

Modelling of concrete carbonation; is it a process unlimited in time and restricted in space?

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Abstract. The aim of the article is mathematical modelling of the carbonation process that has been based on results of research conducted both in accelerated and natural conditions. The article covers short characteristic of carbonation, its processes and effects. Also critical review of articles that concern carbonation mathematical models was included in the paper. Assuming the self-terminating nature of carbonation the hyperbolic model of carbonation was formulated. Such a model describes the carbonation progress as the process unlimited in time but with the restricted range in concrete depth that is limited by the value of a model asymptote. Presented results cover research on carbonation of concrete with a different water-cement ratio and different types of binders and duration times of early curing. Investigations have been conducted as accelerated (1% concentration of CO₂) as well as in long-term exposures in natural conditions. The obtained results confirmed statistically that hyperbolic model is a well-founded approach when the modelling concrete carbonation process is concerned.

Key words: concrete carbonation, carbonation models review, hyperbolic model of carbonation, self-terminating nature of carbonation, accelerated testing of carbonation, long-term natural tests of carbonation.

1. Carbonation – mechanism, factors, threat for durability

Carbonation is the combination of physical and chemical concrete transformations under the influence of prolonged exposure to carbon dioxide. A carbon dioxide is always present in ambient air and the internal atmosphere of buildings. In the atmosphere concentration of CO₂ by volume is about 0.04% [1] but in industrial areas or along the roads may be 0.3% and locally even more, so in the concrete with surface uncovered with other the material carbonation process runs continuously [2]. The main causative mechanism of carbonation is the reaction of atmospheric CO₂ with calcium hydroxide, one of the cement hydration products (Fig. 1). The products of this reaction are calcium carbonate and water. Other constituents of the concrete, such as hydrated calcium aluminosilicate contained in the CSH-phase can also carbonate but this process is slow and takes place in a smaller scale. Also its effect on the properties of concrete is visible only when a concentration of CO₂ is high [3].

In the group of external factors, environmental factors and exploitation conditions of concrete and technological factors shaping the concrete properties during its execution are standing out.

Internal factors determining the course of carbonation are properties of concrete components and their proportions in concrete as well as hardened concrete properties. They both are result of the qualitative and quantitative composition, as well as, the conditions of element execution. The proposed classification has no sharp limitations and individual factors are strongly interrelated (e.g. w/c vs. porosity, cracks width

vs. diffusivity, etc.). Classification aims, to identify factors that should be taken into account when course of carbonation in concrete is under considerations at various stages of its life, are including designing, creation and exploitation.

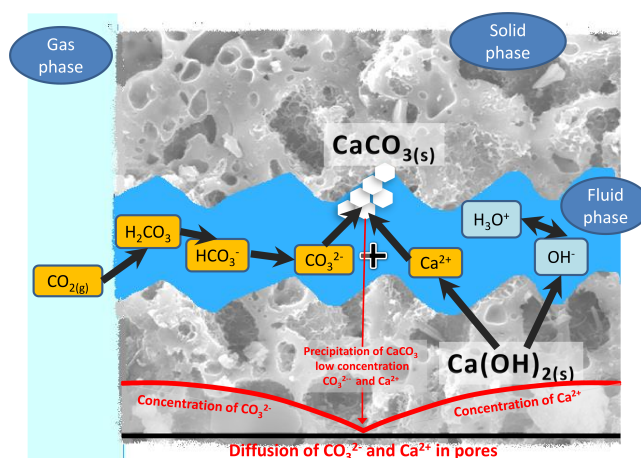


Fig. 1. Mechanism of carbonation

Concrete carbonation is not only dependent on the presence of carbon dioxide in the environment but also its intensity. The extent of carbonation in the concrete strongly depends on a number of factors (Table 1) which can be classified as external – relating to the ambient and internal conditions– related to the composition and microstructure of concrete (Fig. 2).

Progress of carbonation in concrete causes a gradual neutralization of the alkalinity of concrete, due to the change of calcium hydroxide onto the neutral calcium carbonate. As a

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result of this reaction to the alkalinity of concrete is reduced to pH below 10. Consequently, concrete protection of the reinforcing steel is lost. The passivity of the protective layer on steel is destroyed. When steel is depassivated the electrochemical corrosion begins in presence of oxygen and moisture. In the concrete, moist but not saturated with water, the time of carbonation is dependent on the relationship between the rate of diffusion of Ca^{2+} ions and carbon dioxide. When the diffusion of carbon dioxide is faster than Ca^{2+} the carbonation

products crystallize on the surface of portlandite and forms a protective layer that slows down the process. This layer is not completely sealed, so the process is delayed but not stopped. If the Ca^{2+} ions diffuse faster than a carbon dioxide, carbonate crystallization occurs on the surface of CSH and in the capillary pore space that reduce the porosity of the concrete. This mechanism is particularly evident in the case with Portland cement concretes [4] but observed also by many researchers with slag cement [5–7] or with fly ash cement [7–9].

Table 1
 Influence of most important factors on course of carbonation

	Factor	The direction of factor's change	Change of rate of carbonation	Remarks
External	Concentration of CO ₂	↗	↗	Proportionally to the square root of the concentration
	Relative Humidity of the air	↗	0–50% ↗ 50–80% ↔ 80–100% ↘	Humidity of concrete is more important
	Cracking (crack width)	↗	↗	
	Stress state:			Local effects
	Tensile stresses	↗	↗	
	Compressive stresses	↗	↘	
	Freeze/thawing destruction	↗	↗	–
Technological	Ambient temperature	↗	↗	–
	Time of early curing	↗	↘	–
	Temperature of curing (heat treatment)	↗	↗	–
	Water-cement ratio	↘	↘	
Internal	Cement content	↘	↗	
	Alite content in clinker	↗	↘	
	Specific surface of cement	↗	↘	Despite of the type of cement
	Additives for concrete:			
	Type I	↗	↔	Influence depends on additive content
	Type II			
	– as a partial substitution of aggregate	↗	↗	
	– as a partial substitution of cement	↗	↘	
	Polymers presence (PCC)	↗	↘	–
	Air entrainment	↗	↗	–

