Corrosion Rates in Carbonated Low Clinker Cements: Are the New Binders Really Sustainable?

STEFANONI Matteo[1,a] [*], ANGST Ueli[1,b] and ELSENER Bernhard[1,c]

[1]ETH Zürich, Institute for Building Materials (IfB), Stefano-Franscini-Platz 3, CH-8093 Zürich, Switzerland

[a]matteost@ethz.ch, [b]ueli.angst@ifb.baug.ethz.ch, [c]elsener@ethz.ch

*corresponding author

Keywords: Corrosion, Carbonation, SCMs, Sustainability

Abstract

Lowering the clinker content of concrete using SCMs can contribute significantly to reduce the energy consumption and the CO_2 emissions of building materials. Substitution of clinker up to 65% is now possible according to European and Swiss standards. Uncertainty about durability, especially carbonation induced corrosion, is the main factor limiting the practical use of these blended cements: containing less CaO they have less capacity to neutralize CO_2 and thus higher carbonation rate, which may lead to premature corrosion of steel reinforcement.

Results in literature on the corrosion rate in carbonated concrete are rare and refer to ordinary Portland cement only. 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 of the structure.

To be able to collect data of corrosion propagation rates in a reasonable time a new experimental set up has been designed. Parameters that can be measured are electrical resistivity of the sample, corrosion potential and corrosion rate of the steel, oxygen diffusion and consumption rate; their evaluation should allow to investigate the protective nature of the low clinker material for steel in concrete and the mechanism, particularly the kinetics, of carbonation induced corrosion.

The first results show that in certain environments blended cements could be more susceptible to corrosion.

Introduction

In the last years a lot of attention has been directed to environmental issues in building industry. According to *Trends in global CO₂ emissions: 2015 Report* [1] cement production accounts for roughly 8% of global CO_2 emissions. Lowering the clinker content of cements using supplementary cementitious materials (SCM) can contribute significantly to reduce the energy consumption and the CO_2 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 facts, 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 SiO_2-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].

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.
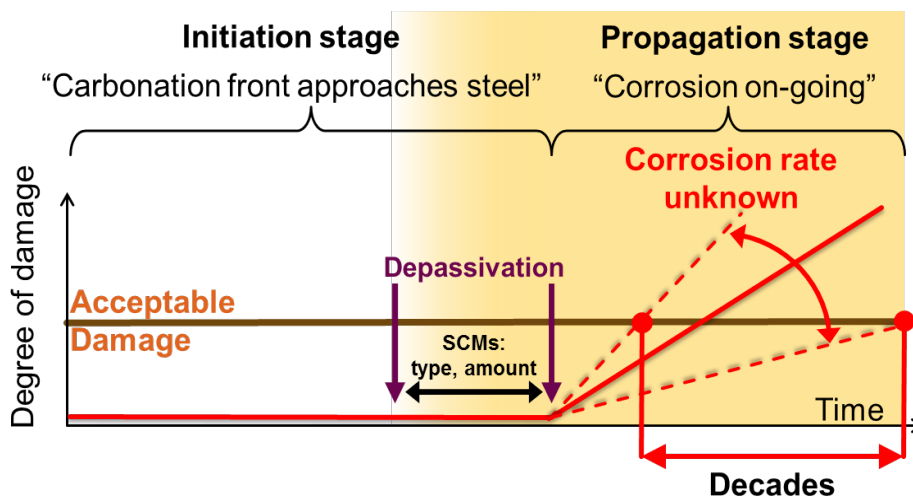

Figure 1: Schematic representation of the service life of a reinforced concrete structure (Tuutti diagram) showing the importance of the propagation-stage of corrosion in carbonated concrete.

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.

