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cemsuisse-Projekt 202004 – Februar 2023

Diese Forschungsarbeit wurde durch cemsuisse, Verband der Schweizerischen Cementindustrie mitfinanziert.



Eidgenössische Technische Hochschule Zürich Swiss Federal Institute of Technology Zurich

Cemsuisse research project 202004

Final report

Ensuring the durability of reinforced concrete structures during carbonation and alternating wet/dry exposure

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February 2023

Summary

This project employed different electrochemical methods to study the penetration of moisture into carbonated concrete and simultaneously monitor the corrosion behavior of embedded carbon steel bars. Mortar specimens with embedded sensors were produced from four different binders (CEM I, CEM II/B-LL, CEM II/B-M (T-LL), and CEM III/B) and with two w/b ratios (0.5 and 0.6). The specimens were carbonated and subsequently exposed to simulated XC4 exposure class conditions. These wetting / drying exposure conditions were simulated in the laboratory based on meteorological date representative for Zurich, which revealed that 95% of all rain events last shorter than 3 hours. In the experiments, it was observed that the cover depth plays an important role in controlling corrosion of steel in carbonated concrete. Appreciable variations in corrosion state of steel electrodes were mostly observed for steel bars at cover depths up to 20 mm. In all studied systems, the steel at a depth of 30 mm were largely unaffected during wetting periods of 3 hours duration. Differences between the mortars were clearly apparent. Carbonated CEM III/B mortars showed the highest water permeability and accordingly exhibited most pronounced reactions in terms of corrosion rates during wetting. Carbonated CEM I mortars showed the lowest water permeability results and accordingly, the reactions of the embedded steel bars to wetting were the least pronounced. Carbonated CEM II/B-LL and CEM II B-M (T-LL) mortars exhibited intermediate behavior. At w/b ratio 0.5, the steel reacted much less pronounced to wetting/drying exposure, compared to ratio w/b 0.6 for all binder types. In agreement with this, carbonated mortars with w/b=0.6 showed higher water permeability results than w/b=0.5. In all systems, the steel bars at a cover depth of 30 mm exhibited corrosion rates lower than 7 μ A/cm² (upon long wetting). For wetting phases with a duration of 3 hours, the corrosion rate at a cover depth of 30 mm hardly increased in all studied systems. Numerical simulations of moisture transport confirmed the findings of the experiments. The main conclusion is that the moisture state on the steel surface is one of the decisive factors for steel corrosion. If the moisture state can be well determined, the risk of steel corrosion could be well assessed and further mitigated by the moisture control methods.

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1. Introduction

Reinforced concrete is almost always exposed to the environment with CO₂, which can lead to concrete carbonation and thus potentially to reinforcement corrosion. Therefore, the current European and Swiss standards define exposure classes XC, and the concept of ensuring durability is based on requirements for reinforcement cover and resistance of the cover concrete against carbonation. The latter is ensured by the test method "carbonation resistance", for instance described in Annex I of the Swiss standard SIA 262/1. This approach is intended to ensure that the (mean) carbonation depth does not reach the reinforcement during the planned service life (XC4) or at most very late (XC3). However, the phase in which corrosion progresses after steel depassivation is not explicitly taken into account. After the depassivation of the reinforcement, the rate of corrosion is highly dependent on concrete moisture (environment) and concrete properties (porosity, moisture, etc). In exposure class XC3 in particular, the rate of corrosion remains very slow, while in XC4 a higher rate of corrosion must be assumed, at least temporarily (in the wet phases). In recent years, due to the pressure of reducing CO₂ emissions, various low-clinker cements have been developed. With the conventional normative approach, these new clinkerreduced cements are unequally treated as they are carbonated faster than the high-clinker cements.

In terms of sustainability, it is therefore essential to take reinforcement corrosion into account in the service life calculation using reliable, quantitative approaches. As has been shown, temporary wetting events play an important role (exposure class XC4) [1–3], namely the transport of moisture through the cover concrete and the interaction with the electrochemical corrosion processes on the reinforcing steel. The understanding of these processes is not sufficient today, primarily because the majority of studies on the durability of carbonated concrete focus on the carbonation process itself and less on the processes relevant to corrosion (moisture transport, electrochemistry).

2. Research objective

The aim of this project is to provide an experimental and theoretical basis to ensure the durability of carbonated concrete in exposure class XC4. Specifically, the understanding and modeling of reinforcement corrosion in carbonated concrete in wetting-drying exposure conditions should be improved. Due to the lack of reliable data, the current state of the art does not allow for a sufficient understanding and reliable quantitative description of these processes and the current standard approach leads to an unequal treatment of different cements.