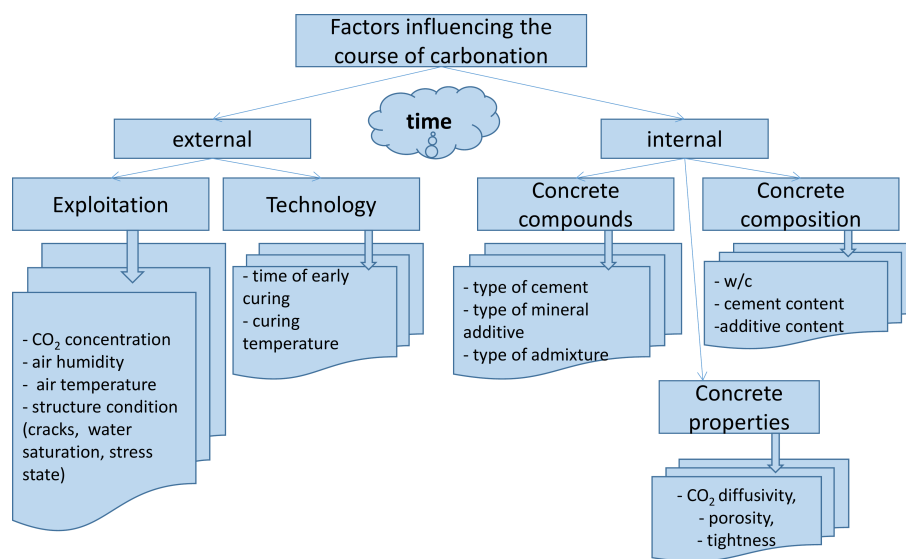


Fig. 2. Classification of factors affecting the carbonation

Table 2
Influence of carbonation of main concrete properties

Property	Influence: + positive - negative = non	Remarks	
Passivation of reinforcement	-	Decrease of pH value under the limit of durability of passive layer on the rebars	
Water absorption	+	Small decrease as a consequence of microstructure tightening	
Compressive strength	Surface layer	+	Small increase as a consequence of increase of porosity
	globally	=	surface effect not affect the result of compressive strength testing on the samples
Depth of water penetration under pressure	+	The result of pores filling with carbonation products	
Frost resistance	-	Decrease, due to the fact that small pores can easier fully fill with water	
Shrinkage	-	Carbonation shrinkage is an element of total shrinkage	
Susceptibility on chloride penetration	-	Increase of susceptibility – synergic effect	

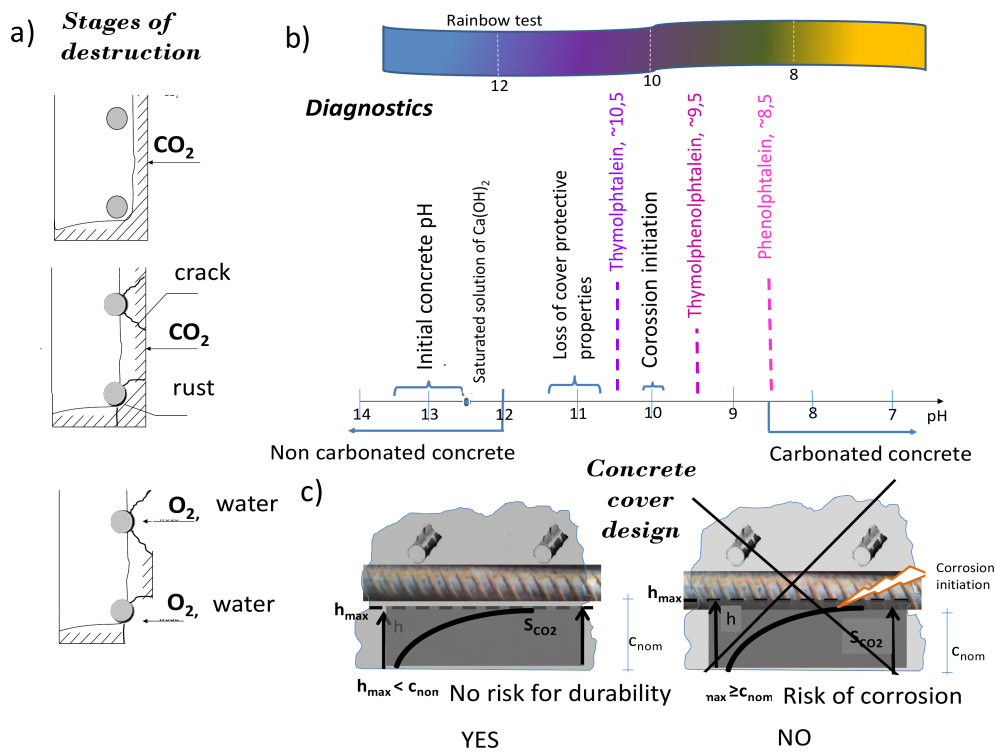


Fig. 3. Stages of destruction (a), diagnostics (b) and cover design (c) under the risk of carbonation

Carbonation has significant effects on most of the technical properties of concrete (Table 2). The indirect technical effect of carbonation is the gradual destruction of reinforced element (Fig. 3a), initiated when the carbonation front reaches a depth equal to the thickness of concrete cover. A depth of carbonation in concrete is evaluated mainly by using pH indicators (Fig. 3b). Simultaneously, carbonation has a positive environmental effect due to sequestration of some volume of CO₂ from the atmosphere [10, 11]. The choice of the cover thickness should ensure that during the designed service life of structure carbonation front has not reach the reinforcement (Fig. 3c). Both, the choice of the depth of cover and prediction of the time when the front of carbonation reaches a reinforcement, require knowledge of the model expressing the change in the depth of carbonation as a function of time.

2. Theoretical foundations of carbonation modeling – Fick’s laws advantages and disadvantages, factors not included in them

Researches on the development of universal models of carbonation, describing its changes in time and taking into account different material and technological variables, are conducted for many years in various research centers. In mathematical modeling of carbonation a key issue is to determine the intensity of the flow of carbon dioxide through the concrete. The starting point is Fick’s law. The diffusion flux in one-dimensional space, in accordance with Fick’s first law, is described by the equation:

$$Q = -D \frac{\partial \varphi}{\partial x}, \quad (1)$$

where Q – is the flow, i.e. the amount of material flowing through a unit cross section per unit time $\text{mol/m}^2\text{s}$, D – is the diffusion coefficient m^2/s , φ – is the concentration of the diffusing substance mol/m^3 , x – is the way of diffusion, m.

Fick's first law allows to describe the diffusion process under a constant, unchanging in time, density of the diffusion flux [12, 13].

In the case where the density of diffusion flux varies over time, the diffusion process is described by Fick's second law, in the form as follows:

$$\frac{\partial Q}{\partial t} = D \cdot F_D \frac{\Delta \varphi}{x}, \quad (2)$$

where Q , D , φ , x – as in Eq. (2), t – time, s, F_D – surface, through which the diffusion occurs, m^2 , $\frac{\Delta \varphi}{x}$ – concentration gradient on the concrete surface and on the depth x .

If x is taken as the depth of carbonation, thus simplifying it can be assumed that φx , i.e. the concentration on the depth x is 0 and then Eq. (2) takes the form (3):

$$\frac{\partial Q}{\partial t} = \frac{D \cdot F_D \cdot \varphi_{\text{ext}}}{x}, \quad (3)$$

where φ_{ext} – CO_2 concentration in the air.

