

CONCRETE CARBONATION PROTECTION SYSTEMS

Marcos da Silva Lopes Simas

ABSTRACT

Concrete has been used for many years in the construction of countless structures since it was simple to maintain and had a highly effective performance. However, when subjected to hard exposure conditions, concrete service life degrades, due to processes like carbonation.

This thesis objective is to assess the relationship between carbonation depth and time of exposure in different types of coatings.

Four different types of surface coatings were tested in order to analyze carbonation progress: a common plastic paint and three paints with anti-carbonation properties. Coatings were applied in concrete samples and later tested in an accelerated carbonation test chamber. The efficiency of protection systems was attested in comparison with unprotected samples.

The influence of concrete cracking in the carbonation progress was also analyzed. These samples were also submitted to accelerated carbonation and the carbonation depth was compared to the non-cracked surface.

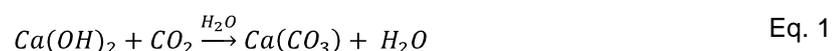
A linear relationship between the carbonation depth and the square root of time was observed, in accordance with several proposed models. Protected samples presented smaller carbonation depths, determined by spraying a phenolphthalein solution. Results seem to indicate that such surface coatings lead to a higher carbonation initiation period. Experimental data supports the hypothesis that carbonation depth is linearly proportional to the crack's width.

Keywords: Concrete, carbonation, surface coatings, cracking

1. Introduction

The majority of concrete deterioration is connected to corrosion of reinforcement due to carbonation or chloride-induced depassivation of steel bars. The carbonation induced corrosion rate is usually low, but due to its uniform distribution along the structure surface, it may lead to severe cracking and spalling. In terms of durability, we can assume that corrosion may begin when the carbonation depth equals the concrete cover (TUUTTI, 1982).

The chemical reaction between carbon dioxide (CO_2) in the air and the hydration products of cement, causes the neutralization of the concrete interstitial liquid phase, saturated of calcium hydroxide and other moisturized alkaline compounds. The initially high pH of the cement paste (typically in a range of 13-14) declines to a pH below 9, affecting the concrete's ability to protect steel reinforcement from corrosion. From among the several reactions that can take place, the one involving calcium hydroxide is the most important. Therefore, the concrete carbonation is usually represented in a simplified way by the reaction:



The CO_2 ingress into concrete occurs mainly by gas diffusion since ion diffusion is much slower (LAGERBLAD 2005). The calcium carbonate crystals ($CaCO_3$) fill the empty spaces in the concrete pore system, increasing its density and therefore reducing the carbonation rate in addition to the greater depth of penetration. Regardless of the quality of the concrete, it quickly forms a thin carbonated surface layer. This “carbonation front” goes deeper with time and separates in two different alkalinity areas: the non carbonated area with $pH > 9$, and the layer considered in somehow carbonated with $pH < 9$.

The traditional way of determining the depth of carbonation is to spray a phenolphthalein indicator onto the surface of a freshly split concrete sample. The solution is a colorless base indicator, which turns purple when the pH is higher than 9. Corrosion may begin when the carbonation front indicated by the phenolphthalein test is about 6 to 8 mm from the steel bar (KASHINO, 1984). Never the less, phenolphthalein gives a good approximation of corrosion’s begin.

Many factors can affect the carbonation rate, and ultimately, the amount of carbonation that can occur with a given cement paste composition. Internal factors that have the greatest impact on carbonation rates include water/cement ratio, chemical composition of mortar and internal relative humidity (RH). External factors include external RH, temperature, CO_2 concentration, and cracks. Water and carbon dioxide carry out the most important role since they are the two of the essential compounds for carbonation reactions. A higher concentration of CO_2 means higher diffusion, but it also means it needs a greater amount of water to dissolve and form the carbonate ions. In a general manner, the rate of carbonation takes its optimum state in natural conditions, to a RH between 50 and 70% (Figure 1). Gaseous diffusion becomes slower for both CO_2 higher rates (in water it’s 10^4 less than in air) and lower ones (not enough water to dissolve CO_2) (VÉNUAT; ALEXANDRE, 1969, BAKKER, 1988). Cracks allow CO_2 to penetrate deep in the concrete, increasing carbonation, as wider the crack’s width.

