

Experimental verification of carbonation models used for estimation of reinforced concrete structures durability

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Abstract. The subject of the article is a comparison of two types of concrete carbonation models: self-limited carbonation and infinite carbonation. The results of the research on the progress of carbonation during six years of sample exposure in natural atmospheric conditions were used to determine the detailed models for a set of concretes with different w/c and different types of cement, and two scenarios of initial curing. It has been established that the model of self-limiting carbonation (i.e. hyperbolic) is more adequate for describing laboratory tests results in natural conditions.

Key words: concrete, reinforced concrete, concrete carbonation, modelling, self-terminating carbonation model, durability, cover thickness.

1. Introduction

Determining carbon dioxide flow rate through concrete is an essential issue in the mathematical modelling of carbonation development. Various scientific centres around the world have been conducting research for years in order to define a universal carbonation model, considering its complex nature and various material and technological variables [1]. A broad discussion on the history and current trends of carbonation modelling, including publications issued until 2013, was conducted by the co-author of this article in monograph [2]. The results of this research include different forms of concrete carbonation models, which can generally be divided into two groups. In the first case, carbonation is treated as an unlimited (infinite) process both in time and in the space of concrete. In the second case, it is considered that the process is unlimited in time, but has a limited (finite, self-limiting, self-terminating) range in concrete. Consequently, the first type of models will be abbreviated as unlimited (or infinite) models, while the second one will be called limited (or self-terminating) models. More important models of carbonation recently used in practice are briefly reviewed in chapter 2 of this paper.

Models are developed either through theoretical considerations or by modelling the results of laboratory measurements. In the first case, they result directly from the laws governing the phenomena of diffusion in porous media (Fick's laws), including changes in the concrete microstructure over time, and also as a result of carbonation reactions. In the second case, mathematical modelling of experimental research results is used, employing regression analysis and curve fitting analyses.

The practical reason for developing carbonation models is the need to use them at the structure design stage (selec-

tion of cover thickness [3]) as well as at the stage of structure exploitation, for diagnostic and prognostic purposes (estimation of reinforcement corrosion initiation time, forecast of element – object durability [4]).

Recently there is a need for developing itemized models for new types of cement composites, for example low-pH cement concretes (Seigneur et al. [5]), recycled aggregate concretes (Grabiec et al. [6]) or in specific environmental conditions (Felix et al. [7]) and specific mode of loading (Chen et al. [8]). The idea of advanced numerical tools, including FEM applied in carbonation modelling is also developed (i.e. Zurek [9]). Different additional variables are added to the models, and their importance for carbonation course is tested, i.e. ambient humidity and temperature and detailed parameters of cement and clinker composition (Jingtao et al. [10], Ta et al. [11]).

However, the vast majority of researchers are focused on developing infinite carbonation models, and this trend is confirmed by a review of modelling directions recently made by Tongaria et al. [12].

The purpose of this paper is to compare the adequacy of the unlimited (infinite) carbonation model and the self-terminating carbonation model in describing the course of concrete carbonation, based on studies of a diverse population of concrete (three levels of water–cement ratio, two types of cement – CEM I and CEM III, two concrete care scenarios). The analysis presented in this paper was based on six years of investigation in natural atmospheric conditions. The paper is also a kind of response to the former demand for “selection for the best less-parameter carbonation depth model“ (M. Bhattacharjee et al. [13]).

2. Review of concrete carbonation models

2.1. Models of concrete carbonation as an unlimited process. When determining the amount of CO₂ permeating through concrete, the law determining the amount of diffusing substance per unit of time over a given surface, i.e. the

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Manuscript submitted 2020-03-27, revised 2020-05-30, initially accepted for publication 2020-06-19, published in October 2020

first Fick's law [2, 14], could be used. It determines that the amount of diffusing substance per unit of time through a surface (perpendicular to the direction of diffusion) is directly proportional to the surface area and gradient of the substance concentration in the system. According to this law, the stream density is given by (1):

$$dQ = DF \frac{c_1 - c_2}{x} dt, \quad (1)$$

where dQ – CO₂ flux density, D – effective carbon dioxide diffusion coefficient through the carbonated concrete layer [cm²/s], F – surface through which diffusion occurs [cm²], c_1 – carbon dioxide concentration near the concrete surface (volumetric content of CO₂ in the air), c_2 – carbon dioxide concentration in the reaction zone, x – depth of carbonated layer [cm], t – time [s].

The amount of CO₂ with which concrete components can react in time dt can be determined from (2):

$$dQ = aFdx, \quad (2)$$

where a – coefficient determining what volume of CO₂ can be bound in a unit of volume of concrete, depending on the type of cement and its amount in concrete, as well as the degree of hydration.