If we assume that the diffused carbon dioxide will be completely used for carbonation, then diffusion flux ∂Q through a given volume of concrete is equal to the maximum potential amount of carbon dioxide that can bind due to carbonation in this volume of concrete:

$$\partial Q = a \cdot F_D \partial x, \quad (4)$$

where a – coefficient determining the amount of CO_2 bound in the way of carbonation by unit volume of concrete in kg/m^3 , calculated acc. to the Bulletin CEB [14] as:

$$a = 0.75 \cdot C \cdot [\text{CaO}] \cdot \alpha_H \cdot (M_{\text{CO}_2}/M_{\text{CaO}}), \quad (5)$$

wherein the C – content of cement, kg/m^3 ; $[\text{CaO}]$ – CaO content in the cement composition; α_H – the degree of hydration of cement; M_{CO_2} and M_{CaO} – molar masses.

Substituting (4) to (3) and integrating over ∂x a basic carbonation model is obtained. This model is used by most researchers, for example, Bars et al. [15], Burkan et al. [16], Hossain et al. [17], Ishida and Maekawa [18, 19], Loo et al. [20], Masuda [21]. These Ming Liang et al. [22], Monteiro et al. [23], Muntean [13], Steffens et al. [24] as a basic model that determines the depth of carbonation x after the time of exposure t in the concentration of CO_2 equal to φ_{ext} :

$$x = \sqrt{\frac{2D\varphi_{\text{ext}}}{a}} \cdot \sqrt{t}. \quad (6)$$

In practice, the most widely used model is greatly simplified. It relates to an average constant RH and carbon dioxide concentration in the environment and can be expressed in the form:

$$x = B - A \cdot t^{1/2}, \quad (7)$$

where A is a constant depending on the diffusion coefficient, the ability of concrete to bind CO_2 and CO_2 concentration in the air whereas B is empirical factor accounting the initiation

period of carbonation. Also a formula in the following form is often used:

$$x = \sqrt{\frac{2Dt[\text{CO}_2]}{[\text{Ca}(\text{OH})_2]}}, \quad (8)$$

where $[\text{CO}_2]$ and $[\text{Ca}(\text{OH})_2]$ – molar concentration of carbon dioxide and calcium hydroxide concentration, D – diffusion coefficient, t – time of exposition.

The models (6)–(8) treat the phenomenon of carbonation as unlimited in the concrete that is exposed to an environment containing carbon dioxide and unlimited in time. It is assumed that the end of carbonation is related only to the exhaustion of reagents available in the system, including mainly calcium hydroxide and in the further horizon other hydrates. An important issue, however, is the accessibility of carbon dioxide in the system, especially, in the deeper zones of the concrete. Diffusion of CO_2 resulting from the concentration difference in the way from the surface into the concrete depends not only on the concentration gradient but also on the concrete microstructure. The models based on Fick's laws assume that the medium in which diffusion takes place does not change over time, which allows the reception of a constant diffusion flux in Eq. (1). This is a significant simplification of the description of the process of carbonation, which does not take into account a number of additional factors, such as changes in diffusivity as a function of humidity, changes in atmospheric concentrations of CO_2 in climatic year, participation in the carbonation of CSH phase and residuals of non-hydrated cement, qualitative and quantitative characteristics of the material composition of concrete (w/c, type of cement, additives, admixtures), technological and environmental factors (curing, temperature, state of stress) and first of all diffusivity changes resulting from changes in time of the concrete microstructure. The latter effect, resulting from the saturation of the pores with carbonation products, limits the possibility of a direct description of a process based on Fick's law. The result of carbonation is a decrease in porosity, in particular capillarity that takes place in addition to the occurrence of carbonation shrinkage, thus reducing the permeability of the concrete and therefore the possibility of diffusion of gases in concrete.

3. Overview of theoretical and empirical models describing carbonation progress in time

The considerations and doubts have led to the formulation of a number of different forms of model expressing the progress of carbonation in time as a function of various factors.

Especially, the modifications of the basic model (see Eq. (6)) are numerous when taking into account the material variables, technological and environmental factors. For example, Nilsson [25] points the need to include changes in diffusivity of concrete with periodic changes of the humidity:

$$x_{\text{CO}_2} = \int_0^t \frac{\varphi_{\text{ext}}}{a} \cdot \frac{1}{\int_{x=0}^{x=x_{\text{CO}_2}} \frac{dx}{D \cdot f(\text{RH})}} dt. \quad (9)$$

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Papadakis et al. after many years of research [26] have developed and published a model that accounts participation of phases other than portlandite in carbonation:

$$x = \sqrt{\frac{2Dt[CO_2]}{[Ca(OH)_2] + 3[CSH] + 3[C_3S] + 2[C_2S]}} \quad (10)$$

This equation was derived with the simplifying assumption that the full carbonation of concrete is not only a complete consumption of calcium hydroxide, but also other mineral phases. However, a very big difference in the rate of carbonation for these phases and portlandite shows that only the carbonation of $Ca(OH)_2$ is important in practice. Groves [27] proves that in Eq. (10) the unreacted components of the cement compounds could be omitted and the equation can be simplified to:

$$x = \sqrt{\frac{2Dt[CO_2]}{[Ca(OH)_2] + 3[CSH]}} \quad (11)$$

In both cases (Eqs. (10) and (11)) models were derived and experimentally verified assuming an initial maximum time of concrete early curing, which in practice is not always possible and expedient. Wang and Lee [28] illustrate a modified version of the model (10) defined for concrete containing up to 15% of microsilica in the form of:

$$x = \sqrt{\frac{2Dt[CO_2]}{0.33[Ca(OH)_2] + 0.214[CSH]}} \quad (12)$$

Models from (6) to (12) are based directly on Fick's laws, so they may be treated as well theoretically established. Many publications also presented empirical models of carbonation, taking into account Fick's law to a limited extent and determined on the basis of test results obtained over a range of variables in material and exposure conditions. For example, Papadakis [26] presented an empirical model of carbonation depth x for concrete with Portland cement, carbonated under natural atmospheric conditions:

$$x = 0.35\rho_C \frac{\left(\frac{w}{c} - 0.3\right)}{1 + \frac{\rho_C w}{1000C}} f(\varphi) \sqrt{1 + \frac{\rho_C w}{1000C} + \frac{\rho_C K}{\rho_K C} c_{CO_2} 5 \times 10^5 t}, \quad (13)$$

where ρ_C , ρ_K – density of cement and aggregates, kg/m^3 ; K , C , W – the content of aggregate, cement and water in the concrete, kg ; c_{CO_2} – concentration of CO_2 in the air, mg/m^3 ; $f(\varphi)$ – influence of relative humidity; t – time of exposure, years.