2. Carbonation modeling

The main mechanism of gaseous CO_2 transport is diffusion. In stable conditions, the amount of ion diffusion is controlled by Fick’s first law. On the other hand, the speed of the process is controlled by Fick’s second law. The generality of prediction models of steel depassivation due to carbonation follow this law, and are presented in the following simplified form:

$$x = K\sqrt{t} \quad \text{Eq. 2}$$

x – depth of carbonation (mm), K – carbonation coefficient ($mm/year^{0.5}$), t – exposure time (t)

This means carbonation depth increases in proportion to the square root of time. Daimon et al. (1971) considered the existence of an initial period (t_i) during which carbonation is inhibited, due to an initial drying stage when the pores are filled with water (Figure 5). The K value is assumed as a durability parameter, including all the environmental and concrete intrinsic dependent variables. There is some documentation referring K values, depending for example,

on binder type and content, exposure conditions, and some authors also indicate correction factors for surface treatment and cover (LAGERBLAD 2005). In the generality of the proposed models for carbonation prediction, K essentially depends on 3 main variants:

- The amount of concrete substances susceptible to suffer carbonation, or alternatively, the necessary amount of CO_2 for it to happen;
- CO_2 concentration differences between external environment and carbonation front;
- Concrete CO_2 diffusion coefficient.

3. Accelerated carbonation

Another approach available for observing the long-term performance, in addition to predictive modeling and real-time behavior, is to subject materials to accelerated processes. Accelerated carbonation is a way to accelerate the concrete carbonation process. This can be done incubating samples in an environment with an elevated concentration of CO_2 so that the reaction is not limited by the amount available. Samples are usually placed in a chamber with controlled conditions of temperature, RH and CO_2 concentration.

Knowing the rate values of natural (K_n) and accelerated exposure (K_a), it is possible to determine the relationship between the accelerated test time (t_a) and the real exposure one (t_n) to achieve equal penetration ($x_a = x_n$).

$$x_a = x_n \Rightarrow \frac{t_n}{t_a} = \left(\frac{K_a}{K_n}\right)^{1/0,5} \quad \text{Eq. 3}$$

Several researchers have tried to determine the K_a/K_n ratio based on parameters such as curing, compressive strength, binder content and others. However it is a complex task to simulate all the variables involved. Under natural conditions, the low reaction gives the released water in carbonation enough time to diffuse and leave the specimen. In accelerated tests, when a comparable depth of carbonation is reached, the humidity is still very high, suggesting it has not enough time to leave the sample (MUNTEAN, 2005). This causes the translation of carbonation optimum rate to values near 30% RH (SAEKI ET AL., 1971; THIERY, 2005) (Figure 1).

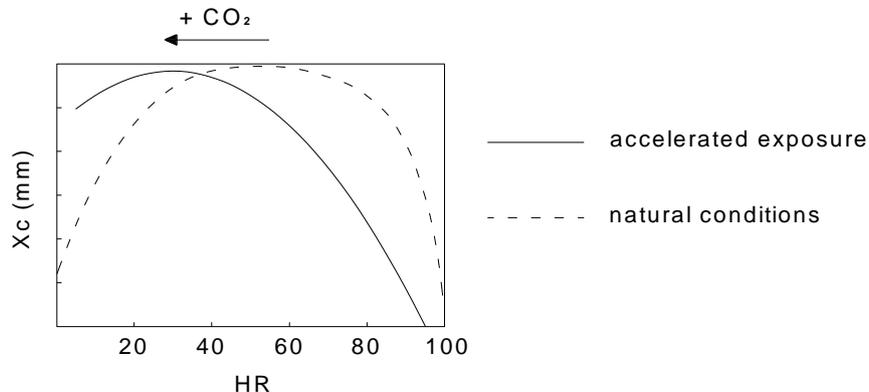


Figure 1. Relation between RH and carbonation depth for natural and accelerated conditions.