In this project, a combined experimental and numerical approach is employed to investigate the moisture transport and corrosion processes, which take place inside the concrete as a result of exposure to the wetting-drying conditions. The corrosion rate of steel in carbonated mortar under cyclic wetting-drying exposure is measured. In particular, the influence of the binder type and the water-to-cement ratio on the corrosion rate is studied. Meteorological data for urban Zurich is analysed to assess how realistic the choice of wetting-drying cycles is, compared to natural rainfall on structures. A numerical model approach with a focus on moisture transport is developed and validated using experiments. This part of the model, i.e. the state of corrosion as a function of moisture development, can also be compared with the electrochemical measurement results.

3. Experimental

3.1 Specimen design

The exposure experiments were conducted on small mortar specimens (one specimen per mortar mix, see section 3.2 for materials). Figure 1 shows the dimensions $(100 \times 40 \times 30 \text{ mm}^3)$ of one specimen. In Figure 1 on the left, the six darker rods with a diameter of 4 mm on the left are carbon steel rods, that are placed at heights of 10, 20, and 30 mm, with two rods at each height. The six smaller rods with a diameter of 2 mm on the right are stainless steel rods, and they are placed at 5, 10, 15, 20, 25, and 30 mm. Both sets of steel bars are arranged in a staircase pattern to acquire data at different heights in the sample. The carbon steel bars are used for monitoring the corrosion potential over time, as well as to periodically determine the instantaneous corrosion rate via linear polarization resistance measurements. The stainless steel bars are used for electrical impedance measurements.



Figure 1. Left: Drawing of the specimen design (unit = mm). Right: Photograph of mortar specimen used for the exposure experiments. The small wires on the bottom are not relevant for the experiments discussed here.

3.2 Materials

Four binder types were used: CEM I and CEM II/B-LL, CEM II/B-M (T-LL), and CEM III/B. Each binder was used for two mortar mixes with water-to-binder (w/b) ratios of 0.5 and 0.6, respectively. The sand-to-cement ratio was 3:1 in all cases (max. grain size 4 mm). The 3 kg batches were mixed in a tabletop mixer according to the following protocol:

- Mix dry materials for 1 minute at the low speed
- Add water and mix for 2 minutes at the low speed
- Wait 2 minutes and continue mixing for 1 minute at the high speed
- Fill mould and vibrate <30 s on a vibration table

To avoid using form oil for demoulding, a reusable Teflon mould was produced. The specimens were demoulded after one day and cured at high relative humidity (>95%) for 2 months. After curing, the specimens were placed in a carbonation chamber with up to 90% CO₂. The carbonation progress was tested twice by spraying pH indicator on reference prisms ($40 \times 40 \times 160 \text{ mm}^3$) produced from the same batch and stored under identical conditions. Since the specimens were smaller than the reference prisms, a fully carbonated reference prism implied that the specimens were fully carbonated too.

Once they were fully carbonated, all four sides lateral of the specimens were covered with epoxy to reduce the effect of water evaporation and to ensure one-dimensional transport (perpendicularly to the embedded electrodes, see Figure 1). Next, the specimens were placed in a desiccator with a fixed relative humidity (RH) of 85% for conditioning, until their weight became stable.

3.3 Measurement setup

The experiments lasted around 48 hours and consisted of three wetting phases followed by drying phases. During the wetting phases, the bottom of the specimen was put in direct contact with water. During the drying phase, the bottom was in contact with air at ambient laboratory temperature and relative humidity. The durations of the drying and wetting phases are shown in Figure 2. The red dots indicate linear polarization resistance (LPR) measurements; these measurements give information with respect to the corrosion rate.



Figure 2. The durations of the wetting and drying phases for the exposure experiments (unit: hour).

Figure 3 shows the setup during the experiment. The reference electrode was placed on the top side of the specimen. Otherwise, the top of the specimen was sealed with parafilm. Therefore, ideally moisture could only enter or leave the specimens from below. During the experiment, two quantities were monitored continuously: firstly, the corrosion potential of the six carbon steel rods against the reference electrode, and secondly, the electrical impedance between four pairs of stainless steel wires. The numbering of the ten measurement channels is indicated in Figure 4. Except during the LPR measurements, which take about 30 minutes, the electrical potential and electrical impedance were acquired every 2 and 5 minutes, respectively.



