

RELATIVE IMPORTANCE OF CORROSION RATE AND EXPOSURE CONDITION ON THE PRACTICAL USE OF NEW ENVIRONMENTALLY FRIENDLY BINDERS

Matteo Stefanoni¹, Ueli Angst² and Bernhard Elsener³

^{1,2,3} ETH Zurich Faculty of Civil Engineering, Institute for Building Materials
Stefano-Franscini-Platz 3, CH-8093 Zürich, Switzerland
e-mail: matteost@ethz.ch, uangst@ethz.ch, elsener@ethz.ch

SUMMARY: Lowering the clinker content of concrete using SCMs can contribute significantly to reduce the energy consumption and the CO₂ emissions of building materials. Uncertainty about durability, especially carbonation induced corrosion, is the main factor limiting the practical use: containing less CaO they have less capacity to neutralize CO₂ and thus higher carbonation rates, which may lead to premature corrosion of steel reinforcement. Results in literature concerning corrosion of steel in carbonated concrete are rare and refer mostly to ordinary Portland cement. Generally, a trend to higher corrosion rates at higher relative humidity was found. To estimate service life of concrete structures made with new blended cements corrosion rate data are urgently needed, because the so called “corrosion propagation stage” might significantly contribute to the total service life. Corrosion rate has to be measured for different blended cements, w/c ratios and exposure conditions. To collect data of corrosion propagation rates in a reasonable time, a new experimental set up has been designed. The new test setup consists of small (8 x 8 cm) and thin (6 mm) mortar samples instrumented with a reference electrode, 5 steel wire electrodes and a stainless steel grid counter electrode. The thin sample allows full carbonation within 1 week (4% CO₂). Parameters that can be measured are electrical resistivity, corrosion potential and corrosion rate, oxygen diffusion. These results should allow to investigate the mechanism, particularly the kinetics, of carbonation induced corrosion. The first results show that new blended cements could be more susceptible to corrosion in certain exposure conditions. Depending on the environment the steel dissolution rate can vary of a factor of 200, from < 0.1 µm/year at 50% RH, to 20 µm/year in wet conditions. To define the application limits of new binders, the interaction with variable exposure conditions has to be carefully evaluated.

KEY WORDS: Corrosion, Carbonation, Durability, SCMs, Exposure conditions.

1 INTRODUCTION

In the past years environmental issues in the building industry have become an increasingly hot topic. According to *Trends in global CO₂ emissions: 2015 Report* [1] cement production accounts for roughly 8% of global CO₂ emissions. The ideal solution touches every step of the production, on the raw materials side lowering the clinker content of cements using supplementary cementitious materials (SCM) can contribute significantly to reduce the energy consumption and the CO₂ emissions of building materials, thus they become environmental friendly. Uncertainty about durability, especially carbonation-induced corrosion, is the main factor limiting the practical use of these blended cements. As a matter of fact, the carbonation rate is faster for blended cements [2] due to their inherent chemical properties, in particular the reduced pH buffering capacity (lower 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 (OPC 65% CaO), variably down to 40% [4-6], depending on the type and amount of substituents;
- Consumption of calcium hydroxide [3,7,8] in presence of SiO₂-rich components by the pozzolanic reactions.

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 of data collected since 1968 for ground granulated blast-furnace slag (GGBS) [9] and for fly ash concrete [10].

Carbonation also influences differently the microstructure properties depending on the type of binder. It is acknowledged that carbonation leads to a reduction in porosity which is ascribed to the positive difference of molar volume between the formed calcium carbonate and the hydration products, and the C-S-H carbonation may significantly contribute to this evolution. Several previous investigations have highlighted the reduction in porosity after carbonation [11, 12-15]. However the influence on the pore size distribution seems to be dependent mainly on the binder considered: apparently the differences are not very relevant with high clinker levels, but lowering the grade of CEM I content a shift of the capillary porosity to coarser distribution was highlighted [15-19] possibly due to the disappearance of the clusters of CH crystals replaced by a packing of calcium carbonate crystals leaving new voids.