4. Anti-carbonation systems

Concrete can be protected against CO_2 ingress by means of surface coatings and/or polymer modified cementitious mortars. Many generic types of coatings are known to be effective barriers to CO_2 diffusion. However, the most efficient way to prevent further carbonation is to apply a surface layer that absorbs CO_2 , for example cementitious mortar or rendering concrete. Aesthetical or other reasons make it often difficult to use cementitious based protection since it needs a certain thickness to function. In these cases a thin layer of coating might be more efficient (REHABCON annex F). Surface protective treatments can be classified in several different ways. European standard prEN 1504-2 uses a classification system that divides surface treatments in "Hydrophobic impregnation", "Impregnation" and "Coating". Hydrophobic impregnation produces a water-repellent surface; impregnation produces a discontinuous thin film (usually 10-100 μm) that partly fills the capillaries; coatings produce a continuous layer (typical thickness 0,1-5 mm) on the concrete surface. These systems can be complemented with one another, when separately they do not fulfill the necessary requirements.

There are several test methods to evaluate the characteristics of a particular anti-carbonation product. Among these, resistance to CO_2 diffusion is one of the most important. The carbonation resistance can be measured in accordance with e.g. prEN 1062. By this standard, a coat's resistance to CO_2 diffusion should be greater than a 50 meters thickness equivalent air layer and, it's calculated as shown in

Eq. 4. An analogous method for water vapor diffusion is assumed, and the equivalent air thickness (R_{H_2O}) should be less than 4 meters (KLOPFER 1978). prEN 1504-2 recommends 5 meters.

Resistance to diffusion = Diffusion coefficient \times Layer thickness

$$(R_{CO_2}) \quad (\mu_{CO_2}) \quad (s) \quad \text{Eq. 4}$$

A repair system applied to an old concrete structure will inevitably affect the inner moisture state of concrete. For example, under unfavorable conditions, drier internal state might increase carbonation rate. Paints based on acrylic polymer emulsion, usually respond with a high resistance to CO_2 ingress and little diminished water vapor transfer.

5. Experimental procedure

5.1 Sample preparation

In sample preparation, a type II ordinary Portland cement (OPC) was used. Two sets of cylinders were cast for this study (Figure 2). Set 1 was prepared to evaluate efficiency between protected and unprotected samples. Set 2 refers to the samples, on which was intended to evaluate the crack effect on carbonation. Both sets were sited into a wet curing period of 28 and

78 days, respectively. Compressive strength tests were carried on 3 150x300 mm cylinders. Mix proportions and compressive strength test results are presented in Table 1 and 2, respectively.

Table 1. Concrete mix proportions.

	Cement (CEMII–32,5 MPa)	Sand	Aggregate 2	Aggregate 1	Water	W/C
kg/m ³	367	624	727	484	187	0,51

Table 2. Compressive strength test results.

Compressive tension (MPa)	
Set 1	Set 2
(28 days cure)	(78 days cure)
23,3	29,2

Set 1 consisted of 21 150x40mm cylinders sawn from the original specimens. Both ends of each cylinder were coated with epoxy resin to ensure that CO_2 would only diffuse in the samples, in a two-dimensional mode. Four different types of commercially available surface coatings were tested (Table 3). Sikagard paints were classified as anti-carbonation coatings, and Dyrup paint as a common plastic paint, therefore cheaper, with no concerns to restricting carbonation. The remaining samples were kept unprotected and four of them contained embedded steel bars.

Set 2 samples consisted of 15 150x70mm cylinders. These specimens were split in a diametral compression test, obtaining two similar pieces. These two were later united with a little epoxy adhesive. By doing this, was intended to obtain a controlled crack width. The maximum crack width (w_{max}) recommended in EN 1992-1-1, for any exposure class is 0,4mm. The halves were pressed together in order to fall within these limits as much as possible and crack width assessed with an optical crack microscope. Both ends of each cylinder were coated as done previously.