By comparing (1) and (2), equation (3) is obtained:

$$dQ = aFdx = DF \frac{c_1 - c_2}{x} dt, \quad (3)$$

and then (4):

$$x dx = \frac{D}{a} (c_1 - c_2) dt. \quad (4)$$

The difference in CO₂ concentrations can be taken as not changing over time. If we take the concentration of carbon dioxide in the reaction zone as 0 ($c_2 = 0$), after integration we get equations (5) and (6):

$$\int x dx = \int \frac{D}{a} c_1 dt, \quad (5)$$

$$\frac{x^2}{2} = \frac{D}{a} c_1 t, \quad (6)$$

and hence (7):

$$x = \sqrt{\frac{2Dc_1}{a}} t. \quad (7)$$

Taking the symbol A according to (8):

$$A = \sqrt{\frac{2Dc_1}{a}}, \quad (8)$$

we will get the commonly used equation to determine the progress of concrete carbonation over time (9) [15]:

$$x = A\sqrt{t}. \quad (9)$$

Equation (9) indicates the infinite progress of carbonation, which reaches increasingly deeper areas of concrete. Coefficient A depends on the effective carbon dioxide diffusion coefficient in concrete, as well as the concentration and amount of CO₂ that can be bound in concrete. The equation for the dependence of carbonation depth on time can also be written in the form of equation (10) [15]:

$$x = A\sqrt{t} + B, \quad (10)$$

where B – coefficient depending on the pore structure, or in the form of equation (11):

$$x = \sqrt{\frac{2Dt[\text{CO}_2]}{[\text{Ca}(\text{OH})_2]}}, \quad (11)$$

in which [CO₂] and [Ca(OH)₂] – molar concentrations of carbon dioxide and calcium hydroxide, D – effective diffusion coefficient, t – exposure time.

Different versions of more or less general unlimited carbonation models are known, considering various factors. Woyciechowski [2] cites many versions of the infinite carbonation model, based on various sources, among others:

Papadakis et al. [16–20] derived an equation that considers the participation in carbonation of other concrete phases (after portlandite) (12):

$$x = \sqrt{\frac{2Dt[\text{CO}_2]}{[\text{Ca}(\text{OH})_2] + 3[\text{C S H}] + 3[\text{C}_3\text{S}] + 2[\text{C}_2\text{S}]}}. \quad (12)$$

Groves [21] showed that the C₃S and C₂S phases do not participate in carbonation, and simplified the equation (12) to the form (13):

$$x = \sqrt{\frac{2Dt[\text{CO}_2]}{[\text{Ca}(\text{OH})_2] + 3[\text{C S H}]}}. \quad (13)$$

Wang and Lee [22] modified the Groves equation to obtain the expression (14):

$$x = \sqrt{\frac{2Dt[\text{CO}_2]}{0.33[\text{Ca}(\text{OH})_2] + 0.214[\text{C S H}]}}. \quad (14)$$

Further development of this type of models was done by Torres et al. [23], including the effect of porosity changes in time due to the carbonation products crystallization.

Papadakis [17] also proposed another model – empirical – for concretes with Portland cement, carbonating in natural atmospheric conditions (15):

$$x = 0.35\rho_C \frac{\left(\frac{w}{c} - 0.3\right)}{1 + \frac{\rho_C W}{1000C}} f(\varphi) \cdot \sqrt{1 + \frac{\rho_C W}{1000C} + \frac{\rho_C K}{\rho_K C} C_{CO_2} 5 \cdot 10^5 t} \quad (15)$$

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

Bulletin 238 CEB [24] presents a probabilistic model according to which it was assumed that (16):

$$x = \sqrt{2k_1 k_2 k_3 \Delta c} \sqrt{\frac{D_{nom}}{a}} \left(\frac{t_0}{t}\right)^n, \quad (16)$$

where D_{nom} – CO_2 diffusion coefficient in concrete (determined under RH conditions $\approx 65\%$, $t \approx 20^\circ\text{C}$) [mm^2/year], Δc – difference in CO_2 concentration in the concrete environment and at the carbonation depth, a – amount of CO_2 needed for full carbonation of concrete [kg/m^3], n – coefficient of the impact of periodic variability of ambient conditions (the greater the variability of conditions, the higher the n), t_0 – reference period (in natural conditions $t_0 = 1$ climate year), t – exposure time [years], k_1 – concrete moisture impact factor (0.3–1.0), k_2 – factor of initial curing time impact (1.0 or 2.0); k_3 – factor considering the susceptibility of concrete to bleeding (1.0–1.5).

In the literature, there are also charts and nomograms used to estimate the carbonation depth depending on one parameter, e.g. concrete strength class [25], as well as considering many additional factors (w/c ratio, humidity, type of cement,

curing time, exposure conditions) affecting the carbonation process [2, 25].