The underlined changes in the material microstructure can be of main importance in defining the adsorption and diffusion properties of water and oxygen in the concrete matrix, influencing the corrosion rate as a consequence.

Considering the schematic representation of the service life (Fig. 1), increasing SCMs addition leads to a shorter induction period for the onset of a corrosion process (depassivation) and it becomes obvious that the corrosion rate of steel in carbonated concrete becomes a critical factor for reaching the expected service life of a structure. However, results in literature on the corrosion rate of steel in carbonated concrete are rare and refer mostly to ordinary Portland cement.

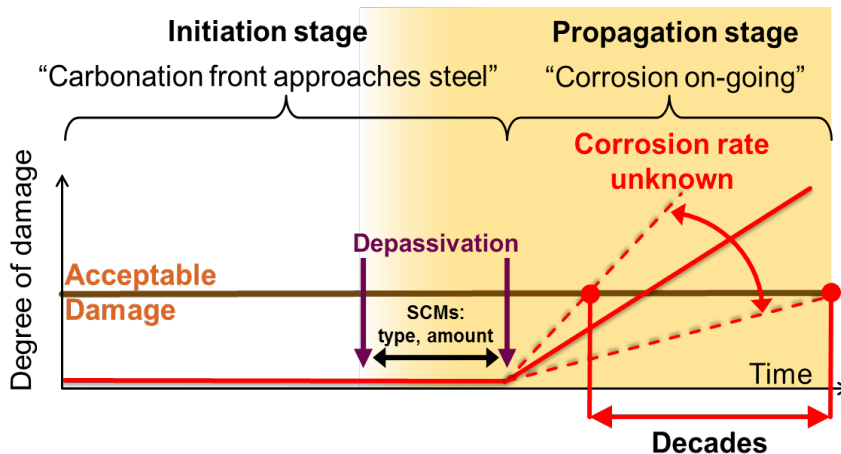


Figure 1: Schematic representation of the service life of a reinforced concrete structure (Tuutti diagram) showing the importance of the propagation-stage of corrosion in carbonated concrete.

For service life prediction of concrete structures with new, blended cements, corrosion rate data are urgently needed because the so-called “corrosion propagation stage” might be a significant part of the total service life. Being the corrosion process a system property, influenced both by the material and the environment, the

combination of different materials (composition and mix design) together with different exposure conditions (constant RHs and wet-dry cycles) have to be studied.

The final objective is to evaluate the application limit, case by case, and develop guidelines for the use of new blended cements. In this paper an approach for carbonated mortars is presented, aiming to achieve fast testing of corrosion properties, thanks to an innovative sample setup. The relative importance of type of binder, w/c ratio and exposure condition, with respect to corrosion propagation rate, is evaluated.

2 MATERIALS AND METHODS

2.1 Sample design

To be able to collect data of corrosion rate of steel in carbonated mortar in a reasonably short time, a new experimental set up has been designed. The new test setup consists of small (8 x 8 cm) and thin (6 mm) cement mortar sample instrumented with a reference electrode, 5 steel wire electrodes and a stainless steel grid counter electrode (Fig. 2). The thin sample allows rapid full carbonation (max 3 weeks in 4% CO₂) and rapid equilibration of environmental humidity (checked by the sample weight). 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 consumption rate. From these data the mechanism of steel corrosion in carbonated concrete made of different blended cements can be evaluated.