Russell et al. [29] propose an empirical model defined on the basis of samples prepared in order to achieve a uniform level of humidity in its entire volume:

$$x = \beta_0 + \beta_1[\log(Pl)] + \beta_2(f_{cu}) + \beta_3(RH_{10}) + \varepsilon_1, \quad (14)$$

where Pl – initial air permeability through the concrete, RH_{10} – relative humidity in the pores of the concrete to

a depth of 10 mm, f_{cu} – compressive strength, β_i and ε_i – coefficients of the model.

Meanwhile, authors [29], verifying above findings showed limited compliance of this model with the results obtained for the different concretes – yielding correlation coefficients not exceeding the value of 0.7.

Uomoto et al. [30] presented a complex model of carbonation as a function of w/c , CO_2 concentration, temperature and exposure time:

$$x = (2.084 - 0.8471 \log C_{CO_2}) \times e^{8.748 - \frac{2563}{T}} \times \left[2.39 \left(\frac{w}{c}\right)^2 + 0.446 \frac{w}{c} - 0.398 \right] \times \sqrt{C_{CO_2} \times t}, \quad (15)$$

where C_{CO_2} – CO_2 concentration, %; T – ambient temperature, K; t – time of exposure, years, w/c – water-cement ratio. The model was determined on the basis of research in the natural and accelerated conditions (elevated CO_2 concentrations), but only on samples with a high degree of saturation with water (about 80%), which limits the versatility of the model.

Kishitani [31] published formulas determined on the basis of long-term studies in natural conditions, binding a carbonation depth with the w/c value and exposure time t , and pointing out the threshold value of $w/c = 0.6$, significantly changing the nature of this relationship. Kishitani's Model is a pair of equations:

$$\begin{cases} \text{if } \frac{w}{c} < 0.6 \text{ then } x = R1 \times \sqrt{t} \times \sqrt{0.639 \frac{w}{c} - 0.244} \\ \text{if } \frac{w}{c} \geq 0.6 \text{ then } x = R2 \times \sqrt{t} \times \sqrt{\frac{\left(\frac{w}{c} - 0.25\right)^2}{0.345 + \frac{w}{c}}} \end{cases} \quad (16)$$

wherein $R1$, $R2$ – coefficients of the type of cement. The model was determined on the basis of concrete with Portland cement, for which the values of $R1$ and $R2$ are equal to 1; for other types of binders the model was not generalized.

The Bulletin 238 Comité Euro-Internationale du Béton [14], developed by the Working Groups CEB 5.1 Modeling of Material Behavior Exposed to the Environment and the Environmental Actions 5.2, presents a probabilistic model in the form:

$$x = \sqrt{2k_1 k_2 k_3 \Delta c} \sqrt{\frac{D_{nom}}{a}} t \times \left(\frac{t_0}{t}\right)^n, \quad (17)$$

where D_{nom} – diffusion coefficient at $RH \approx 65\%$ and $t_{ext} \approx 20^\circ C$, $mm^2/year$; Δc – difference of CO_2 concentration on the surface of concrete and inside the concrete; the authors suggest to assume te value of concentration equal to 0 at the depth of carbonation range, and then Δc in Eq. (17) is equal to c_0 – concentration of CO_2 in the air, kg/m^3 ; a – amount of CO_2 for concrete full carbonation, calculated with Eq. (5) kg/m^3 ; n – coefficient of influence of changes in external conditions; for laboratory conditions $n = 0$, for natural conditions $n \leq 0.3$ (the higher the changes of conditions the higher value of n); t_0 – reference period – in natural conditions $t_0 = 1$ climatic year; t – time of exposition, years;

k_1 – coefficient of concrete humidity, from 0.3 to 1.0; k_2 – coefficient of time of early curing; 1.0 for “good” curing or 2.0 for “bad” curing; there is no definition of “good” and “bad” curing; k_3 – coefficient of concrete bleeding, equal from 1.0 (minimum of bleeding) to 1.5 (for high degree of bleeding).

This model is an attempt to take into account all important factors that determine the course of carbonation in the structure. This direction of carbonation modeling was developed in further works of RILEM and Fédération of Internationale du Béton, among others, in the document “Predictive and Optimised Life Cycle Management” edited Sarja [32] and then subsequent FIB code drafts: Model Code for Service Life Design (2006), Model Code 2010 – First complete draft vol1 & 2 (2010) and more recently Model Code 2010 – Final draft vol1 & 2 (2012) [33].

A probabilistic model of carbonation given in [32] after Schiessl and Lay [34], in subsequent versions of these documents was slightly different, and ultimately in the draft Model Code [33] it is given in a form that combines the mechanisms of diffusion and chemical bonding of carbon dioxide and external influences (including weather conditions). It defines resistance to carbonation as a measurable value, expressed as a function depending on factors such as performance of works, exploitation environment and the impact of concrete carbonation test method. Modeling of carbonation shown in the FIB code is complex, requires knowledge of the many complex factors and difficult to carry out (for example the experimental determination of the diffusion coefficient of carbonated concrete).

The models published in the form of indicative nomograms are also found in the literature. They allow to determine predicted carbonation depth basing on the knowledge of selected materials and environmental characteristics, such as a nomogram quoted in [35], which allows to predict the depth of carbonation after specified time of exploitation, based on the w/c ratio, the type of cement and the type of environment. Vague definition of cement types included in the diagram, makes the obtained result a poor approximation thus determination of the level of the estimation uncertainty is impossible.

In many studies, models describing the approximate course of carbonation with time t as inversely proportional to the concrete compressive strength are published. For example, Brown [36] gives the relationship:

$$x = \frac{(K_C \times t^{1/2})}{f_c}, \quad (18)$$

where f_c – compressive strength, MPa; t – time of exposition, years; K_C – rate of carbonation, which depends on type of cement, mm/years^{1/2}.

Related models are also included in [15, 37, 38]. Czarnecki and Emmons [38] presented indicator K values and a graphical form (Fig. 4) of Eq. (18) – generalized without distinguishing the type of cement. Developing this idea, based on the exposure classes specified in PN EN 206-1 (Fig. 4b), may provide a basis for estimating the required thickness of coatings [41].