2.2. Self-terminating carbonation model. Since concrete is a material that undergoes physicochemical changes, including those caused by the carbonation process itself, it is necessary to look at the problem of carbonation more broadly than just from the point of view of the diffusion process in the porous medium.

The time-varying arrangement of pores in concrete, carbonation products that fill pores, as well as temporary changes in the level of moisture in concrete are the main reasons for the change in the permeability [26] and rate of effective diffusion of carbon dioxide over time [2]. This, in turn, can slow down the rate of neutralisation until it stops completely, and the carbonation front is fixed at a certain invariant border depth in concrete (Fig. 1) [27].

Having considered the changes in the porosity of concrete over time and the progress of carbonation, Woyciechowski [2] modified the carbonation model from the general model (7) to the form (17):

$$x = \sqrt{\frac{2Dc_1}{a}} \frac{\partial D}{\partial t} \sqrt{t}, \quad (17)$$

where $\frac{\partial D}{\partial t}$ describes the changes in the diffusion coefficient of concrete subjected to carbonation over time, t .

Based on the conducted research, Woyciechowski [2] showed that, along with the progress of carbonation into the concrete, the value of the diffusion coefficient tends to zero asymptotically. This indicates that carbonation progress causes concrete self-sealing, which leads to the cessation of diffusion of carbon dioxide. This statement was the foundation for Woyciechowski's definition of a new general carbonation model, which assumes that the depth of carbonation h , is a hyperbolic function of carbonation time, t (18):

$$h = a - \frac{b}{\sqrt{t}}, \quad (18)$$

where h – carbonation depth, a, b – material and technological coefficients, t – exposure time. The hyperbolic model has a time axis parallel asymptote that corresponds to the maximum possible carbonation depth, h_{max} (19):

$$h_{max} = \lim_{t \rightarrow \infty} h(t) = a. \quad (19)$$

By introducing additional material and technological variables (water–cement ratio, w/c , initial curing time, t_{ec}) into the equation of the general model, the relationship describing the carbonation depth as a function of three variables was obtained – water–cement ratio, curing time, exposure time to CO_2 (20):

$$h(w/c, t_{ec}, t) = h(f(w/c), f(t_{ec}), f(\sqrt{t})), \quad (20)$$

where h – carbonation depth, w/c – water–cement ratio, t_{ec} – curing time (days), t – exposure time (years or days).

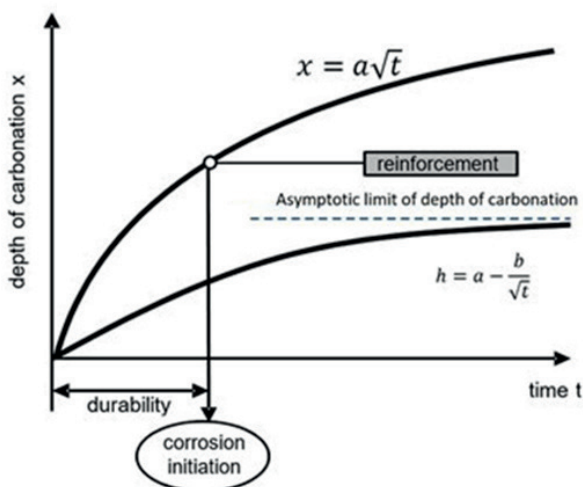


Fig. 1 The idea of self-terminating carbonation according to Fagerlund (based on Woyciechowski [2])

By differentiating equation (18), which is a general Woyciechowski's model of carbonation [2] after time t , an equation describing the speed of carbonation front progress (21) is obtained:

$$\frac{\partial h}{\partial t} = \frac{1}{2} \frac{b}{\sqrt{t^3}} \quad (21)$$

This equation calculates the instantaneous rate of carbonation development at any time. Instantaneous carbonation rate b is helpful in comparing carbonation development for different concretes or under different conditions. Woyciechowski's research [2] confirmed that the effective CO_2 diffusion coefficient decreases over time, which supports the validity of the self-terminated carbonation model.

3. Investigation of concrete carbonation and modelling of its course

3.1. Scope and test methods. The carbonation tests were conducted on the concretes listed in Table 1.

Table 1
Concrete compositions

Compounds content, kg/m^3						
w/c	CEM I 42.5R	CEM III A 42.5R	water	sand 0/2 mm	gravel 2/8 mm	gravel 8/16 mm
0.35	510	–	179	696	331	713
	–	510				
0.45	460	–	207	683	325	700
	–	460				
0.55	410	–	226	680	323	697
	–	410				

Samples in the form of beams with dimensions of $100 \times 100 \times 500$ mm, hardened in water for $t_{ec} = 2$ or 7 days and then up to 28 days in dry air laboratory conditions, were exposed to atmospheric conditions, typical for the centre of Warsaw, for up to six years. Carbonation tests were conducted using the phenolphthalein method, in accordance with PN-EN 14630. The workability of all the tested mixes was good enough for compaction of the specimens on the vibrating table. Two examples of specimens after phenolphthalein test are visible in the picture (Fig. 2 – CEM III on the left, CEM I on the right). The casting edge of the specimen is on the top of the picture. The microstructure of the specimen is dense and shows the expected effect of compaction.