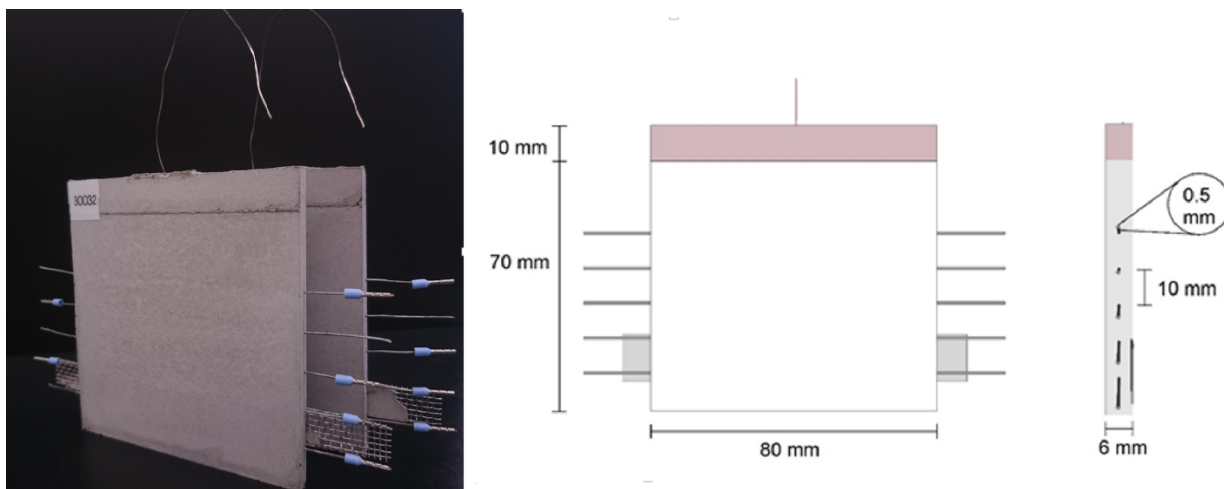


Figure 2: Final sample and schematic representation of dimensions.

2.2 Materials

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 mix design was chosen to allow the best fluidity while maintaining a high stability of the cementitious suspension. 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 increase the fluidity and be able to fill the mould.

2.3 Carbonation procedure

The samples were carbonated in a carbonation chamber at 65% relative humidity and 4% CO₂ concentration in the controlled atmosphere. The time used for complete carbonation was:

- 2 weeks for CEM II mortars;
- 3 weeks for CEM I mortars.

Complete carbonation was ensured by the phenolphthalein test.

2.4 Exposure conditions

The corrosion behavior of the carbonated samples was studied in different exposure conditions. The first tests were performed in controlled and 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 (Fig. 3). The cycles have been carried out by placing 3 mm of water on the samples and let it adsorb, the parameters have been monitored over time from the water adsorption to the drying of the sample.

2.5 Electrochemical tests

All the electrochemical experiments were performed using a potentiostat Metrohm Autolab PGSTAT30. 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. One steel wire was used as working electrode and the stainless steel grid (or other steel wires) were used as counter electrode depending on the test performed. The measurements were repeated over time for each exposure condition.

Corrosion rate: the instantaneous corrosion current density was determined by polarization resistance measurements. The polarization resistance R_p of the single steel wires was measured with the stainless steel grid as counter electrode at ± 10 mV around the open circuit potential with a scan rate of 0.1 mV/s. The IR-drop in the mortar was taken into account indirectly. Impedance measurements were performed right before each polarization resistance test, and the ohmic resistance obtained was subtracted from the result each time at the end of the tests.