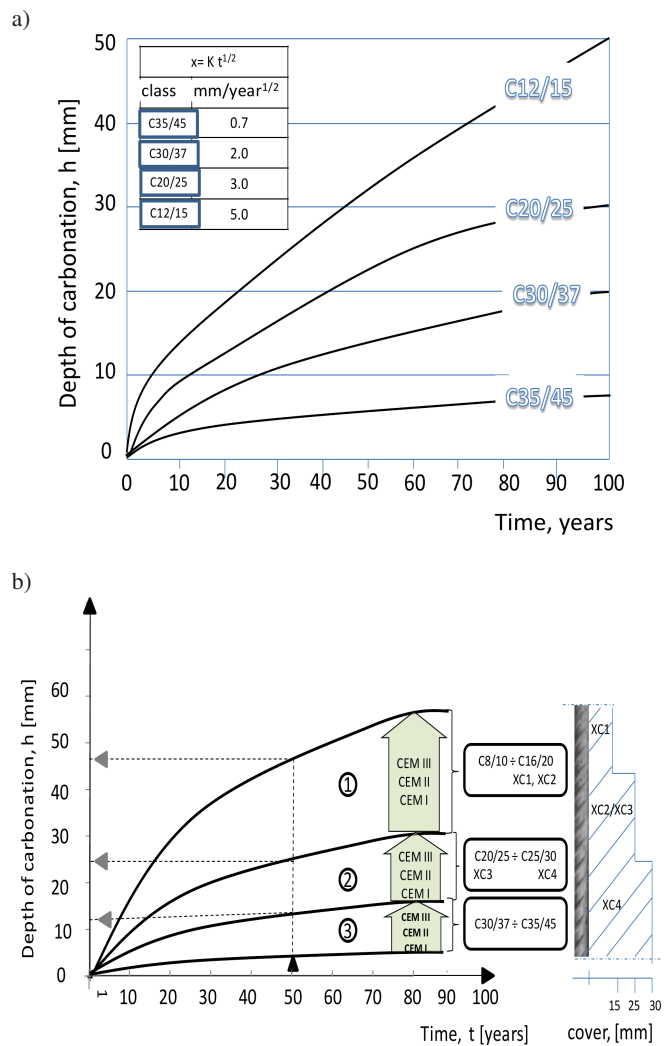


Fig. 4. a) Approximate depth of carbonation for different concrete strength classes (based on [37]), b) required thickness of concrete cover due to the indicative range of carbonation for concrete strength classes and type of cement (based on Ref. 40)

Duval [40] states the relation between the depth of carbonation and the strength of concrete as the exponential function with the power of -0.5 :

$$x = \sqrt{365t} \left(\frac{1}{2, 1\sqrt{f_{c28}}} - 0.6 \right), \quad (19)$$

where f_{c28} – compression strength after 28 days, MPa; t – time of exposition, years.

Jiang et al. [42] presented the model in the form of equation:

$$x = 839(1 - RH)^{1.1} \times \sqrt{\frac{\frac{w}{r_c C} - 0.34}{r_{HD} r_c C}} \times \varphi \times \sqrt{t}, \quad (20)$$

where RH – relative humidity, w and c – cement and water content in concrete, φ – CO₂ concentration, r_c – coefficient of type of cement, r_{HD} – degree of cement hydration. In further studies, the same authors [41] modified model (20) into

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a form suitable for so-called high volume fly ash concrete (HVFA):

$$x = 839(1 - RH)^{1.1} \times \sqrt{\frac{\left(\frac{w}{B}\right)^* - 0.34}{\alpha_H \times (1 - \beta \times k) \times C}} \times \varphi \times \sqrt[3]{t}, \quad (21)$$

where α_H – the degree of hydration of cement, k – coefficient taking into account the mass content of reactive pozzolans in the ashes, β – the degree of hydration of ashes, $(W/B)^*$ – efficient water-binder ratio, taking into account the reactivity of the ashes and its maximum amount that can react due to the pozzolanic mineralogical composition of the ash and cement.

In the works of Houst and Wittmann [42] and Saetta et al. [43] carbonation models do not describe changes in the depth of carbonation front but changes of the rate of the process v , determined on the basis of the Arrhenius function. Most often cited is the following form of the model:

$$v = \alpha \times A \times \exp\left(-\frac{E_0}{RT}\right) f_H f_K f_{K_r}, \quad (22)$$

where α – coefficient of pores microstructure; A – the number of collisions of reactive particles per unit of time 1/s; E_0 – energy of reaction activation, J/kg; R – gas constant; T – temperature, K; f_H, f_K, f_{K_r} – coefficients of, respectively – humidity, concentration of CO_2 and concentration of $Ca(OH)_2$ in pores. Coefficients f_K and f_{K_r} are the ratio of free and bond CO_2 in pores to the concentrations of CO_2 in the air. Coefficient f_H has a value from 0 to 1 and depends on humidity as follows:

$$f_H = \begin{cases} 0 & : \varphi < \varphi_{\min} \\ 2.5 \times (\varphi - \varphi_{\min}) & : \varphi_{\min} < \varphi < 0.9 \\ 1 & : 0.9 < \varphi \end{cases} \quad (23)$$

where φ – relative humidity; φ_{\min} – minimum humidity at which the reaction is possible (usually assumed as 0.5). The assumption that at the relative humidity above 90% the reaction rate will be the highest ($f_H = 1$) is true, but it ignores the fact that with such a high saturation of pores with water, the diffusion of CO_2 in pores is extremely slowed down, which may lead to a sharp reduction in the reaction rate, as a result of depletion of the main reagent.

4. Hypothesis of the carbonation self-terminating nature

With the progress of a carbonation rate the process decreases. In the literature one can find suggestions that the rate may decrease to zero, which would mean the reduction of diffusivity of concrete. In effect, carbon dioxide could not reach the noncarbonated area of concrete. Such a hypothesis is given in Fagerlund’s paper (Fig. 5a) [44] and it is confirmed by some investigations of the long-term exploited concrete structures [36]. According to Fagerlund, the reason for this may be the diffusion of alkali in the direction from the interior of concrete to the surface, which is opposite to the diffusion of CO_2 .

Determining the equilibrium of these phenomena causes the stabilization of the carbonation front in concrete [44].