3.2. Results and discussion. Table 2 summarises the average carbonation depths measured after subsequent exposure periods for each series of samples. Each result is an average for 3 specimens. For each specimen 20 measurements were taken in each

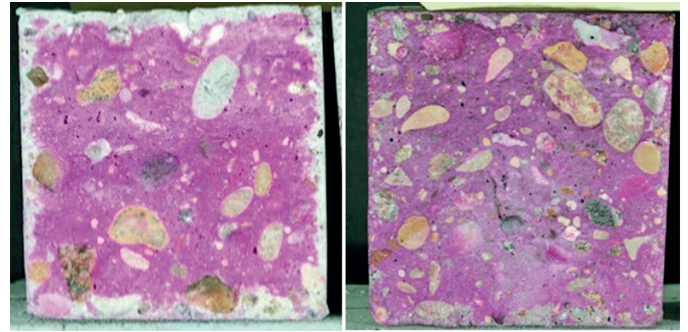


Fig. 2 An example of measurements of depth of carbonation with phenolphthalein test. Casting edge on the top of the picture. Left – $w/c = 0.45/\text{CEM III}$; right – $w/c = 0.45/\text{CEM I}$

term of testing, in accordance with the standard procedure. Variation coefficient for depth of carbonation was ranged in 9–13% limits – the expected variability for alkalimetric methods.

Table 2
Average depths of concrete carbonation in natural conditions

Cement type	Time of exposure for carbonation, years	Depth of carbonation, mm, for concrete with w/c :					
		0.35		0.45		0.55	
		t_{ec} days	t_{ec} days	t_{ec} days	t_{ec} days	t_{ec} days	t_{ec} days
CEM I 42.5R	1	1.1	0.2	1.3	1.1	2.2	2.0
	3	1.3	0.4	2.2	1.8	4.1	3.3
	4	1.7	1.5	2.5	1.9	4.1	3.7
	6	1.8	2.2	4.2	3.1	Nt	5.3
CEM III A 42.5R	1	0.7	0.8	2.8	3.3	5.5	3.3
	2	0.6	0.8	4.3	4.5	6.4	6.9
	3	1.4	1.0	6.2	5.0	7.4	10.4
	5	1.7	1.5	6.1	4.1	6.8	9.8

t_{ec} – time of early curing in water, days

nb. – lack of measurement result after subsequent period of exposure

The obtained results allowed us to determine carbonation models of infinite type in accordance with equation (10) – Table 3 and self-terminating type, in accordance with equation (18) – Table 4.

It was noted that when using both the infinite and self-terminating models, higher carbonation rates were obtained as the w/c increased. This is in line with the expectations, because a higher w/c ratio makes concrete more porous, which is why it has a higher CO_2 diffusion coefficient. In most cases, it was noted that a longer initial curing time reduced the carbonation rate – longer curing was conducive to sealing the concrete. An unexpected effect was observed for CEM III concrete with the highest w/c ratio – the longer period of initial curing has no positive impact on the resistance to carbonation. Such a high w/c ratio in case of slag cement leads to low quality of

Table 3
Models of infinite carbonation (acc. to equation (10)) for tested concretes

Cement type	w/c	Time of initial curing, days	Depth of carbonation as a function of exposure time	Correlation coefficient, R	Rate of carbonation
CEM I	0.35	2	$x = 0.55 + 0.51 \cdot t^{0.5}$	0.94	$\partial x / \partial t = 0.26 \cdot t^{-0.5}$
		7	$x = -1.46 + 1.41 \cdot t^{0.5}$	0.91	$\partial x / \partial t = 0.71 \cdot t^{-0.5}$
	0.45	2	$x = -0.83 + 1.88 \cdot t^{0.5}$	0.94	$\partial x / \partial t = 0.94 \cdot t^{-0.5}$
		7	$x = -0.34 + 1.29 \cdot t^{0.5}$	0.94	$\partial x / \partial t = 0.65 \cdot t^{-0.5}$
	0.55	2	$x = 0.24 + 2.05 \cdot t^{0.5}$	0.97	$\partial x / \partial t = 1.03 \cdot t^{-0.5}$
		7	$x = -0.36 + 2.19 \cdot t^{0.5}$	0.98	$\partial x / \partial t = 1.10 \cdot t^{-0.5}$
CEM III	0.35	2	$x = -0.37 + 0.92 \cdot t^{0.5}$	0.90	$\partial x / \partial t = 0.46 \cdot t^{-0.5}$
		7	$x = 0.10 + 0.58 \cdot t^{0.5}$	0.92	$\partial x / \partial t = 0.29 \cdot t^{-0.5}$
	0.45	2	$x = 0.34 + 2.82 \cdot t^{0.5}$	0.91	$\partial x / \partial t = 1.41 \cdot t^{-0.5}$
		7	$x = 3.20 + 0.65 \cdot t^{0.5}$	0.47	$\partial x / \partial t = 0.25 \cdot t^{-0.5}$
	0.55	2	$x = 4.71 + 1.14 \cdot t^{0.5}$	0.74	$\partial x / \partial t = 0.57 \cdot t^{-0.5}$
		7	$x = -1.15 + 5.49 \cdot t^{0.5}$	0.88	$\partial x / \partial t = 2.75 \cdot t^{-0.5}$

