference [10].

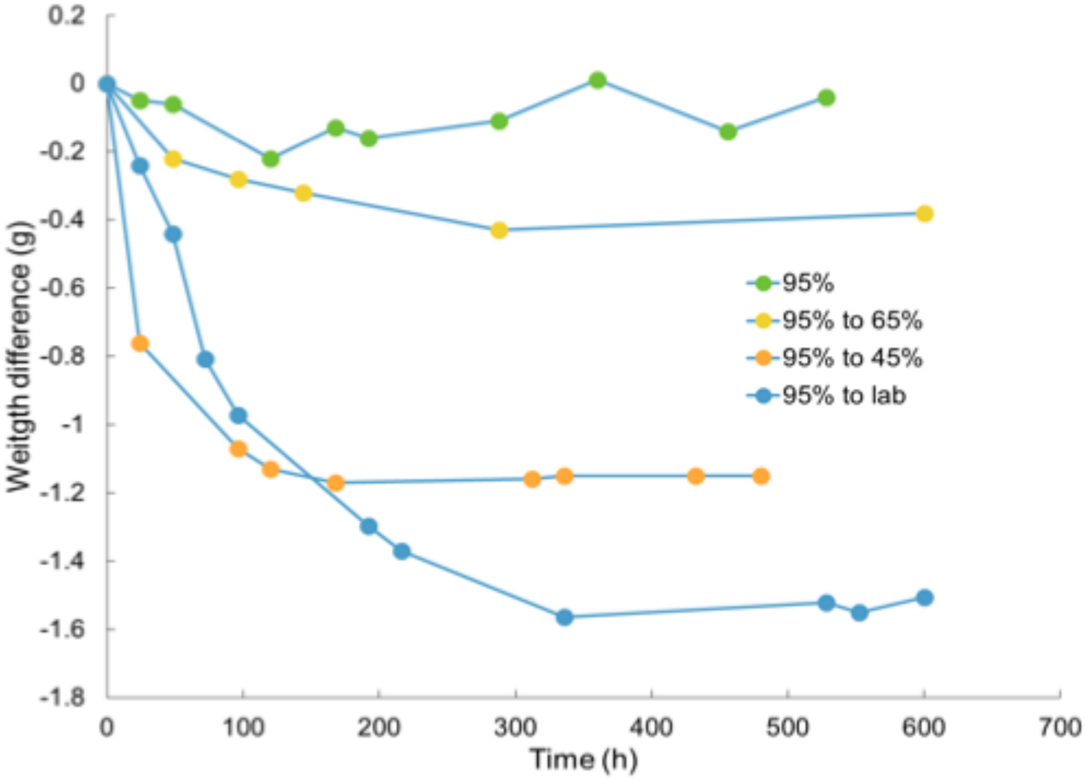

Figure 4: Time to equilibration of the sample weight during change of the relative humidity of the environment.

Mortar mix: For the realization of the mortar samples Holcim Optimo 4 cement (CEM II/B-M (T-LL) 42.5) and Holcim Normo 5R (CEM I 52.5 R) were used. The w/b ratios tested were 0.4, 0.5 and 0.6; the sand/binder ratio was 2 and the sand had a maximum particle diameter of 1mm. A poly-carboxylate ether superplasticizer with de-foaming agent was added to the mix in order to control the fluidity and be able to fill the mould. The mix design was chosen to allow good fluidity while maintaining a high stability of the cementitious suspension.

Carbonation and exposure: The samples were carbonated in a carbonation chamber with controlled atmosphere at room temperature, 65% relative humidity and 4% CO_2 concentration. The time required for complete carbonation was 2 weeks for CEM II mortars and 3 weeks for CEM I mortars. Complete carbonation was ensured by the phenolphthalein test.

The carbonated samples were exposed to different constant environments (50% and 95% relative humidity and 20 °C). Another series of experiments studied the response to wet and dry cycles, samples have been provided with a silicon sealed wall for the ponding solution (more details see in [11]).

Corrosion rate measurements: Open circuit potential (OCP) and linear polarization resistance (LPR) were measured with a Metrohm Autolab PGSTAT30 potentiostat. The embedded Ag/AgCl sensor was always used as reference electrode and its reference potential was checked by means of an external Ag/AgCl reference electrode. LPR measurements were performed at ± 10 mV versus OCP with a sweep rate of 0.05 mV/sec. The corrosion rate of the steel in carbonated mortar, i_{corr}, was calculated with the Stern-Geary equation from the polarization resistance Rp

$$i_{corr} = B / Rp$$

with B = 0.026 V (actively corroding steel) after correcting the measured polarization resistance for the ohmic drop [11].