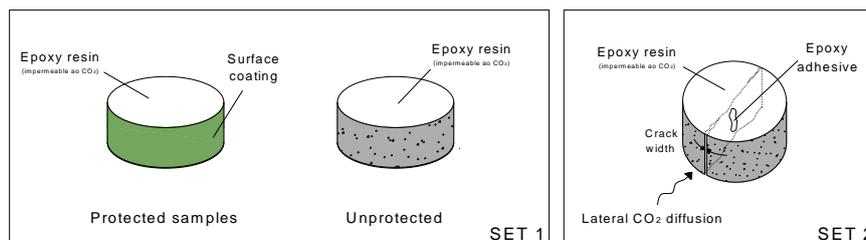


Figure 2. Prepared samples: Set 1 - uncracked samples; Set 2 - cracked samples.

Table 3. Characteristics of the tested surface coatings.

Coatings	Sikagard® 660 ES (S660)	Sikagard® 670 W (S670)	Sikagard® 680-ES Betoncolor (S680)	Dyrup Dyrurway ref. 5780 (Dyrup)
Base	Solvent acrylic resin dispersion	Solvent acrylic resin dispersion	Solvent acrylic resin dispersion	Aqueous acrylic resin dispersion
CO_2 diffusion resistance	120 μm ~ 290 m $\mu(CO_2) = 24,2 \cdot 10^5$	187 μm ~ 88 m $\mu(CO_2) = 4,7 \cdot 10^5$	130 μm = 420 m $\mu(CO_2) = 32,3 \cdot 10^5$	-
Water vapor diffusion resistance	120 μm ~ 2,8 m $\mu(H_2O) = 23333$	$s_D(H_2O) = 0,75$ m $\mu(H_2O) = 4200$	130 μm = 2,2 m $\mu(H_2O) = 16923$	-
Liquid water permeability	$W = 0,003 \text{ kg}/(\text{m}^2 \cdot \text{h}^{1/2})$	Impermeable to rain	Resistant to weather conditions	-

5.2 Accelerated testing

After curing, the specimens were transferred to a sealed chamber mode and subjected to carbonation at 26°C in temperature, 60% RH and a CO_2 concentration of 20% by volume. Samples from Set 1 were measured from a period of 7 to 39 days (group A, Figure 4) and later on, from a period of 199 to 329 days (group B, Figure 4). During this intermission, no measurement was possible. Samples from Set 2 were measured after a period of 27 and 53 days inside the carbonation chamber.

5.3 Carbonation depth measure

After the accelerated carbonation exposure, samples were removed from the chamber, sawcut in two pieces and the new exposed surfaces were sprayed with a phenolphthalein indicator (Figure 3). Carbonation front depth was then measured. In Set 1 samples, depth was measured in several points to determine median penetration (x). In Set 2, samples were sawcut to produce measurement surfaces perpendicular to both the material face and the crack. In these, data was taken into the crack surface (b) and along the uncracked surface (a), to each crack width (w).

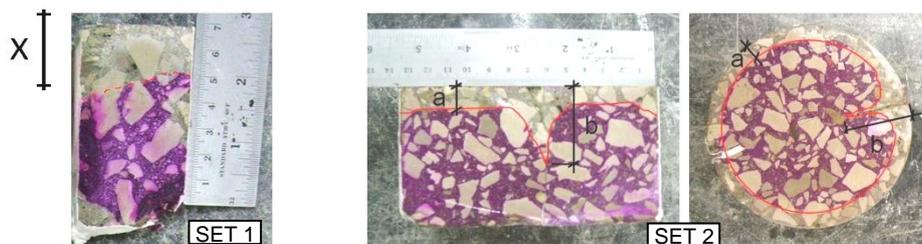


Figure 3. Carbonation depth procedure.