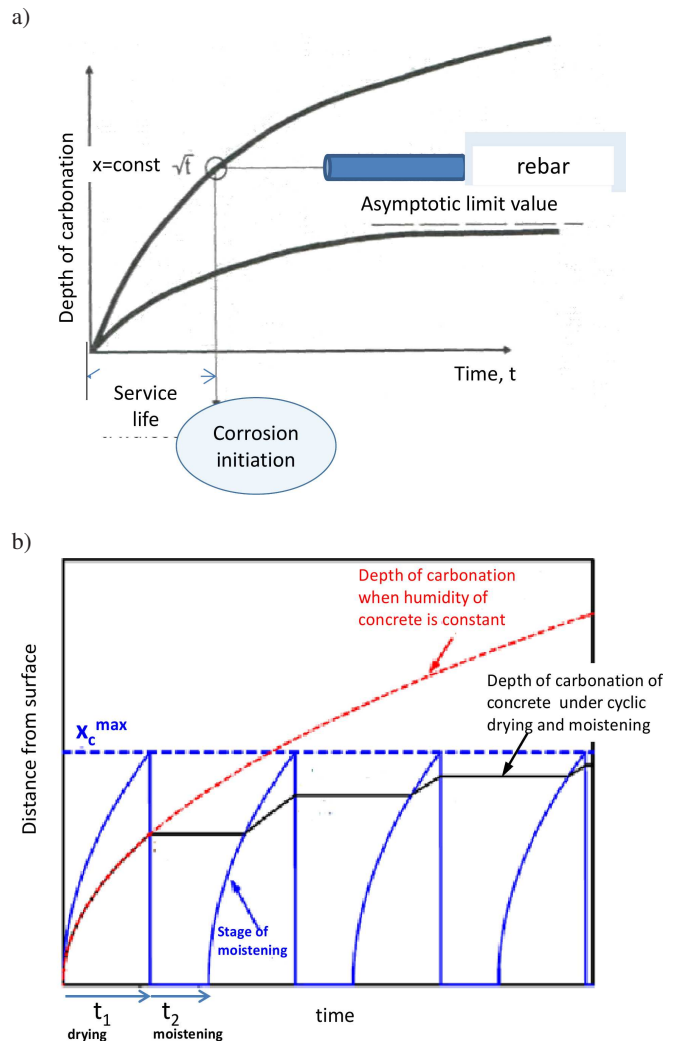


Fig. 5. a) The idea of carbonation limited in time by Fagerlund (based on Ref. 44), b) effect of alternating cycles of drying and moistening of concrete on the depth of carbonation, by Bakker (based on Ref. 45)

Bakker [45] also gives the suggestion of a gradual stabilization of the carbonation depth at a constant maximum level. However, he justifies his thesis with the fact that in natural conditions the concrete is alternately dry and wet and the carbonation can be continued into the concrete until the re-wetting front reaches the current carbonation depth, so any subsequent cycle lasts longer. If periods of concrete dampening are too short, the carbonation will not proceed and as a consequence the front will set at a constant level (x_c^{max} in Fig. 5b) [45].

This theory is also confirmed by Hergenröder [46] and L.-O. Nilsson [25]. The later one also introduces function R_{CO_2} as “moisture-dependent diffusion resistance” [25]:

$$R_{CO_2} = \int_{x=0}^{x=x_{CO_2}} \frac{dx}{D_{CO_2}(RH(x))}, \quad (24)$$

where D_{CO_2} – initial diffusion coefficient; $RH(x)$ – concrete humidity at the depth of carbonation x_{CO_2} and recommends the introduction of this variable to the equation discussed earlier in the form (6). Cited authors emphasize, however, that these theories are not yet confirmed in a satisfactory manner.

In the light of the foregoing, it can be assumed that a change of the characteristics of the concrete pore structure in time, pores overgrowing with carbonation products, as well as, periodic changes in the moistening of concrete cause changes of CO_2 diffusion coefficient. Taking into account, the concrete diffusivity changes over time (and with progress of carbonation depth) would require modifying the general model of carbonation depth (6) to the form:

$$x = \sqrt{\frac{2\varphi_{ext}}{a}} \cdot \frac{\partial D}{\partial t} \cdot \sqrt{t}, \quad (25)$$

where symbols in the model (29) are the same as in the model (6), and operator $\frac{\partial D}{\partial t}$ describes changes of diffusion coefficient in concrete with progress of carbonation. In the authors' opinion described processes may cause a reduction of the rate of carbonation gradually down to zero. It leads to stabilization its front on a fixed maximum depth in concrete.

So the factor $\frac{\partial D}{\partial t}$ should have such a form that the function (25) is characterized by asymptote, ordinate of which would naturally limit the depth of carbonation in concrete. In this perspective, the process of carbonation - remaining unlimited in time, could be regarded as limited in the space of concrete, in the zone from the surface to a depth equal to the asymptote ordinate. Authors' research of diffusivity conducted by concept contained in EN 1062-6:2003 (method A – Gravitational: steady flow of carbon dioxide through the sample of concrete with a thickness of approximately 10 mm at the difference in CO_2 concentrations of 10%, i.e. 180 g/m^3), for many types of concrete, including different cements types

and different w/c ratio, carbonated in natural and accelerated conditions, indicate that the nature of the diffusion coefficient changes is the power function of time [11] In the various conditions of tests the best fit of the model to the test results is obtained in the case of hyperbolic functions (Fig. 6).

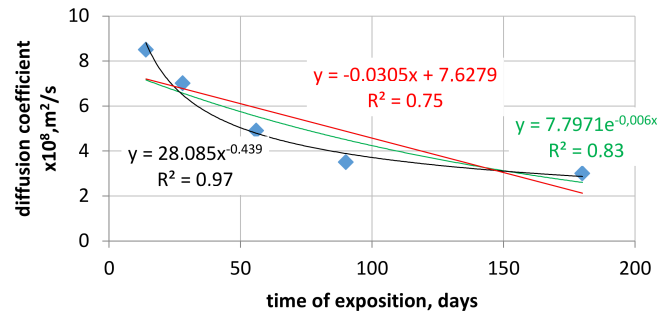


Fig. 6. Statistical modeling of CO_2 diffusion coefficient changes in concrete for concrete with cement CEM II/A – 42.5 and $w/c = 0.55$, as a function of time in the of carbonation chamber with CO_2 concentration = 1%; linear model – red color, the exponential model – green, hyperbolic model – black, lab results – blue; the form of models and coefficients of determination are given

The presented reasoning was the basis for the formulation of a general hyperbolic model of carbonation, according to which change in the depth of carbonation h is a function of time t and can be expressed in the general form:

$$h = a - b \times t^{-0.5}, \quad (26)$$

where a, b – characteristic coefficients of the function.

5. Experimental verification of the hypothesis

Research program. Experimental verification of the proposed model of carbonation was carried out in the framework of several independent research programs. The flow chart was