Figure 3. A specimen during the wetting phase. The bottom of the sample is in contact with water. The stainless steel rods are connected to four channels of an impedance measurement board. The carbon steel bars on the right and the reference electrode are connected to six channels of a Keithley multimeter.



Figure 4. Measurement setup. The carbon steel bars on the left imitate steel reinforcements. The stainless steel bars on the right are connected in pairs to monitor the electrical impedance between them (the purple numbers indicate where the 2-point impedance measurements were taken).

3.3.1 Potential measurements

The electrical potentials of the six carbon steel bars (numbered 1-6 in Figure 4) were measured using a saturated silver/silver chloride/potassium chloride reference electrode (Ag/AgCl/sat. KCl, here referred to as SSE). A small sponge, wetted with tap water, on top of the specimen established the electrolytic contact. In addition, two additional capillaries with 0.01 M KCl solution were used to reduce the possibility of chloride contamination of the concrete surrounding the area where contact was established with the reference electrode. The sponge and the reference electrode were sealed as tight as possible to avoid the sponge drying out too quickly, as the influx of water from above had to be minimized to avoid influencing the electrical impedance measurements.

The 6 carbon steel bars were monitored simultaneously; two for each cover depth, that is, at distance 10, 20, and 30 mm from the bottom surface of the specimen. These measurements were implemented using a Raspberry Pi and a Keithley multimeter with a multiplexer. The measurement frequency was set to 2 minutes.

3.3.2 Impedance measurements

The electrical impedance measurements were realized with a proprietary impedance measurement board provided by the ETH spinoff Duramon. The board offers four channels, which can be set to read the impedance value once every 5 minutes. The board performs two-point AC impedance measurements at a given frequency of 1 kHz. The channels were used as indicated in Figure 4, with channel 1 corresponding to the pair of stainless steel rods at 5 and 10 mm and so on in 5 mm increments (i.e. channel 4 measures between 20 and 25 mm).

The electrical impedance measurements were converted to the resistivity of the mortar using cell constants that consider the difference geometries in the arrangements shown in Figure 4. These cell constants were obtained from a numerical model (finite element calculations).

3.3.3 Linear polarization resistance measurements

The linear polarization resistance measurement (LPR) is a technique to obtain the instantaneous corrosion rate. Using the electrochemical workstation *Metrohm Autolab*, the carbon steel rods were polarized a few mV in vicinity of the open circuit potential. The slope of the linear part of the plot was considered the sum of the resistance of the pore solution R_{Ω} and the polarization resistance, R_p . The resistance of the pore solution (R_{Ω}) is estimated from electrochemical impedance spectroscopy measurements (EIS), by taking the real component of the impedance value in the frequency range of 100-1000 Hz. The corrosion rate was computed via the Stern-Geary equation,

$$i_{\rm corr} = \frac{26 \,\mathrm{mV}}{R_p \cdot A}$$
,

where *A* is the area of the electrode. The reference electrode was the same as the one used for the potential measurements, and the two left-most stainless steel rods were used as counter electrodes. To save time, LPR measurements were only performed for steel rods 1, 3, and 5 in Figure 4. To perform the linear polarization resistance measurements, the other rods were temporarily disconnected to avoid interference between the different devices.

3.4 Characterization of moisture transport and retention properties

To predict the moisture state at the steel surface, the measured sorption isotherm (describing the relation between degree of saturation and relative humidity, RH) is needed as the input data (see the next section for the moisture transport model). In this project, the desorption isotherm was measured on the carbonated materials. The measurements employed 2-mm thick slices, which were kept at different RH until the mass equilibrium. Three slices for each RH and each material were tested to have statistical results.

For model calibration, the water absorption measurements were conducted on short cylindrical carbonated specimens with a height of 4 cm and a diameter of 3 cm, which were core drilled from the reference prisms. Two specimens were used for each material. The cylinders were pre-dried at 65°C till mass equilibrium. Then, one end of the cylinder was in contact with liquid water and

the other surfaces were sealed by aluminum sheet. The details of these measurements can be found in the publication [4].

