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1 **Model for Practical Carbonation Depth Prediction for High Volume Fly Ash Concrete**
2 **and Recycled Aggregate Concrete**

3

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1 **Abstract**

2 The reuse of industrial residue streams such as fly ash (FA) or waste materials such as
3 recycled concrete aggregate (RCA) can be beneficial both from an economic and an
4 ecological point of view. Extensive research, investigating different properties of these
5 concrete types, has been carried out so far. However, durability remains a key property
6 ensuring sustainable application of these materials in the construction sector that still needs
7 more research to be fully understood. The main objective of this study was to evaluate the
8 application of widely used models for carbonation depth prediction—defined for ordinary
9 Portland cement concrete with natural aggregate (NAC)—to high volume FA concrete
10 (HVFAC) and recycled aggregate concrete (RAC). The research presented in this paper was
11 conducted in two steps. First, an experimental programme was designed to provide better
12 understanding of the influence of different CO₂ concentrations on the carbonation process
13 kinetics in HVFAC, RAC and NAC. This was performed using accelerated carbonation tests
14 (CO₂ concentrations of 1%, 2%, 4% and 16%) and natural carbonation tests (duration 21 and
15 48 months). Furthermore, a database of previously published results of HVFAC and NAC
16 carbonation depths was made in order to analyse the application of carbonation depth
17 prediction defined by Tuutti and given in the *fib* Model Code 2010. It was shown that the
18 existing models, providing the relationship between accelerated test results and natural
19 carbonation depth, are applicable to NAC and RAC but not to HVFAC. Modifications of the
20 above mentioned models were proposed in order to enable a more accurate and reliable
21 prediction of the HVFAC carbonation depth under natural exposure conditions.

22 **Keywords**

23 Fly ash; Recycled aggregate; Carbonation; CO₂ concentration; Accelerated test; Natural test;

24

1 **1. Introduction**

2 The immense impact of the construction industry on the environment is mainly caused by the
3 extremely large use of raw materials, energy consumption and waste production. The concrete
4 industry, with an annual production of almost 20 billion tons [1], is responsible for a large
5 portion of these impacts. The use of natural stone aggregates and large carbon dioxide (CO₂)
6 footprint from cement production are the main problems of non-sustainable concrete
7 production. The high consumption of these natural resources causes an impact on the
8 environment and significant greenhouse gas emission – it is estimated that 7–10% of all CO₂
9 emissions of anthropogenic origin is due to the production of cement [2]. A lot of effort is
10 now being invested in finding alternatives to traditional processes and materials used in the
11 current cement industry: alternative fuels, transport efficiency, raw materials and clinker
12 substitution.

13 In order to preserve natural resources and lower cement consumption, different supplementary
14 cementitious materials like fly ash (FA), blast furnace slag and silica fume are being used.

15 Supplementary cementitious materials are usually by-products obtained from different
16 industries that possess pozzolanic activity potential. The main difference between them is
17 their source material and process of production, resulting in different physical and chemical
18 properties of different supplementary cementitious materials which will further affect
19 concrete properties in different manners. Possible application of these materials is also
20 influenced by their available amount and price. The use of blast furnace slag in concrete
21 usually requires additional grinding in order to get the appropriate fineness. On the other
22 hand, silica fume is a by-product but has relatively high commercial price. The diversity of
23 FA types available world-wide is very vast, but most of them can be used without additional
24 treatment, they have relatively low price and above all, large quantities are still available.

1 Having all that in mind, it is not surprising that FA is one of the mostly-used supplementary
2 cementitious materials, reaching its full potential when used in high volume FA concrete
3 (HVFAC). There are different definitions of what HVFAC is: Malhotra [3] defined it as a
4 concrete with a large amount of FA, usually between 40% and 60% of total cementitious
5 materials mass, while the ACI (American Concrete Institute) Committee 232.3R-14 [4]
6 defined it as a concrete with 37% or more of FA in the total mass of cementitious materials.
7 Another way to preserve natural resources and make concrete more environmentally friendly
8 is the application of recycled concrete aggregates (RCA) that is beneficial both from
9 economic and ecological points of view [5]. However, replacement of natural aggregate (NA)
10 with RCA or replacement of cement with FA greatly influences concrete's physical,
11 mechanical and durability properties. In order to ensure sustainable application of these green
12 alternatives to cement concrete production, durability properties of both recycled aggregate
13 concrete (RAC) and HVFAC along with existing models for service life prediction must be
14 evaluated.