Corrosion rate of steel in carbonated mortar

Exposure conditions XC3 – constant relative humidity

At 50% RH the corrosion rate of steel in carbonated CEM I (ordinary Portland cement) and CEM II samples (specifically CEM II/B-M (T-LL) 42.5, containing limestone and burnt oil shells) at all w/c ratios from 0.4 to 0.6 was lower than 0.01 $\mu A/cm^2$ (lower then 0.1 µm/year), thus negligible (Fig. 5). Initially the corrosion rate slightly increased over time, together with the corrosion potential shifting to slightly more negative values for both cement types. At 50% RH no significant influence of the w/b ratio in terms of final corrosion rate was found.

At 95% RH corrosion rates were higher for samples made with blended cement (CEM II) and higher w/c ratio, but overall found to be lower than 0.1 µA/cm^2 (1 µm/year) (Fig. 5). Also in this case, in the first period of exposure, the corrosion rate increased slightly with time and the corrosion potential decreased, for both cement types.

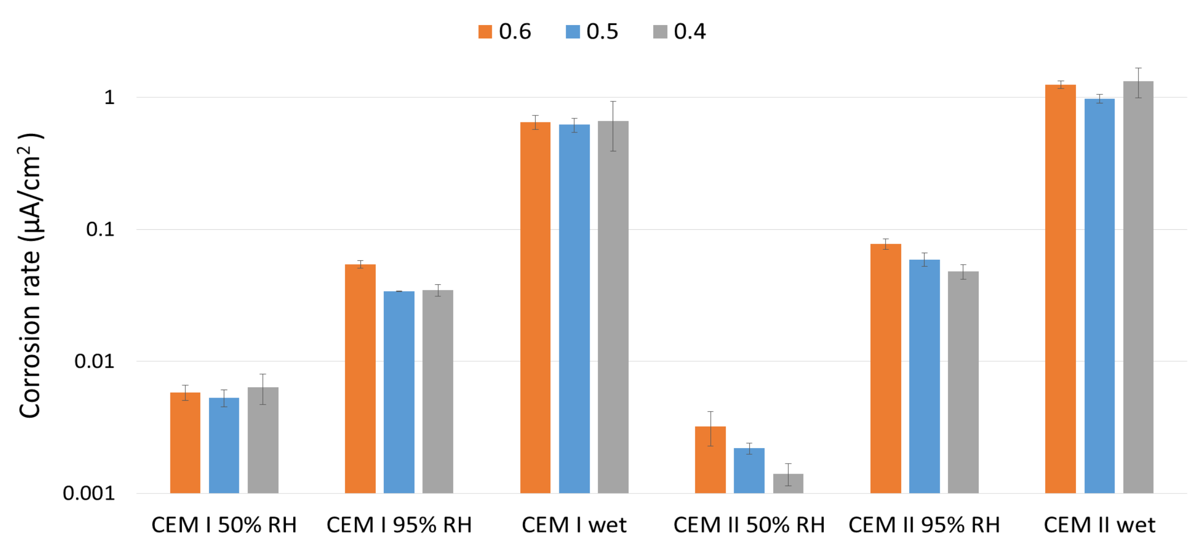

Figure 5: Corrosion rates measured for exposure condition XC3 with 50% and 95% relative humidity for w/c ratio 0.4, 0.5 and 0.6 and two types of binder (for wet-dry cycles the maximum value for each cycle was taken).

The parameter that is decisive for the corrosion rate of steel in carbonated concrete is the relative humidity of the environment – the corrosion rate increases strongly with RH. The other parameters such as w/b ratio and cement type are less important. Nevertheless it can be stated that for the specific type of blended cement used in this study the corrosion rates are about twice as high as in samples made of CEM I.

Exposure conditions XC4 - wetting and drying

In wet or partially immersed conditions (exposure class XC4) where liquid water arrives at the reinforcement, corrosion rates of steel in mortar made of CEM I were found from 2 to 4 times higher than in high humidity environment [9]. This suggests that the contact with water is the most aggressive condition in terms of carbonation-induced corrosion. The new test-setup allowed studying also the behavior during wetting and drying of the mortar samples. As shown in Fig. 6, wetting leads to a rapid and drastic decrease in the polarization resistance from about 2 MΩcm^2 to 20 kΩcm^2, corresponding to an increase in corrosion rate from 0.01

μA/cm^2 to about 2 μA/cm^2 (maximum corrosion rate 20 μm/year) in CEM I (Fig. 6). The open circuit potentials during wetting decreased to nearly – 1.0 V vs SCE.