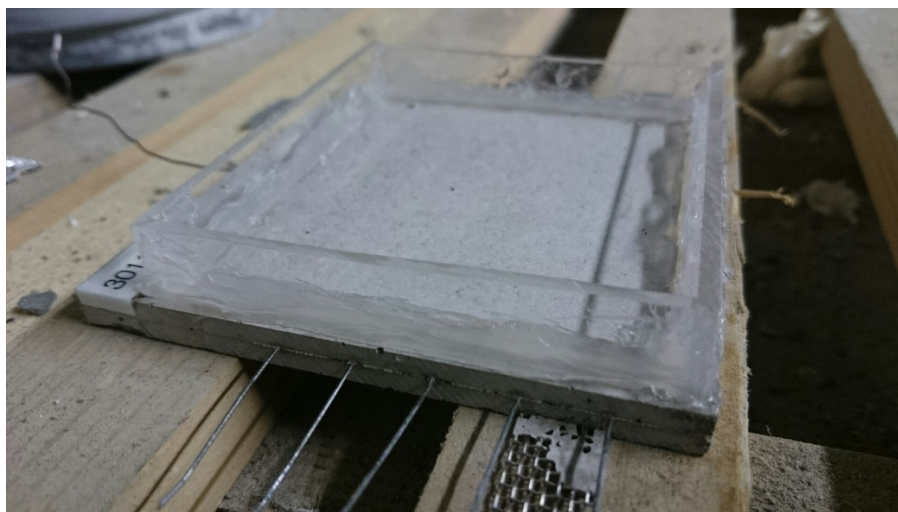


Figure 3: Samples used for wet and dry cycles.

3 RESULTS

Linear polarization measurements allowed the calculation of an electrical resistance R_p' that is the sum of the polarization resistance R_p of the steel wires and the ohmic resistance R_Ω between working electrode and counter electrode.

Electrochemical impedance spectroscopy tests were performed in order to measure the ohmic resistance. The values obtained were subtracted from the total resistance to get the real polarization resistance values.

The corrosion rate was then calculated using the Stern Geary relation (1):

$$i_{corr} = \frac{B}{R_p} \quad (1)$$

Where R_p is the polarization resistance and B is a parameter depending on the electrochemical properties of the considered system; for iron in active corroding state a value of 26 mV is commonly used.

At 50% RH the corrosion rate both of CEM I and CEM II at all w/c ratios from 0.4 to 0.6 were lower than $0.01 \mu\text{A}/\text{cm}^2$ (lower than $0.1 \mu\text{m}/\text{year}$) (Fig. 4). 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/c ratio in terms of final corrosion rate was found.

At 95% RH corrosion rates were higher for samples made with blended cement and higher w/c ratio, but overall found to be lower than $0.1 \mu\text{A}/\text{cm}^2$ (ca. $1.2 \mu\text{m}/\text{year}$) (Fig. 4). Also in this case, in the first period of exposure, the corrosion rate increased with time and the corrosion potential decreased, for both cement types.

Samples exposed to wetting showed a very rapid decrease of the open circuit potential and of the polarization resistance (Fig. 5), the maximum value of the corrosion rate after wetting was $1.7 \mu\text{A}/\text{cm}^2$ (ca. $20 \mu\text{m}/\text{year}$) (Fig. 4). The process of drying out took much more time, at the end the corrosion potential and polarization resistance reached values similar to 50% RH. The w/c ratio did not seem to play a decisive role in defining the maximum corrosion rate in the wet state. On the contrary the type of binder did play a role, for CEM II higher corrosion rates were measured in the wet phase and it was also noticed that CEM II showed a faster drying. In figure 6 the averaged corrosion rates for the two binders is reported for a wetting and drying cycle.