Experimental

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% CO_2) 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.
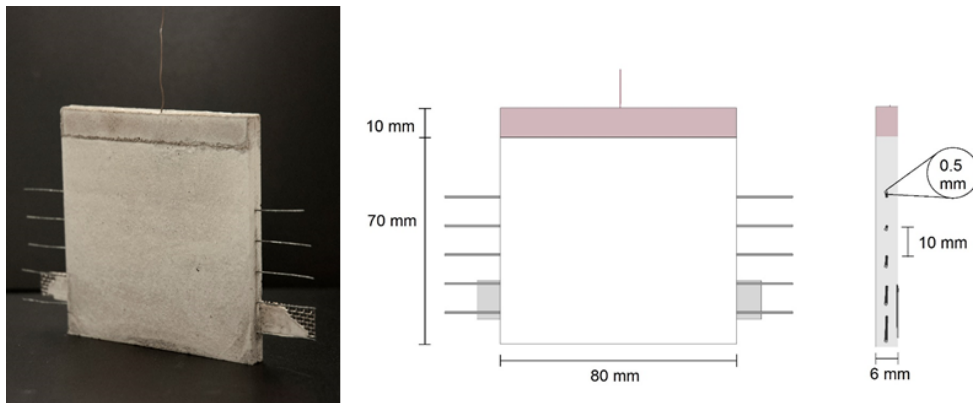

Figure 2: Final sample and schematic representation of dimensions.

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.

Carbonation procedure.

The samples were carbonated in a carbonation chamber at 65% relative humidity and 4% CO_2 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.

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 car-

ried 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.

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. The steel wires were used as working electrode and the stainless steel grid was used as counter electrode. The measurements were repeated over time for each exposure condition.

Electrochemical impedance spectroscopy was performed using as working and counter electrode the steel wires two by two, positioned at 1 cm distance from each other. The AC amplitude was set at 10 mV around the open circuit potential and the impedance was measured at frequencies between 10^5 and 0.1 Hz.

The polarization resistance (inversely proportional to the corrosion rate) was measured with the stainless steel grid as counter electrode, varying the potential in anodic and cathodic direction from the open circuit potential by 10 mV at a scan rate of 0.05 mV/s.
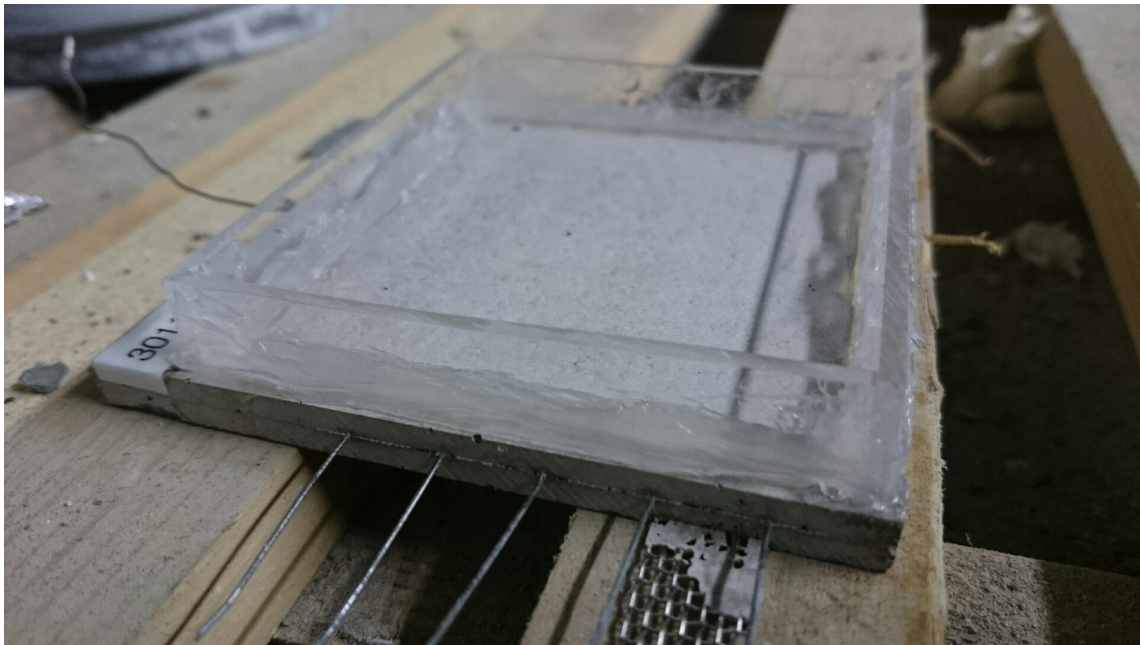

Figure 3: Samples used for wet and dry cycles.