Table 4
Models of self-terminating carbonation (in acc. with equation (18)) for tested concretes

Cement type	w/c	Time of initial curing, days	Depth of carbonation as a function of exposure time	Asymptote, mm	Correlation coefficient, R	Rate of carbonation
CEM I	0.35	2	$x = 2.3 - 1.5 \cdot t^{-0.5}$	2.3	0.94	$\partial x / \partial t = 0.75 \cdot t^{-3/2}$
		7	$x = 0.7 - 0.5 \cdot t^{-0.5}$	0.7	0.86	$\partial x / \partial t = 0.25 \cdot t^{-3/2}$
	0.45	2	$x = 4.0 - 2.9 \cdot t^{-0.5}$	4.0	0.98	$\partial x / \partial t = 1.43 \cdot t^{-3/2}$
		7	$x = 3.0 - 2.0 \cdot t^{-0.5}$	3.0	0.91	$\partial x / \partial t = 1.00 \cdot t^{-3/2}$
	0.55	2	$x = 7.9 - 6.2 \cdot t^{-0.5}$	7.9	0.97	$\partial x / \partial t = 3.10 \cdot t^{-3/2}$
		7	$x = 5.6 - 3.8 \cdot t^{-0.5}$	5.6	0.95	$\partial x / \partial t = 1.90 \cdot t^{-3/2}$
CEM III	0.35	2	$x = 2.9 - 1.7 \cdot t^{-0.5}$	2.9	0.96	$\partial x / \partial t = 0.85 \cdot t^{-3/2}$
		7	$x = 1.6 - 0.8 \cdot t^{-0.5}$	1.6	0.86	$\partial x / \partial t = 0.40 \cdot t^{-3/2}$
	0.45	2	$x = 10.9 - 8.4 \cdot t^{-0.5}$	10.9	0.97	$\partial x / \partial t = 4.20 \cdot t^{-3/2}$
		7	$x = 9.2 - 6.2 \cdot t^{-0.5}$	9.2	0.93	$\partial x / \partial t = 3.10 \cdot t^{-3/2}$
	0.55	2	$x = 11.6 - 6.6 \cdot t^{-0.5}$	11.6	0.95	$\partial x / \partial t = 3.30 \cdot t^{-3/2}$
		7	$x = 19.4 - 16.4 \cdot t^{-0.5}$	19.4	0.99	$\partial x / \partial t = 8.20 \cdot t^{-3/2}$

concrete and high porosity – the extended period of curing is not helpful in this case, if the tests begin after 28 days of hardening. In the future, it would be reasonable to use the idea of equivalent time (in acc. with EN 206) for carbonation testing of CEM III concretes. In most cases, it was noted that the carbonation rate was higher in concrete with slag cement (CEM III), which led to a greater final depth of carbonation of concrete with this cement. In all cases, high correlation coefficients (0.86–0.99) were obtained with the model of self-terminating carbonation. It means that self-terminating model is adequate for experimental results. When using the

infinite model, however, the effects of regression analysis were varied – the correlation coefficient ranged from 0.47 to 0.98. It means that the infinite model is not adequate for experimental data in all cases – especially for concretes with slag-cement. A conclusion can be drawn that the self-terminating model is better suited to describe the carbonation process of the tested concretes. The depths of carbonation of the concrete following a long time of exposure to CO₂ according to the infinite carbonation model are much greater than the values of the depth which carbonation pursues according to the self-terminating carbonation model (Figs. 3 and 4).