4. Moisture transport modeling

To test the idea that the moisture state can directly affect the steel corrosion behavior, moisture transport through the concrete cover and the moisture state at the steel surface can be determined by a moisture transport model. The numerical simulations of this project were conducted by adapting a moisture transport model that has been commonly used for cementitious materials [5,6]. This model is a two-phase transport model, including liquid phase and water vapor, which thus can simulate moisture transport in the existing test specimens and under different boundary conditions, including wetting and drying cycles. In 1D, the mass balance equation can be expressed as follows:

$$\frac{\partial S}{\partial t} = \frac{\partial}{\partial x} \left(-\frac{D_0 f(S,\phi)}{\phi \rho_l} \frac{\partial \rho_v}{\partial x} - \frac{k_l k_{rl}}{\phi \eta} \frac{\partial P_l}{\partial x} \right)$$

where S is the water degree of saturation in the porous material; D_0 is the free vapor diffusion coefficient in air; $f(S, \phi)$ is the resistance factor for vapor diffusion; ϕ is the porosity of the material; ρ_l is the density of liquid water; ρ_v is the density of water vapor; k_l is the intrinsic water permeability of the porous material; η is the relative permeability of the porous material; η is the viscosity of liquid water, and P_l is the liquid pressure.

The resistance factor $f(S, \phi)$ and the relative permeability k_{rl} can be calculated by empirical and theoretical models, respectively (see [5,6] for equations). The main unknown in this model is the intrinsic permeability k_l . Many methods, including direct and indirect methods, can be used to determine k_l [7]. In this project, we used an indirect method, called "inverse analysis" to determine k_l , in which the mass change of a specimen obtained from the water absorption measurement was used to back calculate the permeability.

5. Results

5.1 Potential measurements

Figure 5 shows the evolution of the potentials during the experiment, relative to their starting value. The absolute values can be found in the appendix (Figure 16). All the potential measurements were performed using an Ag/AgCl/sat. KCl electrode (SSE). For brevity, the unit of the potential will be referred to as mV_{SSE} in the following. The gaps in the potential curves correspond to the LPR measurements, during which the cables were disconnected. For the specimen shown on the bottom right in Figure 5, the later measurements were excluded because the resulting values indicated a measurement error.



Figure 5. Potential differences with respect to the first measured potential for the eight specimens. The left column belongs to samples with w/b ratio 0.5, whereas the right column is from specimens with w/b ratio 0.6. The blue areas indicate the wetting phases.

Overall, it can be observed that the lower the cover depth of the embedded carbon steel bars, the earlier they exhibit changes in potential. These observed potential changes in negative direction may indicate a change in the corrosion state of the steel bar. A likely explanation for the behavior shown in Figure 5 is that upon exposure of the specimen to wetting, the water penetrates the cover concrete and once it reaches the steel bar, corrosion occurs more actively than in the initial dry state. The higher the cover depth, the longer it thus takes for the water to reach the steel bars. An

alternative explanation for the potential changes may be streaming potentials arising in the concrete when liquid water moves through the pore system [8]. These effects cause a change in the measured potential as soon as moisture surrounds the steel electrode under question. Thus, similarly to the first explanation (change in corrosion state), this effect also would indicate that moisture has arrived at the steel electrode once its potential exhibits a change.

The potential changes for CEM I specimens are shown in the top row of Figure 5. For the specimen with a w/b ratio of 0.5, the potential of the lowest steel rods, channel 1 & 2 (red), at 10 mm height decreased by about 120 mV. For the remaining channels 3 to 6, at higher cover depths, a relatively similar drop of the potentials during the first wetting phase occurred. Following the end of the first wetting phase, the measurements were interrupted for LPR measurements. For the remainder of the experiment, the potentials of channels 3 & 4 (green, at 20 mm cover depth) became slightly more negative by about 50 mV. Channels 5 & 6 (30 mm cover depth) behaved differently; the potential of channel 5 changed by about –75 mV while channel 6 exhibited only about half of that value in potential decrease. For its w/b 0.6 counterpart, a similar picture presents itself. Again, the steel bars with the smallest cover depth were the first to show a negative trend. The other potentials only started to become significantly more negative after the second wetting phase.

For CEM II/B-LL, the w/b 0.5 specimen, the potential curves resemble those of the CEM I specimens. However, the potentials of the w/b 0.6 specimen reacted more quickly to the wetting, with potentials starting to drop earlier compared to the w/b 0.5 ones.

For CEM II/B-M (T-LL), the w/b 0.5 specimen had relatively high initial potential values, except for channel 5, which is a clear outlier (c.f. Figure 16). The potential of channel 5 was measured to be around 400 mV more negative than channel 6 at the same height. This can most likely be explained by undesired corrosion effects. For this reason, this channel will be excluded for the interpretation. The potentials at the lowest cover depth (10 mm, channels 1 & 2) decreased most significantly. For the 20 mm steel rods, channels 3 & 4, the potential was relatively stable. For CEM II/B-M (T-LL) w/b 0.6 the first wetting stage exhibited somewhat surprising potential values, with an overall very similar behavior of all rods (this may be due to issues related to the reference electrode). After the interruption for the LPR measurements at around t = 5 h, the rods showed a more reasonable trend with the ones at cover depths >20 mm being at higher potentials and the ones at 10 mm cover depth decreasing. Those values are shown in the third row of Figure 5.