15 In reinforced concrete (RC) structures, reinforcement is physically and chemically protected
16 by the surrounding highly alkaline concrete environment and a thin oxide layer – passivation
17 layer [6]. If the pH value drops below approximately 9.5, the reinforcement passivation layer
18 breaks down (depassivation) and the corrosion of reinforcement can start. One of the most
19 important depassivation processes in RC structures is carbonation. It represents the process of
20 cement matrix neutralization that leads to the decrease of pH in concrete (from 13 to below 9),
21 which reduces the chemical protection of reinforcement. Carbon dioxide (CO₂) from the
22 atmosphere penetrates through concrete pores and dissolves in the pore solution. Afterwards,
23 it reacts with the highly alkaline components in concrete like calcium hydroxide (Ca(OH)₂)
24 and hydrated calcium silicate (C-S-H). It is then transformed into calcium carbonate crystals

1 (CaCO₃) [7] changing the chemistry balance between pore solution and hydrates. When CO₂
2 is dissolved in the pore solution, carbonic acid reacts with the alkalis in the concrete matrix
3 and lowers the pH value of concrete. Creation of non-soluble salts such as CaCO₃ partially
4 fills capillary pores which lead to a decrease in concrete porosity in ordinary Portland cement
5 concrete, which prevents the CO₂ and O₂ from further diffusing into the concrete [7].
6 The formation of CaCO₃ does not stop when all the Ca(OH)₂ is dissolved. Calcium ions
7 (Ca²⁺) are further separated from the C-S-H bond leading to decalcification [8]. The C-S-H
8 bond formed in the pozzolanic reaction is subjected to decalcification during the carbonation
9 process more than the C-S-H bond formed by the hydration of cement [9]. During the
10 pozzolanic reaction, a large amount of non-crystalline and non-alkaline C-S-H products with
11 a large specific surface area are formed, making the calcification process easier.
12 Several studies tested the carbonation resistance of RAC, but a clear conclusion cannot be
13 made based on the data from the literature. Some researchers have found that the impact of
14 coarse RCA on carbonation resistance of concrete is negative and that RAC is more
15 vulnerable to carbonation compared with the reference NA concrete [10–15]. The increase in
16 carbonation depth of RAC varied within the range of 1.8 [11] to about 2.5 times [12,13]
17 compared with the reference NA concrete. It should be noted that concretes used in these
18 studies had the same amount of cement [10,11], effective [12] or total [14,15] w/c ratio, but
19 not the same compressive strength. For practical purposes it is important to have the results of
20 a comprehensive analysis and a comparison of different types of concrete with the same
21 compressive strength. Compressive strength is the most common indicator of concrete quality
22 and the property typically specified when the concrete is ordered from the producer. Usually,
23 more cement is needed for producing RAC with the same compressive strength as the
24 reference NA concrete [16,17]. A higher amount of cement leads to a higher amount of alkalis

1 that can be carbonated in the concrete cover and thus prevents the increase of carbonation
2 depth [18,19]. In most of the studies where RAC and reference NA concrete had a similar
3 compressive strength, RAC showed the same or slightly higher carbonation depth compared
4 with reference NA concrete [13,20,21]. In these studies 20–100% of coarse NA was replaced
5 with RCA. In some cases where 20–50% of coarse NA was replaced with RCA, the
6 carbonation depth was lower for RAC compared with reference concrete [22].

7 The results from literature show opposing conclusions regarding carbonation resistance of
8 concrete made with FA as a cement replacement. This is expected having in mind the
9 opposing effects of FA on carbonation – denser concrete structure and lower amount of
10 $\text{Ca}(\text{OH})_2$ [23]. The increase of FA amount (up to 60%) leads to the increase in carbonation
11 depth [23–30]. Some experimental results showed that HVFAC made with 50% of cement
12 replacement had a lower or equal degree of carbonation compared with ordinary Portland
13 cement concrete, while HVFAC with 70% of cement replacement showed a greater degree of
14 carbonation [31]. Some research has shown that, for the same concrete strengths, concrete
15 with high amounts of FA (50% or more) exhibited almost the same carbonation resistance
16 compared with ordinary Portland cement concrete [28]. Having in mind the limited amount of
17 available research that uses the approach of similar compressive strength, further analysis is
18 needed.