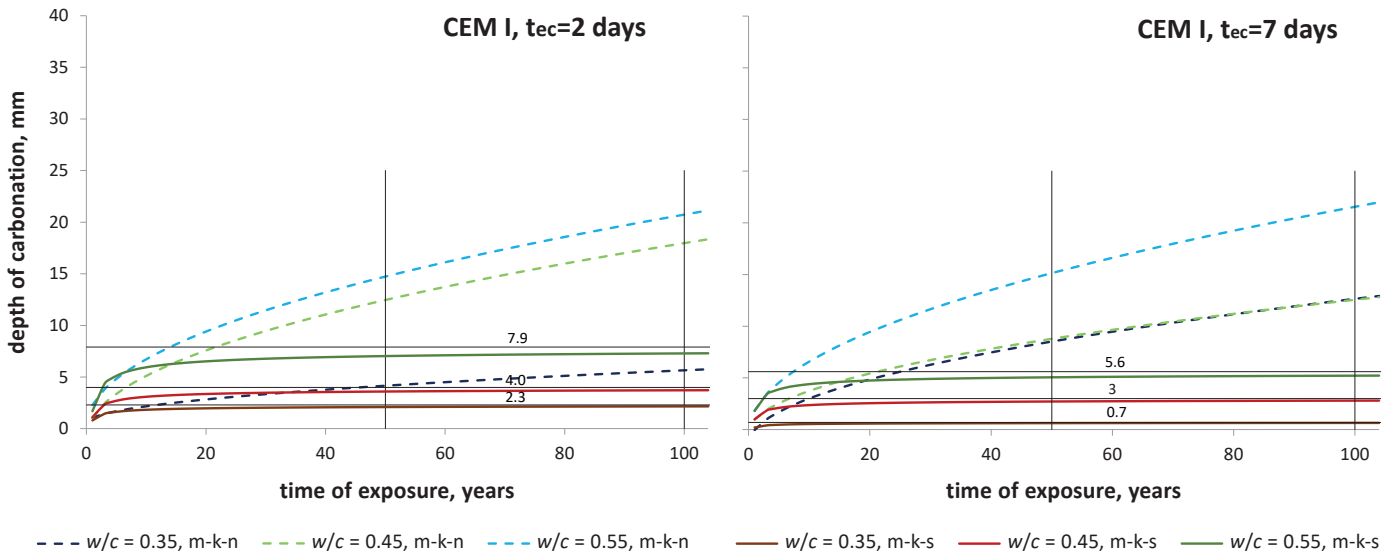


Fig. 3 Models of carbonation for concrete with Portland cement (CEM I): dashed lines – infinite models in acc. with eq. (10); continuous lines – self terminating models in acc. with eq. (18); t_{ec} – time of early curing in water; asymptotic values in millimetres are shown

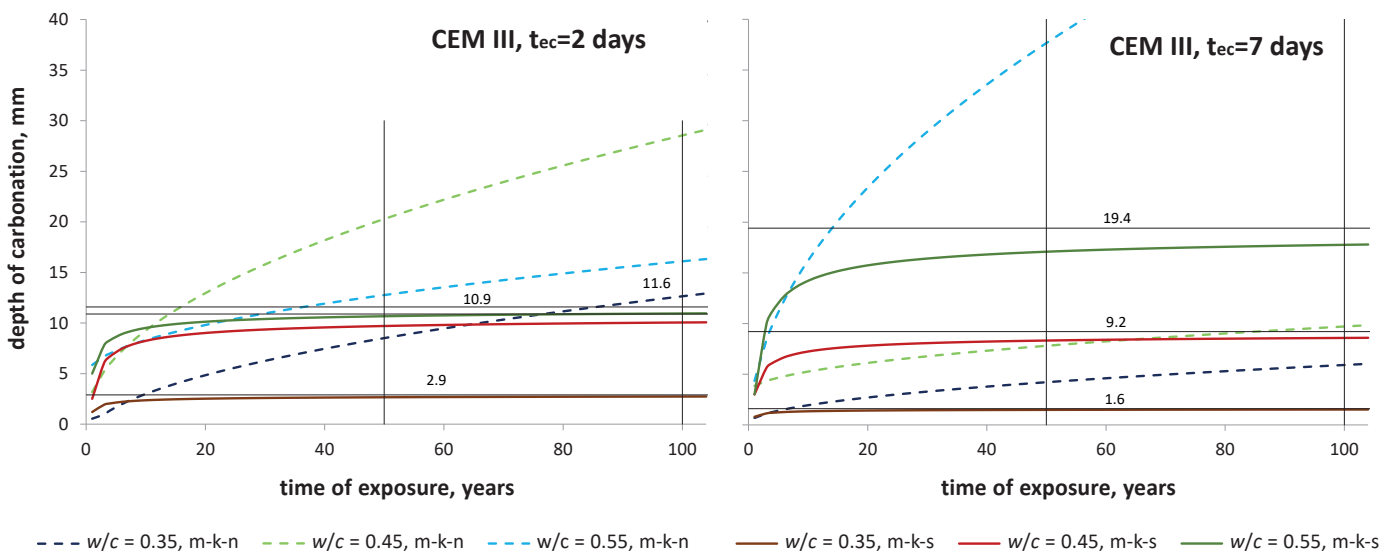


Fig. 4 Models of carbonation for concrete with Slag cement (CEM III): dashed lines – infinite models in acc with eq. (10); continuous lines – self terminating models in acc. with eq. (18); t_{ec} – time of early curing in water; asymptotic values in millimetres are shown