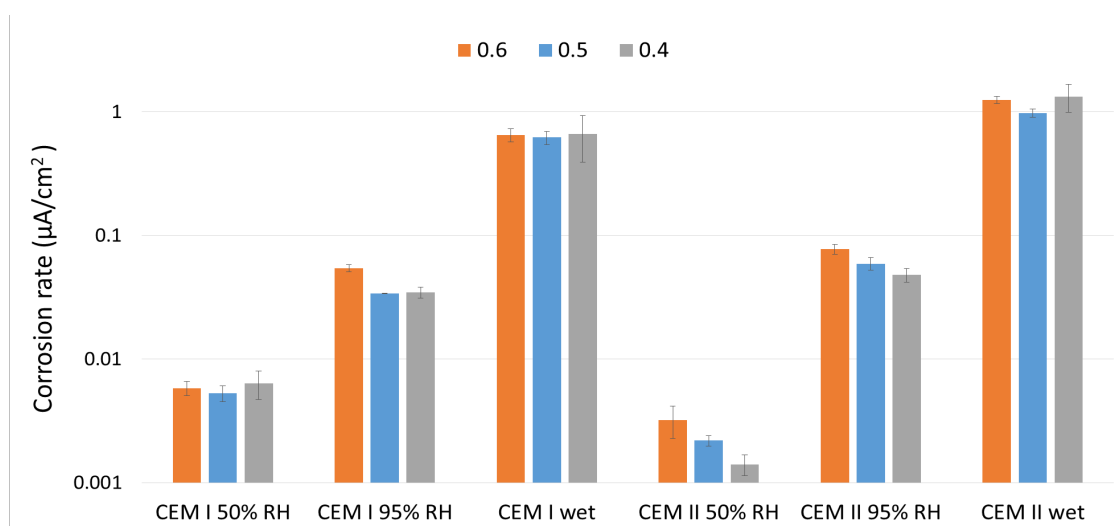


Figure 4: Corrosion rates measured for every exposure condition, w/c ratio and type of binder (for wet-dry cycles the maximum value for each cycle was taken).

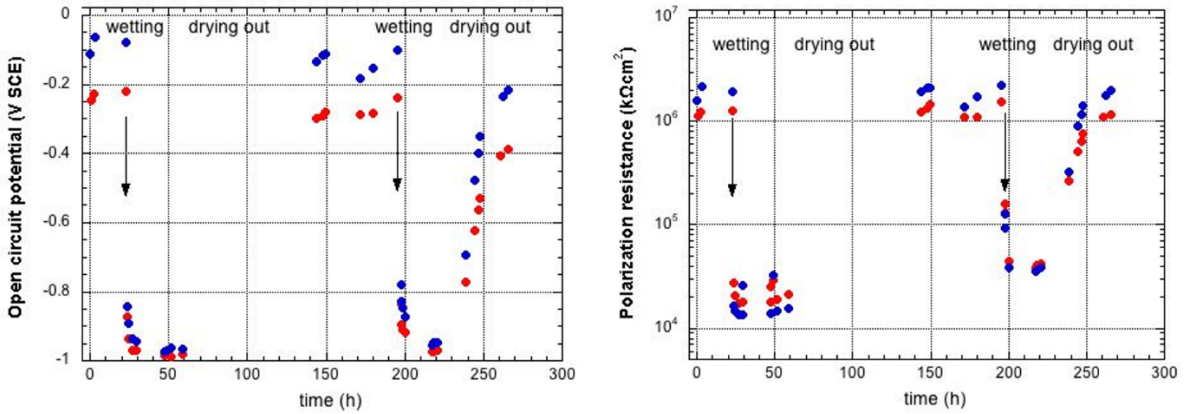


Figure 5: Variation of the open circuit potential and the corrosion rate during wet-dry cycles (measurements on two steel wires per sample).

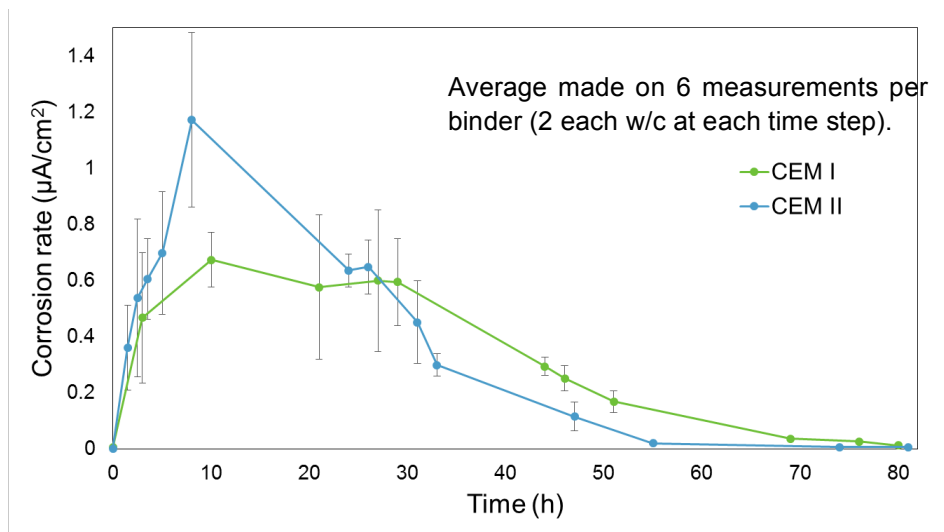


Figure 6: Averaged corrosion rates for the two different binders (all w/c included) in the wetting and drying phases.