6. Results and Discussion

6.1 Unprotected systems

The results from Set 1 unprotected samples are presented in Figure 4. Parameter (a) from set 2 is also included since it relates to a median carbonation depth measured in an uncracked surface (values measured at 27 and 53 days time of exposure). Carbonation depth values are represented in a square root time scale which indeed gives a good representation of the measurements. Two linear trend lines were outlined for group A and B and one third regression to both groups (A+B). In this last one, the coefficient of determination (R^2) presents a higher value (88,5%), but during the period when effectively measurements were made (from 7 to 53 days and from 199 to 329 days) it evidences less adaptability. Since group A and B show different K values ($K_A = 1,884$, $K_B = 6,205$), a mixed model was proposed, based on Eq. 2 and Daimon et al. (1971) model (Figure 5). This representation allows explaining an initial phase of carbonation, during which the phenomenon is slowed down, but not fully ceased. In a natural environment, the water that is produced by the carbonation releases slowly in the atmosphere. In a accelerated carbonation process, water doesn't have enough time to leave the specimen. Thus, a higher inner moisture state delays carbonation because CO_2 diffusion in water is much slower than in air (10^4 times slower). When the inner and the outer moisture of the specimen reach an equilibrium state within the chamber, carbonation may reach a higher rate ($K_B > K_A$). In group A, a small carbonation, prior to the entrance in the chamber, seems to exist ($x_0 = 3,707mm$). Some dispersion on penetration is observed. In spite of the same mix proportions, the corresponding preparation for the various specimens took place in distinct occasions, possibly deriving in slight mortar differences. Phenolphthalein method may also provide some dispersion, since carbonation front frequently reveals an irregular boundary.

The relationship between laboratory and field data is highly dependent on the K_a/K_b rate (Eq. 3), determined based on the carbonation field performance tests. In the present study it was not possible to do such kind of analysis. The model here presented shows two different rates of carbonation. However, in a real environment and for considerable period of service life of the structure, the single carbonation rate calculated based in Eq. 2 may provide a good approximation about carbonation depth.

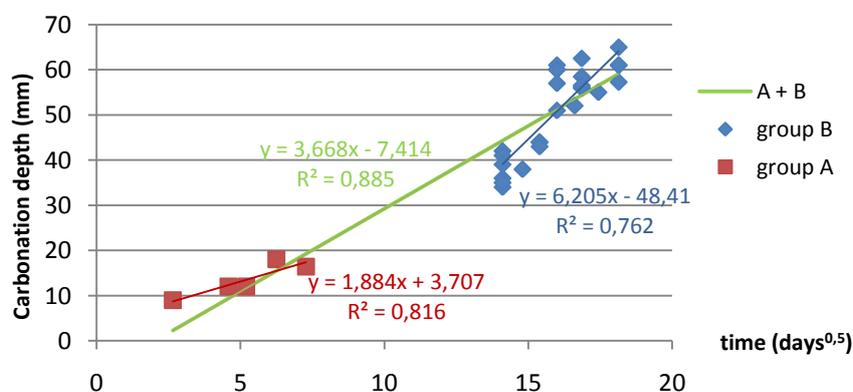


Figure 4. Carbonation depth in unprotected samples (Set 1).

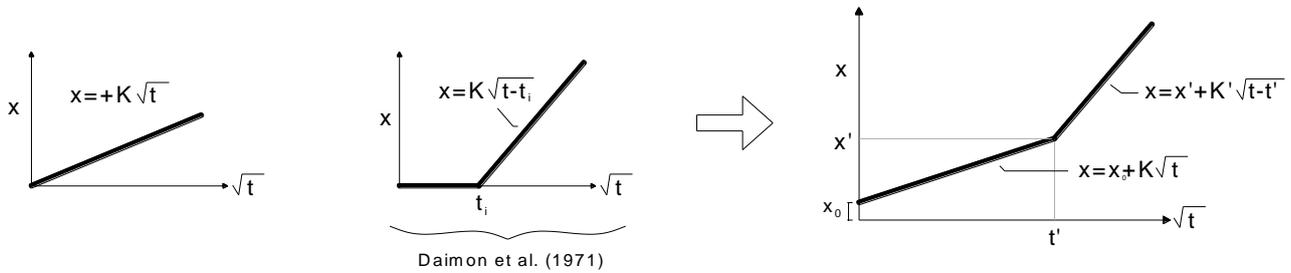


Figure 5. Proposed model for carbonation depth.