For the CEM III/B specimens, the largest potential drops were recorded. For both w/b ratios, the potential of the lowest steel rods dropped by about 250 mV during the course of the experiment. For the w/b 0.6 specimen, the signal suffered from increased noise compared to the other measurements. In addition, after the second wetting phase, the signals of all channels showed an increase in value, with all channels except for channel 5 plateauing at a similar value, which might be due to bad electrolytic connection between the reference electrode and the mortar surface. Given the results for the w/b 0.5 specimen and the experience from previous measurements, the values for steel bars 1–5 are expected to remain at this relatively low value, whereas steel bar 6 will have eventually decreased to lower values too.



Figure 6. Maximum potential change of the steel bars observed over the course of the experiment. The error bars indicate the standard deviation for the two steel bars at the same cover depth.



Figure 6 gives an overview of the maximal potential drop due to the water exposure. Clearly, the most significant decrease in potential value occurs for the CEM III specimens. For the three remaining binder types, the values are comparable. In general, it is observed that increasing cover depths give rise to a lower effect of the water exposure on the potential.

5.2 Impedance measurements

The results of the impedance measurements (electrical mortar resistivity) are presented in Figure 7 (relative to the first measurement) and in the appendix in Figure 17 (absolute values). Since the pore solution pH can be assumed similar for all the different mixes in their carbonated state, the change in resistivity is considered to primarily reflect a change in moisture state. Lower resistivity means higher moisture content in the mortar.



Figure 7. Changes in the electrical resistivity of the carbonated mortars with respect to the initial condition. Note that the rows have different *y*-axis scales.

For all measurements, the impedance exhibits a downwards trend over the wetting/drying exposure. For most specimens, this effect is observed first at shallow cover depths. Due to issues with the data acquisition, unfortunately the impedances could not be measured for all channels without interruption.

5.3 Corrosion rate measurements

Figure 8 shows the corrosion current densities obtained through the LPR technique. The corrosion current density corresponds to the instantaneous corrosion rate. Values lower than 1 μ A/cm² indicate negligibly low instantaneous corrosion rates. The lowest corrosion current density was observed on the CEM I w/b 0.5 specimen with values stagnating around 0.2 μ A/cm² over the entire experimental time. The highest values were obtained for the CEM III/B specimens, with both the w/b=0.5 and 0.6 series reaching peaks of 5 to 7 μ A/cm². The highest corrosion rates are summarized in Figure 9.

Except for steel rod 5 on the CEM II/B-M (T-LL), which already exhibited outlier behavior discussed in the potential measurements section and is excluded here, the corrosion rate tended to be higher for the 0.6 w/b ratio specimens. However, no steel reached corrosion current densities above 7 μ A/cm², which is still a relatively low corrosion rate for practical applications. Note that 7 μ A/cm, assuming it occurs constantly over an entire year, would correspond to approximately 80 micrometers of thickness loss. Under wetting / drying exposure, however, as can be seen from the results shown here, the average corrosion rate over a year will be much lower and the peak values will only be reached during wetting periods.



Figure 8. Corrosion rate measurements for the carbon steel electrodes in the carbonated mortars.



Figure 9. Maximal instantaneous corrosion current densities reached after the third wetting phase in carbonated mortars.