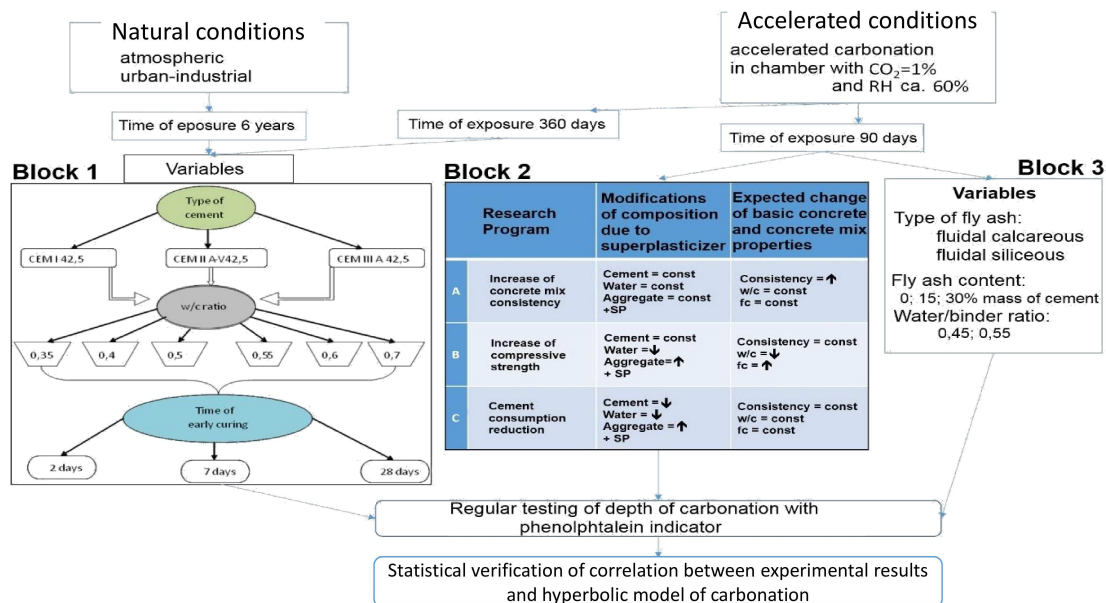


Fig. 7. Program of experiments

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similar in each of the programs: progressive measurements of depth of carbonation were carried out during the exposition in the assumed exposure conditions and then the convergence of the results with the hyperbolic model was verified using the statistical tests. A wide range of variables in the individual blocks of testing (w/c ratio, type of cement, the type and amount of mineral additives, modifications of concrete with superplasticizer used in different functions, different early curing time, different exposure conditions) were chosen to

ensure that the results obtained can be considered as universal (Fig. 7).

Materials and methods. The materials used in the investigation (cement, fine and coarse aggregate, fly ash, superplasticizer) were consistent with the relevant EN standards governing the requirements for the concrete components according to EN 206-1 and came from a commercially available trade offer. Characteristics of concrete compositions used in each testing program are given in the Tables 3–5.

Table 3
Concrete composition – testing program I and II

w/c	Concrete mix composition, kg/m ³							Slump mm
	CEM I 42.5R	CEM II A-V 42.5R	CEM III A 42.5R	Water	Sand 0/2 mm	Aggregate 2/8 mm	Aggregate 8/16 mm	
0.35	510	–	–	179	696	331	713	210
	–	510	–					160
	–	–	510					150
0.45	460	–	–	207	683	325	700	130
	–	460	–					130
	–	–	460					140
0.5	435	–	–	218	680	323	697	150
	–	435	–					160
	–	–	435					170
0.55	410	–	–	226	680	323	697	180
	–	410	–					170
	–	–	410					200
0.60	385	–	–	231	683	325	700	200
	–	385	–					200
	–	–	385					210
0.70	335	–	–	235	696	331	713	240
	–	335	–					240
	–	–	335					240

Table 4
Concrete composition – testing program III

Symbol	Concrete mix composition					Consistence, slump, mm
	w/c	Cement, kg/m ³ CEM II A-V42,5R	Water, kg/m ³	Aggregate, kg/m ³ 0/16 mm	SP, % c.m. melamine-naphthalene.	
0	0.50	435	218	1700	–	150
V	0.425	435	185	1788	0.67	150
S	0.425	435	185	1788	–	30
C	0.425	365	155	1927	1.27	150

Table 5
Concrete composition – testing program IV

Compound	Concrete mix composition, kg/m ³									
	w/(c+p)=0.55					w/(c+p)=0.45				
Cement CEM I 42.5R	320	272	272	224	224	360	306	306	252	252
Calcareous fluidal fly ash	0	48	0	96	0	0	54	0	108	0
Siliceous fluidal fly ash	0	0	48	0	96	0	0	54	0	108
Water	176	176	176	176	176	162	162	162	162	162
Sand 0/2 mm	597	594	594	592	592	595	594	594	591	591
Gravel 2/16 mm	1268	1263	1263	1258	1258	1264	1262	1262	1255	1255
Superplasticizer	2.9	2.9	2.9	2.9	2.9	3.2	3.2	3.2	3.2	3.2
p/(c+p), %	0	15	30	0	15	30	0	15	30	30

Investigations were performed on the concrete elements with dimensions 10×10×40 cm exposed in a vertical position. Exposure to natural conditions took place in an urban-industrial center of Warsaw, in the place unsheltered, exposed to all the weather (rain, frost, sun). Exposure in accelerated conditions took place in a specialized chamber with CO₂ concentration = 1% in the air, at about 20°C and a relative humidity of about 60%, in accordance with the procedure laid down in EN 13295:2005. Measurement of the depth of carbonation was performed regularly after successive periods of exposure, each time for a fresh break of the sample, using phenolphthalein indicator, allowing to find the front range of pH = ~8.5 [2].

Results and discussion. The results of each series of concrete in each test block were analyzed to verify the truth of the hypothesis about their convergence with a model in the general form (30). For this purpose for the Eq. (30) it was estimated by calculating a coefficient of significance and fraction of explained variation with the method of least squares, in relation to the resulting regression. Then the hypothesis was verified with the test F assuming the 95% confidence level. A sample set of test results for concrete with cement CEM I 42.5, carbonated at an accelerated rate, with different w/c ratio, and different time of early curing, is shown in a graphical form (Fig. 8).

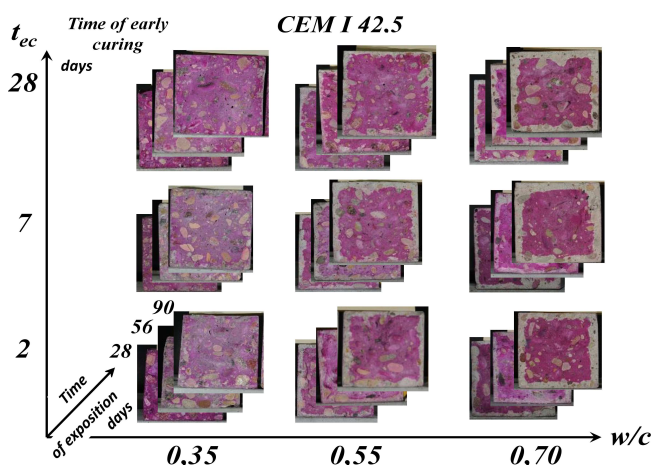


Fig. 8. The research program divided into research blocks

The effect of statistical modeling of regression based on research results (example Fig. 9) in all the examined cases led to a hyperbolic model with regression coefficient R exceeding the value of 0.85, regardless of the concrete compositions, material used, its mode of curing or the carbonation conditions. It is possible to refine the model by introducing to the equation the components taking into account the dependence of depth of carbonation not only on time but also on the w/c ratio and the time of the early curing, what the authors have shown in previous publications [47, 48].