4. Consideration and Conclusions

Based on the analysis of relationships describing the progress of the depth of carbonation of concrete over time, determined on the basis of infinite and self-terminating carbonation models, the following conclusions were drawn:

- Estimated values of concrete carbonation depth after a long carbonation time are significantly higher when using the infinite carbonation model than the self-terminating carbonation model (both based on the results of carbonation tests under natural conditions) and, thus, assessment of the structure durability on their basis provided a greater safety margin.

- In relation to the examined sets of concretes, better statistical compatibility of the test results with the mathematical model of the carbonation process, measured by correlation coefficients, was obtained when the self-terminating carbonation model was used.

Even as the self-terminating model of carbonation was verified by the authors as the most adequate for the experimental results, the answer to the question about its significance in design practice is ambiguous. Ian Hacking, in the Introductory Essays to the 50th Edition of Kuhn's "The Structure of Scientific Revolution", stated that the old theory was not replaced by a new one because it was true, but rather because it was farther from a less adequate conception [28].

The model of the progress of concrete carbonation in time is not only a mathematical description of the physicochemical phenomenon, but also, and perhaps above all, a tool for engineering structure design and prediction of its actual durability.

The self-terminating model of carbonation, which described the process as infinite in time but finite in the space of the concrete, expressed by the hyperbola equation, shows better compliance with experimental results than the classical infinite model. At the same time, it leads to predicting lower carbonation depths after a given exposure time. This was demonstrated in the research presented in this article and also in previous publications of the authors [29–31].

In the context of engineering applications, mathematical models of carbonation should be considered not only in terms of the accuracy of the description of the phenomenon, but also from the point of view of the structure safety, as well as in economic terms. Engineering design requires strict, deterministic responses, considering specific reliability and, therefore, construction safety in the assumed durability period. The classic infinite carbonation model, by its mathematical nature (striving for infinity with time), provides a specific safety factor that increases over time. This specific factor is understood as the difference between the measured value and the value calculated from the model at a certain point in time. This approach to the phenomenon of carbonation underlies the determination of the minimum reinforcement cover thicknesses recommended in accordance with Eurocode EC2 in exposure classes XC. An example of such a consideration for typical reinforced concrete element was shown by authors in one of the previous papers [3].

Material/process modelling is a probabilistic activity based on defining the range of impact factors, and the accuracy (trueness and precision) of the obtained data [28]. The obtained results followed by the analysis lead to the authors' opinion that the self-terminating carbonation model, whose valuation was presented in this article, holds trueness of the phenomenon in a better way than the infinite model.