5.4 Assessment of typical rain events in Zurich

The duration of water exposure applied in the experiments ideally represents a realistic scenario of a wetting event. In XC4 exposure conditions. This typically means concrete exposure to rain or splash water. In this project, we examined meteorological data of Zurich to determine the likely rain duration, which could lead to a wetting event due to rain on a facade or balcony slab, or similar structure. Meteorological data collected by the city of Zurich [9], in contrast to other data, which only contains information about the quantity of rain (e.g., in mm per day), this "city of Zurich data set" provides the rain duration. The data set comprises measurements from three measurement stations in urban locations in Zurich, with each station acquiring the cumulative rain duration once every hour between 1992 and 2022. The values are organized into rain events. It uses a rather simple algorithm; for each non-zero rain duration value, the subsequent non-zero rain value counts toward the same rain event. This implicitly assumes that the rain duration lies at the end of the first hour, and at the start of the second hour. If the second rain duration lies above 58 minutes, continuous rain is assumed, and the next non-zero rain duration is added to the rain event duration, etc. The result of this procedure, that is, accumulating the single entries of rainfall per hour into separate rain events, is depicted in Figure 10. Three quantiles are computed, 50%, 75%, and 95%. This simple analysis shows that, for all three locations, about 95% of all rain events last shorter than 3 hours. Therefore, the three-hour wetting duration selected in this project is considered as representative of a relatively long wetting event (95% fractile) for the urban area of Zurich. In fact, in most cases, the duration of a rain event would be shorter than 3 hours. Rain events lasting longer than 8 hours—the longest wetting duration in the experiment—were only rarely recorded: for example, only 17 such events have been registered at Rosengartenstrasse during the period 1992–2022, thus on average approximately one such event every two years.



Figure 10. Rain events at three locations in Zurich. The three indicated quantiles are shown as dotted lines (note the logarithmic scale).

5.5 Moisture transport and retention properties

The measured desorption isotherms for carbonated mortars with different w/b ratios are provided in Figure 11, which shows that the curves for CEM I mortars for both w/b ratios are higher than the other curves, meaning that they have higher moisture retention capacities. This may be due to the high content of clinker in CEM I so that more carbonation products created more small pores that can retain moisture at the moderate RH. The moisture retention capacity decreases with the increasing w/b ratio, which is caused by the different pore structures as the materials with more water contain more large pores.



Figure 11. Measured desorption isotherms for the different carbonated mortars.

The mass change curves during water absorption are shown in Figure 12 (the mean curve of two measurements and error bars are shown). An absorption curve generally consists of two stages, the first stage and the secondary stage [10,11]. For a homogeneous porous material, the first stage is a linear curve as most curves shown in Figure 12. The water transport in this stage is controlled by capillary actions which is the main transport mechanism. The water transport in the secondary stage is very slow, which is believed to be caused by the redistribution of trapped air, the rearrangement of hydration products, and the complex microstructure. Therefore, to determine the intrinsic permeability, we only take the first linear stage.

As mentioned above, the first stage reflects the rate of water transport under capillary pressure, so by fitting this stage with a linear curve, we can then obtain the slope of the curve, which is known as water absorption coefficient.

$$I = S_p \sqrt{t} + a$$

where *I* is the cumulative water uptake (kg/m²), *a* is a coefficient counting the surface effect and S_p is the water absorption coefficient (kg/m²/h^{1/2}).



Figure 12. Measured water absorption curves and fitted by the moisture transport model for carbonated mortars. The error bars of measured data are added, which are very small, meaning a very good reproducibility of water absorption measurements.

5.6 Numerical analyses of material properties

Table 1 summarizes all determined water absorption coefficient S_p and intrinsic permeability k_l , which are also compared in Figure 13. For the high w/b materials (w/b=0.6), S_p and k_l are higher than the low w/b materials (w/b=0.5), which agrees with the general theory that the high w/b induces more capillary pores and thus moisture can penetrate the concrete cover and reach the steel surface. Therefore, concrete with high w/b ratios are generally less durable than the low w/b concrete. For the same w/b, mortars made from CEM III/B have highest values of S_p and k_l , followed by CEM II/B-LL, CEM II/B-M and CEM I, as well shown in Figure 13. The moisture transport in these materials follows the same tendency, which also matches well the contents of clinker in these cements. The conclusion is that, after carbonation, cementitious materials with high content of clinker may have a better durability performance than these with low clinker contents.

	w/b	CEM I	CEM II / B-M	CEM II / B-LL	CEM III / B
Water absorption coeffi-	0.5	0.3759	0.3587	0.3785	0.4056
cient (kg/m²/h ^{1/2})	0.6	0.425	0.5612	0.9663	0.9965
Intrinsic permeability	0.5	1.0	3.9	8.5	10.5
(x10 ⁻¹⁹ m ²)	0.6	8.0	8.9	87.1	136.0

Table 1 Measured water absorption coefficient and intrinsic permeability



Figure 13 Comparison of water absorption coefficient with intrinsic permeability. The clear trend is that they increase with each other.