Results

Linear polarization measurements allowed the calculation of an electrical resistance Rp' that is the sum of the polarization resistance Rp 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:

$$i_{corr} = \frac{B}{R_p}$$

(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 µA/cm^2 (lower then 0.1 µm/year) (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/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 µA/cm^2 (1 µm/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.
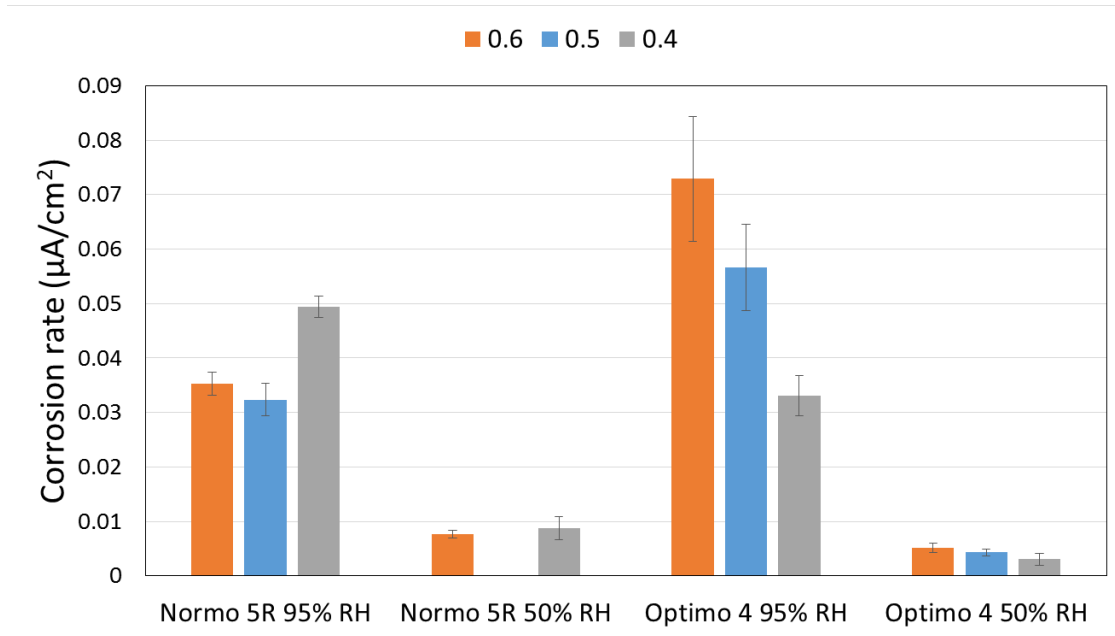

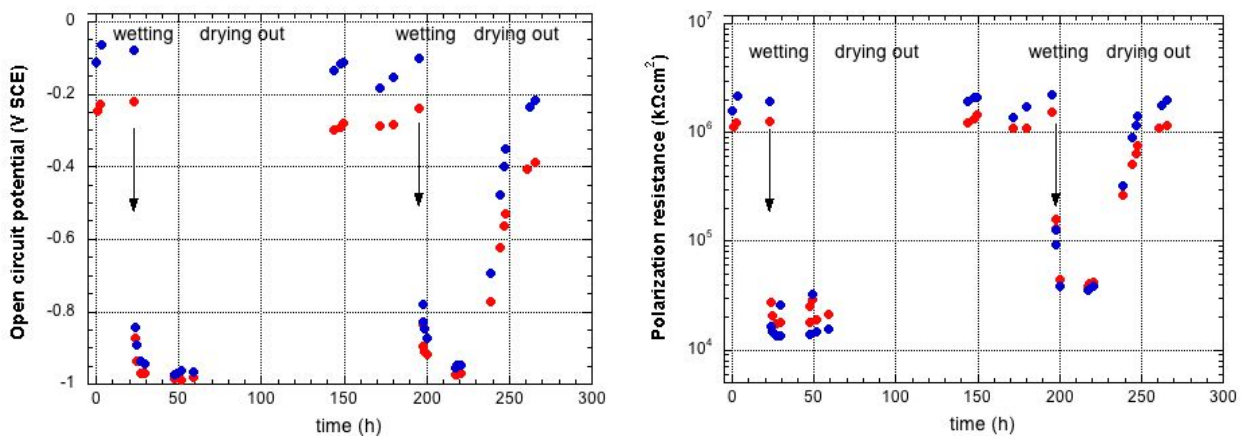Figure 4: Corrosion rates of the tested CEM I and CEM II at 50% and 95% RH.