6.2 Protected systems

The same square root proportionality between time and carbonation depth is observed, as before to unprotected samples. The fact that small depths were measured (13 mm for S660 and S680) by the time of the first essay at 219 days of exposure may indicate that carbonation only begins after a certain period of time. This comes in accordance with Daimon et al. (1971) proposed model. The Sikagard coatings (no information about the Dyrup coating obtained from manufacturer) are permeable to water vapor. However, they can always offer some kind of resistance, increasing the inner moisture during the initial carbonation phase, amplifying the effect described before in 6.1. The epoxy resin applied on both edges of cylinders, revealed to be extremely effective blocking the CO_2 ingress. Analyzing the characteristics of each coating (Table 3), in decreasing order of resistance to CO_2 diffusion (R_{CO_2}), we have: S680 (420m), S660 (290m), S670 (88m) and Dyrup (admitting that this last one does not possesses any pretension at this point). This is precisely the order observed in Figure 6. Dyrup paint exhibits higher carbonation depths, followed by S670 and the coatings S660 and S680 with close values. In spite of the better characteristics of S680 (higher R_{CO_2} and smaller R_{H_2O}) comparing to S660, S680 may had an inferior thickness (s) than the one specified in the product's technical note, causing the approximately carbonation depths. The gradients calculated to each coating linear regression, relate to the K coefficient in Eq. 2. Gradients are relatively similar, varying from $K_{660} = 8,611 mm/day^{0,5}$ to $K_{680} = 10,27 mm/day^{0,5}$. One could say that coatings with higher R_{CO_2} should have minor carbonation rates, and that's in fact true, but due to the reduced number of samples, it would be risky to formulate further hypothesis about the tested coatings efficiency.

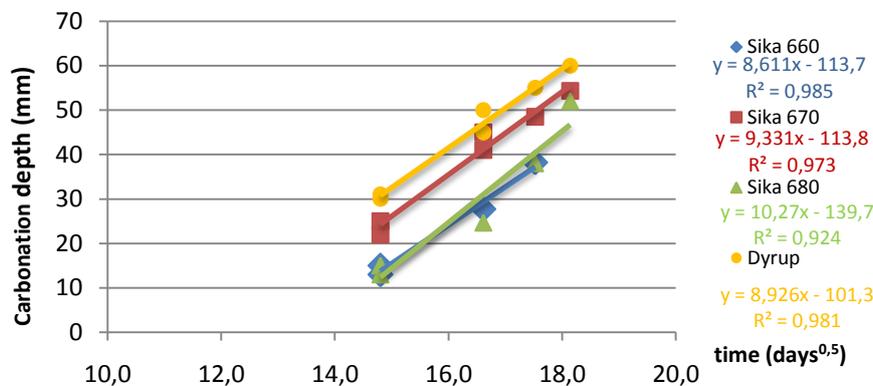


Figure 6. Carbonation depth in protected samples.

6.3 Systems comparison

The uncoated and coated samples were simultaneously tested during the effective period between 219 and 329 days. The coated samples presented inferior carbonation depths (Figure 7). The K value in unprotected samples ($K = 6,205 \text{ mm}/\sqrt{\text{day}}$) is inferior to protected ones. The tested coatings act as a CO_2 diffusion barrier but they can also act as a barrier to water vapor.