The changes of measured electrochemical results, in particular for the measured corrosion rate, can be explained by the numerical simulation results, which were performed under drying-wetting cycles with the same durations as the experiments. The simulations were done for all tested materials, but the mass changes of mortars with w/b=0.5 are much smaller than these with w/b=0.6; therefore, we only present the simulation results for materials with w/b=0.6. The simulated mass change curves for these mortars in Figure 14 show that the CEM III/B material has the highest change of mass due to moisture gain during water absorption and mass loss during drying. This is understandable as the water absorption coefficient and the intrinsic permeability of CEM III/B are high as displayed in Table 1. The general trend of the mass of the specimen increases during the wetting-drying cycles, well corresponding to the increase in measured corrosion rates in Figure 8 for the CEM III/B mortar. Even though CEM II/B-LL mortar also has high values of water absorption coefficient and intrinsic permeability, its simulated mass change curve is rather flat, meaning not much water can penetrate. This may be because the measured sorption isotherm is very flat (see Figure 11), which thus could not induce significant changes in moisture content. The small fluctuations can be seen for CEM I and CEM II/B-LL mortars, but there are much smaller than the CEM III/B mortar.



Figure 14. Simulated mass change curves during wetting-drying cycles of different carbonated mortars.

With the numerical simulations, the changes of moisture saturation at different depths can be extracted as shown in Figure 15. Similar to results in Figure 14, the CEM III/B material shows clear changes of saturation, in particular for the depth of 1 cm, while there are no obvious changes for the other materials, meaning that the drying or wetting front cannot reach the depth of 1 cm. For the CEM III/B material, the significant variations of moisture saturation are displayed for the shallow depth and the variations gradually vanish with the increase in depth. In addition, a clear delay can be seen in the changes of moisture saturation at a certain depth after the boundary condition is changed. These observations are caused by the fact that moisture needs time to move, so if the duration of wetting-drying cycle is short, there would be no enough time to let moisture penetrate deeper.

The effects of variations of moisture saturation are also reflected in measured potentials and resistivity curves (see Figure 5 and Figure 7). With the delay effects of moisture transport, the changes of measured potentials and resistivity curves are also delayed. For instance, the measured potentials still decrease (to more negative) during drying because the wetting front still advances. Until the drying front reaches this point, the measured potentials start to increase as the amount of water at this point decreases.



Figure 15. Modeled changes of saturation at different depths for carbonated mortar (w/b=0.6).

6. Discussion

The experiments captured the corrosion behavior of steels under cyclic drying and wetting conditions. Namely, they established the effects of changing moisture conditions on the electric resistivity and the corrosion potential for small-scale mortar samples. LPR measurements determined the corrosion rate at select times during the experiment. In almost all cases, the moisture ingress during the wetting led to an appreciable drop in potential and resistivity. As expected, a higher distance between the water contact surface and the steel—essentially the cover depth—caused a delay in the reaction of the steel to the rise in moisture. However, the acquisition of the impedance measurements was not always optimal, and thus some data is missing in the time series.

The corrosion rate measurements showed that the corrosion rate remained below 7 μ A/cm² for all specimens. Assuming that the corrosion process occurs at this maximum rate constantly over an entire year, this would correspond to approximately 80 micrometers of thickness loss. For practical applications, this value may be considered unproblematic, especially because under wetting / drying exposure, the average corrosion rate over a year will be much lower. As can be seen from the data presented in this report, the peak corrosion rate values will only be reached during wetting periods and for limited time.

Furthermore, in all cases, the steel bar at a cover depth of 30 mm exhibited instantaneous corrosion rates clearly lower than 7 μ A/cm². It may also be worth highlighting that in the first two wetting phases (wetting duration of 3 hours each) the corrosion rate at a cover depth of 30 mm hardly increased at all. These results highlight the importance of an appropriate cover depth. Although the cover depth is already an established design parameter, current standards aim to prevent the carbonation front from reaching the steel surface. In contrast, the current results indicate that the cover depth remains important even after advanced carbonation, because as long as the moisture does not reach the reinforcement, the corrosion rate remains on acceptable levels. In that case, concrete could be allowed to carbonate as long as appropriate measures to control the moisture content are taken. However, the results generated in the present study do not yet provide a conclusive argument. Further studies on the corrosion behavior of larger scale samples using concrete instead of mortar, or naturally carbonated (or less accelerated) specimens are needed.