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

Samples exposed to wetting showed a very rapid decrease of the open circuit potential and the polarization resistance (Fig. 5), the maximum values of the corrosion rate after wetting was 2 $\mu A/cm^2$ (nearly 20 $\mu m/year$)., 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 corrosion rates measured in the wet phase were about 20 times higher compared to 95% RH.

Discussion

Exposure in a constant relative humidity environment up to 95% RH (exposure class XC3) show negligible corrosion rate values (Fig. 4) far from being considered dangerous; current densities lower than 0.1 $\mu A/cm^2$ are generally considered as characteristic of a passive behavior. It can be noted that the corrosion rate of the steel increases by a factor of 10 going from exposure at 50% RH to 95%. The increase of corrosion rate over time observed at 50% RH could indicate that the steel surface, surrounded by a carbonated environment, is slowly activating but the water content is not high enough to give rise to dangerous dissolution rates. The corrosion behavior in environments with constant RH above 95% is under study.

The influence of the cement type and w/c ratio on the corrosion rate seems to be governed by the pore structure controlling the amount of water at the steel surface. 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 [11]. 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 opposite behavior is found, the corrosion rates are higher for blended cement (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 in experiments with wetting and drying cycles (exposure class XC4). In the wet periods maximum values as high as 2 $\mu A/cm^2$ 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 $\mu m/year$, can be very dangerous and limit the service life of a structure. The dissolution rate turns back to negligible values in the drying phase, emphasizing the importance of the presence of free water at the steel surface for the corrosion process.

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, 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.

Conclusions

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 $\mu m/year$ 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. However, the end of service life, thus the tolerable corrosion loss of the reinforcement (in μm), depends on the reinforcement diameter, cover depth and concrete strength.

For exposure conditions XC3 further research is needed in order to determine the maximum relative humidity for the different blended cements that leads to condensation of water in the pore system.

References

[1] Olivier J. G. J. (PBL), Janssens-Maenhout G. (IES-JRC), Muntean M. (IES-JRC), Peters A. H. W. J. (PBL) (2015). Trends in global CO2 emissions: 2015 Report. PBL Netherlands Environmental Assessment Agency The Hague, 2015.

[2] Leemann, A., Nygaard, P., Kaufmann, J., & Loser, R. (2015). Relation between carbonation resistance, mix design and exposure of mortar and concrete. Cement and Concrete Composites, 62, 33-43.

[3] Lothenbach, B., Scrivener, K., & Hooton, R. D. (2011). Supplementary cementitious materials. Cement and Concrete Research, 41(12), 1244-1256.

[4] Younsi, A., Turcry, P., Aït-Mokhtar, A., & Staquet, S. (2013). Accelerated carbonation of concrete with high content of mineral additions: effect of interactions between hydration and drying. Cement and concrete research, 43, 25-33.

[5] Papadakis, V. G. (2000). Effect of supplementary cementing materials on concrete resistance against carbonation and chloride ingress. Cement and concrete research, 30(2), 291-299.

[6] Sasatani, T., Torii, K., & Kawmura, M. (1995). Five-Year Exposure Test on Long-Term Properties of Concretes Containing. In Fly Ash, Blast-Furnace Slag, and Silica Fume in Concrete, Proceedings, Fifth International Conference, Milwaukee, WI (Vol. 1, pp. 283-296).

[7] Wang, S. (2014). Quantitative kinetics of pozzolanic reactions in coal/cofired biomass fly ashes and calcium hydroxide (CH) mortars. Construction and Building Materials, 51, 364-371.

[8] Kolani, B., Buffo-Lacarrière, L., Sellier, A., Escadeillas, G., Boutillon, L., & Linger, L. (2012). Hydration of slag-blended cements. Cement and Concrete Composites, 34(9), 1009-1018.

[9] Lye, C. Q., Dhir, R. K., & Ghataora, G. S. (2016). Carbonation resistance of GGBS concrete. Magazine of Concrete Research, 1-34.

[10] Lye, C. Q., Dhir, R. K., & Ghataora, G. S. (2015). Carbonation resistance of fly ash concrete. *Magazine of Concrete Research*, *67*(21), 1150-1178.

[11] Alonso, C., Andrade, C., & Gonzalez, J. A. (1988). Relation between resistivity and corrosion rate of reinforcements in carbonated mortar made with several cement types. *Cement and concrete research*, *18*(5), 687-698.