The presence of a coating besides reducing the CO_2 ingress, it can also affect the specimen moisture. Any inner moisture test was carried in the present study but, let us allow the following hypothesis to be made: inner moisture of specimens locates between 30 and 60% RH. Uncoated samples will balance their inner moisture with the chamber (60% RH). Coated samples however will take longer to do so, and thereby their inner moisture will be for a longer period closer to the optimum RH for carbonation to occur (Figure 1). This would lead to a higher carbonation rate for the coated samples, though in a real environment the opposite could happen. This simple example shows how accelerated carbonation can distort results.

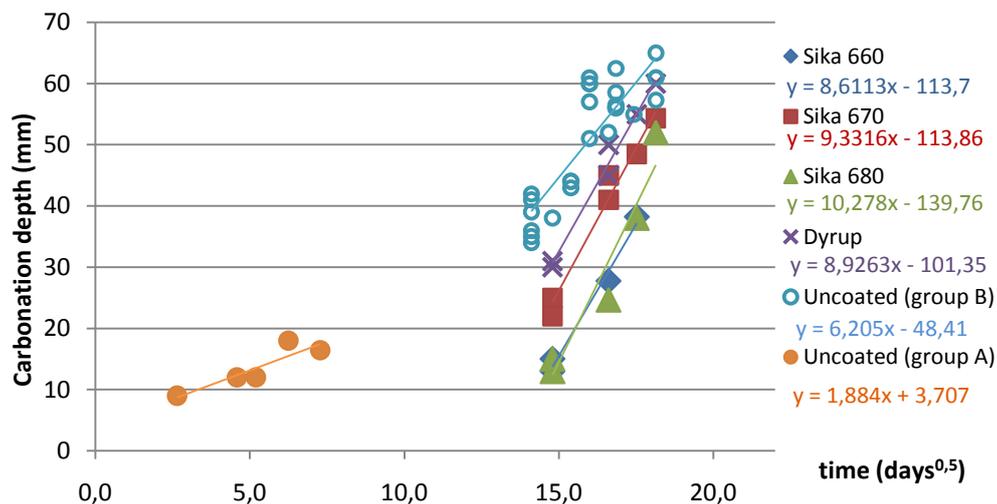


Figure 7. Carbonation depths for coated and uncoated samples.

6.4 Cracked samples

The a and b values for Set 2 samples are presented in Figure 8. Median carbonation depth in uncracked surface (Figure 8 *a*) at 27 and 53 days is, respectively, 11,8 mm and 16,4 mm. Penetration through crack (Figure 8 *b*) increases to larger widths (w). The b and w values seem to be linearly related which is in agreement with previous studies (SULLIVAN-GREEN, 2005). Extrapolating regression lines to $w = 0$, we obtain $b > 0$, which indicates further penetration near the crack's exposed surface. By relating $(b - a)$ with w , it is possible to evaluate crack's penetration isolated from the sound surface penetration, which leads to higher correlation.

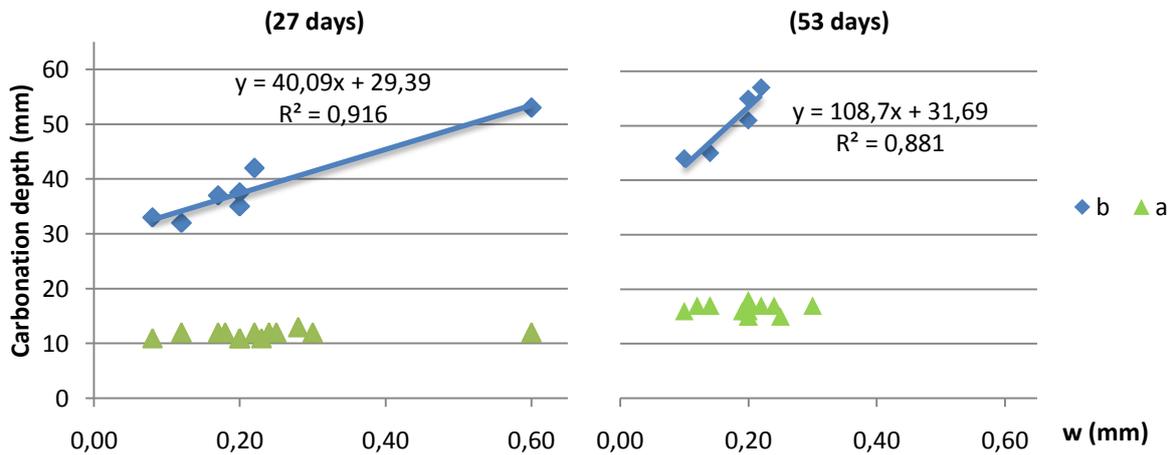


Figure 8. Penetration values for Set 2 sample.