4 DISCUSSION

The influence of the cement type and w/c ratio on the corrosion rate seems to be governed by the pore structure conformation post-carbonation that was discussed in the introduction. Being corrosion an electrochemical process that needs an electrolyte to take place, the condensation behaviour of water in the pores is likely the limiting factor in non-saturated conditions. At 50% RH CEM I samples show a higher corrosion rate than samples made with blended cement (Fig. 4), this is in agreement with data present in the literature [20]. The reason could be found in the finer pore structure of CEM I carbonated mortars that would allow some water condensation also at such low relative humidity. At 95% RH the dissolution rate is higher in CEM II mortars (Fig. 4). Also this fact might be attributed to the pore structure, being coarser for carbonated blended cement: larger pores would increase the amount of water in contact with the steel surface at high relative humidity.

The highest corrosion rates were found during wet and dry cycles (exposure class XC4). In the wet periods

maximum values as high as $1.7 \mu\text{A}/\text{cm}^2$ were measured. The corrosion rate in the wet phase is up to 20 times higher than at constant 95% RH. These values, which can be converted to about $20 \mu\text{m}/\text{year}$, can be very dangerous and drastically limit the service life of a structure. The dissolution rate turns back to negligible values in the drying phase, which seems to be faster in the case of CEM II mortar where the more open structure allows for a faster water evaporation.

It finally turns out that the claimed better durability performances provided by blended cements, because of a finer pore structure and lower permeability [11, 21-23], is perhaps applicable only in a pre-carbonation stage. After carbonation the coarser pore size distribution that is formed seems to rule the corrosion behaviour of steel embedded, leading higher dissolution rates in a humid/wet environment (Tab. 1). Taking the extreme values that were measured, steel embedded in the blended cement used showed a corrosion rate higher than ordinary Portland cement up to a factor of 2, in wet conditions.

Table 1: Averaged corrosion rate values for each binder in each exposure condition (average over minimum 6 measurements). Ratio of dissolution rate of the steel embedded in the two binders for each exposure.

Corrosion Rate ($\mu\text{A}/\text{cm}^2$)	CEM I	CEM II	CEM II/CEM I
50% RH	0.0058 ± 0.0011	0.0023 ± 0.0005	0.39
95% RH	0.0410 ± 0.0025	0.0617 ± 0.0067	1.50
WET	0.6436 ± 0.1416	1.1842 ± 0.3116	1.84

Reminding that, for blended cements, the moment at which corrosion of the reinforcement starts to play an import role comes at earlier ages, and having recorded dissolution rates ranging in a window as wide as a factor of 200 and up to 2 times higher than Portland cement, it is clear how important the evaluation of the exposure conditions is in order to evaluate the safeness of using blended cements for a certain application.

It also has to be underlined that, from the recorded data, carbonation induced corrosion seems to be influenced to a greater extent by the type of binder than by the water to cement ratio.

5 CONCLUSIONS

Stating that the steel corrosion rate is higher for a certain binder with respect to another is finally too much of a generalization and technically wrong. It was shown that the main factor influencing carbonation induced corrosion is the exposure condition, the type of binder only comes second. Having said this, it is also necessary to think about what initially mentioned, the time to depassivation is substantially shortened in blended cements leading to a greater importance of the corrosion behaviour in terms of final service life. Careful evaluation of carbonation rate and corrosion rate, depending on the local exposure conditions, has to be carried out at priori.

From the results it is obvious that major concern for the application of blended cements in atmospheric exposure conditions is related to wet/dry cycles (exposure class XC4). In wet conditions up to $20 \mu\text{m}/\text{year}$ have been measured in carbonated mortar. The amount of corrosion (in μm) can be calculated knowing the corrosion rate and the time the steel is in wet conditions.

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