REFERENCES

- [1] L. Czarniecki and D. Van Gemert, "Innovation in construction materials engineering versus sustainable development", *Bull. Pol. Ac.: Tech.* 65(6), 765–771 (2017).
- [2] P. Woyciechowski, *Concrete carbonation model*, OWPW Warszawa 2013 [in Polish].
- [3] P. Woyciechowski and J.J. Sokołowska, "Self-terminated carbonation model as a useful support for durable concrete structure designing", *Struct. Eng. Mech.* 63(1), 55–64 (2017).
- [4] L. Czarniecki, P. Woyciechowski and G. Adamczewski, "Risk of concrete carbonation with mineral industrial by-products", *KSCE J. Civ. Eng.* 22(2), 755–764 (2018).
- [5] N. Seigneur et al., "Predicting the atmospheric carbonation of cementitious materials using fully coupled two-phase reactive transport modelling", *Cem. Concr. Res.* 130, 105966 (2020).
- [6] A.M. Grabiec, D. Zawal, J. Starzyk and D. Krupa-Palacz, "Selected properties of concrete with recycled aggregate subjected to biodeposition", *Bull. Pol. Ac.: Tech.* 67(6), 1171–1179 (2019).
- [7] E.F. Felix and E. Possan, "Modeling the Carbonation Front of Concrete Structures in the Marine Environment through ANN", *IEEE Latin Am. Trans.* 16(6), 1772–1779, (2018).
- [8] Y. Chen, X. Chen and J. Bu, "Nonlinear damage accumulation of concrete subjected to variable amplitude fatigue loading", *Bull. Pol. Ac.: Tech.* 66(2), 157–163 (2018).
- [9] A. Zurek, "Numerical approximation of a concrete carbonation model: Study of the law of propagation", *Numer. Meth. Part Differ. Equ.* 35(1), 1801–1820 (2019). DOI: 10.1002/num.22377.
- [10] J. Jiao, B. Diao and Ch. Wang, "The Carbonation Model of Concrete Structures and Its Application", in *International Conference on Civil, Transportation and Environment (ICCTE) Guangzhou, China*, 2016
- [11] K. Tongaria, S. Mandal and D. Mohan, "A Review on Carbonation of Concrete and its Prediction Modelling", *J. Environ. Nanotechnol.* 7(4), 75–90 (2018).
- [12] V.-L. Ta, S. Bonnet, T.S. Kiese and A. Ventura, "A new meta-model to calculate carbonation front depth within concrete structures", *Constr. Build. Mater.* 129, 172–181 (2016). DOI: 10.1016/j.conbuildmat.2016.10.103.
- [13] M. Bhattacharjee et al., "Selection for the Best Less-Parameter Carbonation Depth Model", *Am. J. Eng. Technol. Soc.* 2(6), 167–179 (2015).
- [14] B.S. Divsholi and J.H. Cahyadi, *Concrete carbonation under a wide range of conditions. Modeling the carbonation of PC and blended cement concrete under a wide range of conditions*, VDM Verlag Dr. Müller Aktiengesellschaft & Co. KG, Saarbrücken 2009.
- [15] G. Wieczorek, *Reinforcement corrosion initiated by chlorides or cover carbonation*, Dolnośląskie Wydawnictwo Edukacyjne, Wrocław 2002 [in Polish].
- [16] V. Papadakis, C. Vayenes and M. Fardis, "Experimental investigation and mathematical modeling of the concrete carbonation problem", *Chem. Eng. Sci.* 46, 1333–1339 (1991).
- [17] V. Papadakis, C. Vayenes and M. Fardis, "Fundamental modeling and engineering investigation of concrete in relation to CO₂ permeability and degradation of coating", *Constr. Build. Mater.* 22, 2260–2268 (2008).
- [18] V. Papadakis, C. Vayenes and M. Fardis, "Physical and chemical characteristics affecting the durability of concrete", *ACI Mater. J.* 9(2), 186–196 (1991).
- [19] V. Papadakis, M. Fardis and C. Vayenes, "Effect of composition, environment factor and cement-lime mortar coating on concrete carbonation", *Mater. Struct.* 25, 293–304 (1992).
- [20] V. Papadakis and M. Fardis, "A reaction engineering approach to the problem of concrete carbonation", *AIChE J.* 35(10), 1639–1650 (1989).
- [21] G.W. Groves, A. Brough, I.G. Richardson and C.M. Dobson, "Progressive changes in the structure of hardened C₃S cement pastes due to carbonation", *J. Am. Ceram. Soc.* 74(11), 2891–2896 (1991).
- [22] X.-Y. Wang and H.-S. Lee, "A model for predicting the carbonation depth of concrete containing low-calcium fly ash", *Constr. Build. Mater.* 23, 725–733 (2009).
- [23] H. Torres, E. Correa, F. Echeverria and J. G. Castaño, "Simplified Mathematical Model for Concrete Carbonation", *J. Mater. Civ. Eng.* 29(10), 2017.
- [24] "New approach to durability design. An example for carbonation induced corrosion", *CEB Bulletin* 238, Comité Euro-International du Béton (CEB), 1997.

- [25] L. Czarnecki and P.H. Emmons, “Repair and protection of concrete structures”, *Polski Cement* 2002 [in Polish]
- [26] G. Fagerlund, “Concrete structures durability”, Arkady, Warszawa 1997 [in Polish]
- [27] L. Czarnecki and J.J. Sokołowska, “Material model and revealing the truth”, *Bull. Pol. Ac.: Tech.* 63(1), 7–14 (2015).
- [28] L. Czarnecki and P. Woyciechowski, “Concrete carbonation as a limited process and its relevance to concrete cover thickness”, *ACI Mater. J.* 109(3), 275–288 (2012).
- [29] L. Czarnecki and P. Woyciechowski, “Prediction of the reinforced concrete structure durability under the risk of carbonation and chloride aggression”, *Bull. Pol. Ac.: Tech.* 61(1), 173–181 (2013).
- [30] L. Czarnecki and P. Woyciechowski, “Modelling of concrete carbonation; is it a process unlimited in time and restricted in space?”, *Bull. Pol. Ac.: Tech.* 63(1), 43–54 (2015).
- [31] T. Tracz, “Open porosity of cement pastes and their gas permeability”, *Bull. Pol. Ac.: Tech.* 64(4), 775–783, (2016).