The subsequent drying out of the samples took much longer time (about 50 h). Note that here for the first time open circuit potential and corrosion rate data were recorded during the drying out stage of the samples. Repetitive cycling did not influence the open circuit potentials of the steel in carbonated concrete, but the corrosion rate in the wet phase decreased going from the first to the second wet/dry cycle (Fig. 6). The data obtained from two steel wires in the same sample were in good agreement.

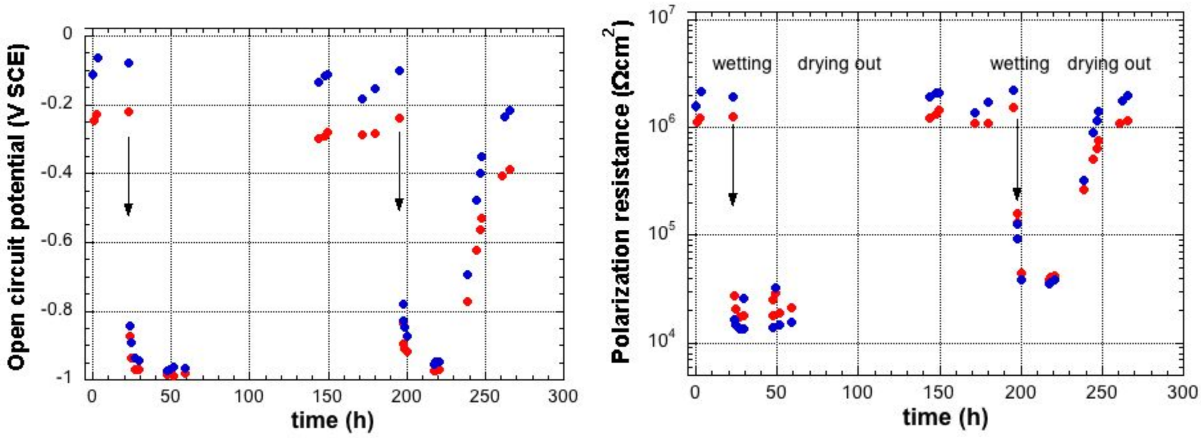

Figure 6: Variation of the open circuit potential (left) and the polarization resistance (right) during two wet-dry cycles on steel in carbonated mortar made of CEM I (measurements on two steel wires per sample)

Practical consequences

After carbonation, blended cements have been found to develop a coarser pore size distribution that might influence the corrosion behavior, leading to a higher dissolution rate in a humid/wet environment. In wet conditions (XC4) steel in carbonated mortar made of the CEM II studied in this work showed a corrosion rate higher by a factor up to 2 compared to mortar made with CEM I. Keeping in mind that depassivation of steel in blended cements occurs at shorter times, the total amount of corrosion in the propagation stage becomes important. In analogy to the “time of wetness” used to assess the total corrosion in atmospheric corrosion, a similar concept could be introduced also for corrosion of steel in carbonated mortar. Thus for a safe, long-term durable and sustainable application of blended cements it might be not sufficient to consider the general exposure class (XC3 or XC4) but a careful evaluation of the site specific conditions (micro-climat) is necessary. The most critical situations might arise when long, dry periods that favor carbonation of concrete are alternating with periods of wetting.

Conclusions

Due to the higher carbonation rate of blended cements the loss of alkalinity at the steel surface might occur before the end of the service life of a structure. The so-called propagation phase might become a substantial part of the service life.

For this reason corrosion rate data of steel in carbonated concrete made of a great variety of cement blends and at different environmental conditions have to be determined.

The new test-setup based on small and thin, instrumented mortar samples as described above, has been found a suitable solution for fast testing of carbonation induced corrosion behavior of new binder compositions.

The corrosion rate of steel in carbonated concrete is mainly governed by the environmental conditions (high RH or wetting), the type of cement and the w/b ratio are less important.

For a safe and sustainable application of blended cements it might be not sufficient to consider the general exposure class (XC3 or XC4) but a careful evaluation of the site specific conditions (micro-climat) is necessary.

Acknowledgements

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