As a result of conducting tests in programs I-IV (Fig. 7) statistically convergence of research results to the general hyperbolic model was confirmed in relation to the 124 variants of material-technological and environmental conditions of carbonation progress. It is, according to the authors, the basis of

the recognition that the hyperbolic model is universal with respect to the cement concrete. A number of other studies carried out by the authors and published among others in [11, 47, 48] also confirm the hypothesis.

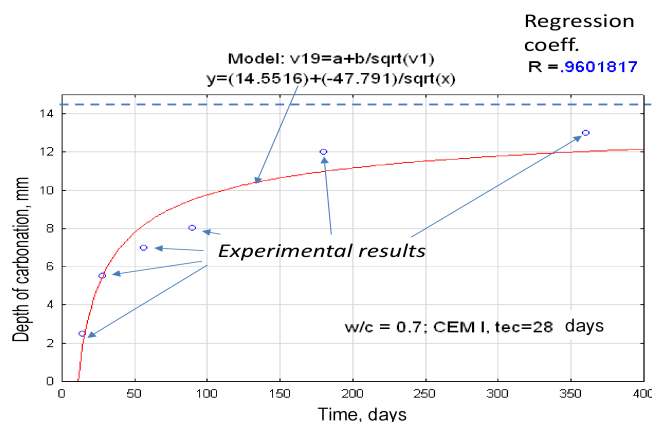


Fig. 9. The effect of statistical modeling of regression based on research results – an example

Models designated for the same concrete but under different conditions of exposure (natural and standard accelerated carbonation) differ significantly (Fig. 1) and the attempt to find an universal correlation binding models “natural” and “accelerated” so far did not give satisfactory results.

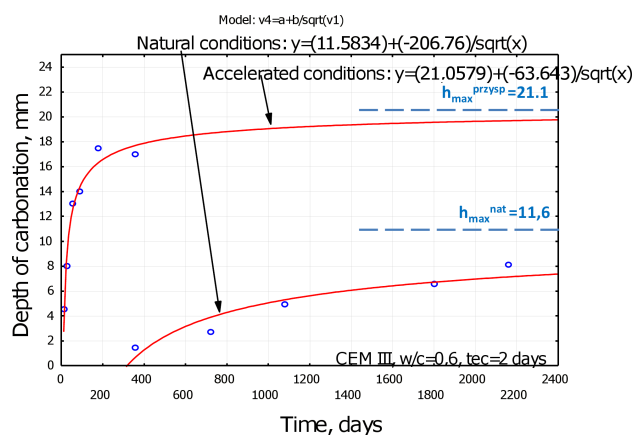


Fig. 10. Comparison of carbonation models obtained in natural and accelerated conditions for concrete with slag cement, w/c = 0.6 and time of early water curing – 2 days

If the mathematical model is determined on the basis of experimental data such model could be useful in case when needed time of exposition is short enough. Thus such approach is adequate only for the models calculated on a basis of experiments conducted in accelerated conditions. It was proved experimentally for a variety of concrete compositions, that – at a concentration of CO₂ = 1% – a period of study after which the carbonation is so advanced that ordinate of model’s asymptote assumes a relatively constant value, is 90 days (example – Fig. 11). Further prolongation of exposure under these conditions does not lead to a significant change in the value of determined asymptote.

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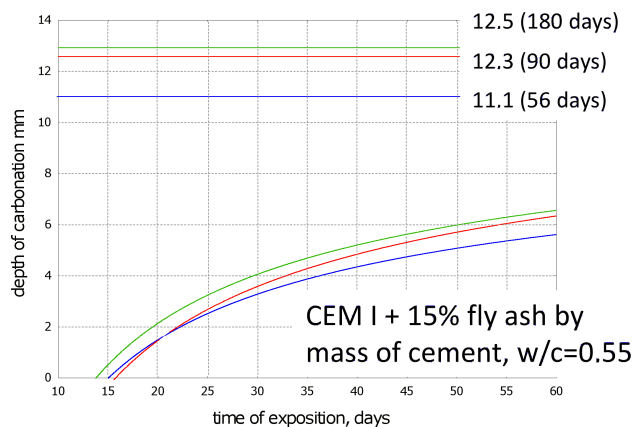


Fig. 11. Comparison of carbonation models obtained for concrete exposed in 1% concentration of CO_2 during 56, 90 and 180 days

In all examined cases, the result of modeling based on accelerated testing results, leads to determine the maximum range of the carbonation depth slightly higher than it was on the basis of results obtained in natural conditions. This leads to the conclusion that the adoption of the test results in an accelerated carbonation conditions for the practical purposes is safe and pessimistic solution, leading at best to adopt a bit too thick covers or too short estimated residual lifetime, if the procedures proposed in [49] are used.

6. Conclusions – model of carbonation as a process unlimited in time but restricted in concrete depth

Many years of research conducted by the authors presented synthetically in this article proved that the process of carbonation, although infinite in time is limited in the space of concrete, as a result of self-limiting nature of the phenomenon (gradual lowering of the CO_2 diffusion ratio and the rate of carbonation tending asymptotically to zero). Endlessness in time of the process is clear from the fact that the maximum depth of carbonation h_{\max} is the asymptote of the hyperbolic function (30), which the carbonation will never reach. This asymptote is described by the equation:

$$h_{\max} = \lim_{t \rightarrow \infty} h(t) = a. \quad (27)$$

Time varying rate of carbonation, which is a derivative of depth h after time t can be described by the equation:

$$\frac{\partial h}{\partial t} = 1/2 \times \frac{b}{\sqrt{t}^3}. \quad (28)$$

Equation (28) can be used to calculate the momentary rate of carbonation at any time t of exposure. The coefficient b in the model (28) can be regarded as an indicator of rate of carbonation, which is useful for comparing carbonation course for different concretes or course of carbonation in different conditions. Lower values of b are the lower values of the initial (early exposure) rate of carbonation but a slower decline in the rate of carbonation in time. General model of carbonation (27) can be expressed in a developed form (29) by introducing additional variables, and then the depth of carbonation is expressed as a function of three variables,

namely exposure time t , water-cement ratio w/c and the time of early curing t_{ec} :

$$h = a_1 \times (w/c) + b \times t^{-0.5} + a_2 \times t_{ec}. \quad (29)$$

The description of a carbonation process with these models correlates well with experimental results. For analysis of the results and practical applications of the model an indicator is a useful tool expressing the progress of carbonation at a given time. It can be calculated as a percentage proportion of the depth obtained after that time towards the value of asymptote obtained from the model developed on the basis of these findings. In the case of a hyperbolic model, the progress in time asymptotically tends to 100%. The further advance the better the statistical representativeness of the model, and predictions made with its use have lower uncertainty.

The discussed model of carbonation can be a useful tool in the design, diagnosis and prognosis of durability of reinforced concrete structures.

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