The calculated moisture distribution by the moisture transport model shows a similar trend as the measured potential and resistivity. The increase in calculated moisture content at a certain depth in a certain carbonated mortar corresponds to the decrease in measured potential and resistivity, and vice versa. This supports our hypothesis and agrees with previous studies [2,3,12] that moisture condition at the steel surface is crucial to control the steel corrosion behavior. Nevertheless, the simulations do not provide consistent results for all studied materials. For instance, the small variations in measured potential and resistivity curves for CEM II mortars are observed (see Figure 5 and Figure 7), but the simulated moisture content does not change much during the wetting-dying cycles. This may be due to the shape of the measured sorption isotherms. As shown in Figure 11, the curves are very flat in the moderate RH range, even water content at 53% RH is lower than that at 44% RH (CEM II/B-M), which is unusual for a sorption curve. The sorption isotherm measurements should be repeated, but the measurements are very time consuming, so there was no enough time to repeat these measurements within the scope of this project.

The change of moisture state can affect the measured potential and resistivity at depths of embedded steel bars as the results in Figure 5 and Figure 7 show. The corresponding corrosion rate is also clearly affected by the change of moisture state (see Figure 8). Therefore, accurately determining the moisture state at the depth of embedded steel bar is able to assess the risk of steel corrosion. This project has tried to determine water content at the steel surface by detailed material characterization and numerical modeling, but a less time-consuming method is needed for general practice.

7. Conclusions

This project employed different electrochemical methods, including potential and resistivity monitoring and linear polarization resistance measurements, to investigate the corrosion behavior of embedded carbon steel bars in carbonated mortars prepared with different types of cement that were exposed to the XC4 exposure class. The following conclusions can be drawn based on the measured results.

1) The corrosion risk clearly responded to the wetting-drying condition. The decrease in measured potential and the increase in measured resistivity was observed during the

wetting period and the reversed tendencies were seen for the drying period. Therefore, wetting increases the risk of steel corrosion.

- 2) The cover depth plays an important role for cyclic wetting and drying exposure conditions. The significant variations in potential and resistivity were mostly observed for steel bars at 10 and 20 mm depth. The steel bars at a depth of 30 mm were largely unaffected, especially for wetting periods of less than 3 hours. It should be mentioned that the meteorological data from Zurich revealed that 95% of all rain events last shorter than 3 hours.
- 3) Differences between different types of cement and w/b ratio were clearly seen.
 - Upon wetting, carbonated CEM III/B mortars showed the most pronounced reactions in terms of potential changes and highest corrosion rates. In agreement with this, CEM III/B mortars showed the highest water permeability results. It should be mentioned, however, that the specimens were carbonated at an age of 2 months, which is relatively young for CEM III/B binder.
 - Carbonated CEM I mortars showed the lowest water permeability results and accordingly, the reactions of the embedded steel bars to wetting were the least pronounced.
 - Carbonated CEM II/B-LL and CEM II B-M (T-LL) mortars exhibited intermediate behavior.
 - At w/b ratio 0.5, the steel reacted much less pronounced to wetting/drying exposure, compared to ratio w/b 0.6 for all binder types. In agreement with this, carbonated mortars with w/b=0.6 showed higher water permeability results than w/b=0.5.
- 4) Even though different corrosion behavior was seen for different cements, under the studied exposure condition, the maximum measured instantaneous corrosion rate observed at 10-20 mm cover depth was 7 μA/cm². The steel bars at a cover depth of 30 mm exhibited corrosion rates lower than 7 μA/cm². It may also be worth highlighting that in the first two wetting phases (wetting duration of 3 hours each) the corrosion rate at a cover depth of 30 mm hardly increased at all in all studied systems. As mentioned above 95% of all rain events in Zurich last shorter than 3 hours.

Numerical simulations of moisture transport confirmed the findings in experimental results as the changes of moisture content at the steel depth match well the measured potential and resistivity curves. The conclusion is that the moisture state on the steel surface is one of the decisive factors for steel corrosion. If the moisture state can be well determined, the risk of steel corrosion could be well assessed and further mitigated by the moisture control methods even in carbonated concrete.

8. Disclaimer and need for further research

This project illuminated the behavior at 4 different cements and two w/b values, as well as an exposure condition representative for the city of Zurich. A transfer of the results to other conditions is not directly possible. Furthermore, the actual damage process (concrete cracking, spalling due to corrosion) could not be studied within the scope of this work.

Nevertheless, the results indicate that further research in this direction is necessary to reconcile the goals of sustainability (low CO2 cements) and durability (corrosion resistance). Further work should provide a fundamental understanding of all the processes involved (electrochemical, chemical, physical such as mass transfer and fracture mechanics), as well as laying the foundations for a normative rethink (test procedures, durability design).

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Appendix

Additional measurement data



Figure 16. Absolute potential measurement data.



Figure 17. Absolute resistivity data. Note the different y-axis scale in the third row.