7. Conclusions and further work

Carbonation seems to progress linearly in a square root time scale.

Smaller carbonation rates have been observed in earlier stages of exposure. A mixed model between $x = K\sqrt{t}$ (initial saturation stage) and $x = x' + K'\sqrt{(t - t')}$ (further exposure) provided a better reading for uncoated samples. A common plastic paint originated higher carbonation depths than anti-carbonation coatings, but even so, smaller than unprotected samples. However the carbonation rate in every case is of the same order of magnitude. In greater μ_{CO_2} coatings, smaller carbonation is expected, but not necessarily. Moisture transfers are a crucial factor affecting carbonation, and in accelerated tests, penetration rates may differ from those in real exposure conditions. Experimental data supports the hypothesis that carbonation depth in crack surface is linearly proportional to crack's width.

A wider set of specimens and a regular plan of measurements would allow a more rigorous carbonation rate determination. The validity of this approach can be fully established only after obtaining some results from the natural carbonation at longer durations.

8. References

BAKKER, R.F.M., *Initiation period. In: Corrosion of Steel in Concrete*, P Schiessl, RILEM, 1988, pp. 22–54.

DAIMON, M., AKIBA, T. Et KONDO, R., *Through pore size distribution and kinetics of the carbonation reaction of portland cement mortars*, *Journal of the American Ceramic Society*, 54(9):423-428, 1971

KASHINO, N., *Investigation Into the Limit of Initial Corrosion Occurrence in Existing Reinforced Concrete Structures*, 3rd International Conference on the Durability of Building Materials and Components, Espoo, Vol 3, 176-186, August, 1984.

KLOPFER, H., *The carbonation of external concrete and how to combat it*, *Bautenschutz and Bausanierung* 1, n.03, 1978

LAGERBLAD, B., *Leaching performance of concrete based on samples from old concrete constructions*, SKB TR-01-27, Report series of Swedish Nuclear Fuel and Waste Management CO, Stockholm, Sweden, 2001

MUNTEAN, A., BROHM, MEIER, S. A., PETER, M. A., , M, *Modelling and simulation of concrete carbonation with internal layers*. Berichte aus der Technomathematik 05-02, ZeTeM, University of Bremen, 2005.

prEN 1504 *European Standards for Concrete Repair*, EN

prEN 1062, *Paints and Varnishes: Coating Materials and Coating Systems for Exterior Masonry*

REHABCON IPS-2000-00063, *Strategy for Maintenance and Rehabilitation in Concrete Structures*, DG Enterprise of the European Commission, 2000-2004.

SAEKI, T., OHGA, H. et NAGATAKI, S., *Mechanism of carbonation and prediction of carbonation process of concrete*. Concrete Library of J.S.C.E., 12 (414): 23-26, 1991

SULLIVAN-GREEN, Laura E, *Effect of crack width on carbonation: implications for crack dating*, Master Degree Thesys, Northwestern University, Evanston, 2005

THIERY, Mickaël, *Modélisation de la Carbonatation atmosphérique des matériaux cimentaires*, Thèse pour obtenir le grade de docteur de l'Ecole des Ponts et Chaussées, 2005

TUUTTI, K. *Corrosion of steel in concrete*. Stockholm, Swedish Cement and Concrete Research Institute, 1982.

VENUAT, M., ALEXANDRE, J., 1968, *De la carbonatation des bétons*, CERILM, Publicação n.º195, 30 p, França, 1969.