19 There are many factors that affect the carbonation process but the most important ones are:
20 binder content, concentration of CO_2 , humidity, temperature, curing conditions and concrete
21 porosity. The time required to determine the carbonation depth under natural conditions is
22 measured in years— CO_2 concentration is approximately 0.03% in rural and 0.3% in urban
23 areas [32]. Having this in mind, the usual quantification of concrete carbonation resistance is
24 done through accelerated carbonation tests. The acceleration of the carbonation process is

1 achieved primarily by increasing the CO₂ concentration. In different standards and technical
2 recommendations a great variety of CO₂ concentrations are prescribed, ranging from 1% to
3 50% [33]. Some studies showed that the application of extremely high CO₂ concentrations
4 (10%, 25%, 50% and 100%) for ordinary Portland cement concrete led to a change in process
5 kinetics [8,34]. On the other hand, there is still a lack of comparative tests examining the
6 influence of relatively low CO₂ concentration (1–4%) (which can be found in the most
7 prominent (pre)standards and guidelines [35–37]) on the carbonation process of RAC and
8 HVFAC. Having this in mind, the question regarding the suitable CO₂ concentration during
9 accelerated tests on ordinary Portland cement concrete, RAC and HVFAC is still open.
10 Although there is a wide range of models for carbonation depth predictions in ordinary
11 Portland cement concrete [35,38–40], there is still a lack of models for practical prediction of
12 natural carbonation in RAC and HVFAC. Existing models [41–43] require values for sets of
13 parameters that are usually not available during the service life design such as the coefficient
14 of the degree of hydration, casting factor, location factor, water absorption of aggregate,
15 carbonation rate constants of Ca(OH)₂ and molar concentration of Ca(OH)₂. For that reason,
16 an analysis and adjustment of existing models used for conventional concrete [35,38] are
17 needed for RAC and HVFAC.

18 **2. Objectives**

19 Carbonation resistance of ordinary Portland cement concrete, RAC and HVFAC during
20 accelerated tests was a topic of many previously published studies. However, there is still an
21 inconsistency in the obtained conclusions regarding the impact of CO₂ concentration on the
22 carbonation process for all three concrete types. Also, a generally accepted model for the
23 application of accelerated test results in the practical prediction of carbonation depth in

1 natural conditions for RAC and HVFAC is not available. Therefore, the main objectives of
2 this study were:

- 3 – To determine the difference in the carbonation resistance between ordinary Portland cement
4 concrete, RAC and HVFAC with the same compressive strength,
- 5 – To assess the influence of CO₂ concentration on the carbonation process kinetic during
6 accelerated tests,
- 7 – To identify the relationship between carbonation depth at different CO₂ concentrations and
8 exposure time for HVFAC and RAC,
- 9 – To determine the prediction of carbonation depth under natural conditions based on
10 accelerated tests on HVFAC and RAC.

11 **3. Methodology**

12 Comparison of the carbonation resistance between different concrete types under the same
13 environmental conditions will be based on the widely used formula proposed by Tuutti (Eq.
14 1) [38] and Eqs. (2)–(4) derived from it. The linear relationship between the carbonation
15 depth (x_c) and the square root of exposure time (t) for certain environmental parameters (CO₂
16 concentrations, humidity, etc.) is defined by the use of a carbonation coefficient (k_c):

$$17 \quad x_c = k_c \cdot t^{0.5} \quad (1)$$

18 The coefficient k_c can be used to effectively compare the carbonation resistance of different
19 concrete types. The time required for determining k_c under natural conditions is measured in
20 years. This is the reason why its use is not suitable for calculation of the concrete cover in the
21 design of concrete structures.

22 Equation 1 can also be written in the following form:

$$23 \quad x_c = K \cdot \sqrt{CO_2} \cdot t^{0.5} \quad (2)$$

24 where,

1 K – coefficient that depends on concrete properties, humidity, temperature, etc.,

2 CO_2 – CO_2 concentration [%].

3 The fact that the coefficient K does not depend on the CO_2 concentration is an important

4 assumption that allows the use of accelerated carbonation tests with different CO_2

5 concentrations. However, the consequences of the use of Eq. (2) in case of RAC and HVFAC

6 will be emphasized.

7 Standards used for carbonation depth calculation define different CO_2 concentrations. In order

8 to compare and correlate the two carbonation depths ($x_{c,1}$, $x_{c,2}$) at different CO_2 concentrations

9 ($[CO_2]_1$, $[CO_2]_2$) and exposure times (t_1 , t_2), for one concrete type, the following relationship

10 derived from Eq. (2) was used:

11
$$\frac{x_{c,1}}{x_{c,2}} = \sqrt{\frac{[CO_2]_1}{[CO_2]_2}} \cdot \left(\frac{t_1}{t_2}\right)^{0.5} \quad (3)$$

12 Carbonation depth under natural conditions at a certain time ($x_{c,NAT}(t)$) can be calculated

13 based on the carbonation depths measured in accelerated tests ($x_{c,ACC}$) by applying Eq. (3) in

14 the following way:

15
$$x_{c,NAT}(t) = x_{c,ACC} \sqrt{\frac{CO_{2,NAT}}{CO_{2,ACC}}} \cdot \left(\frac{t}{t_{ACC}}\right)^n \quad (4)$$

16 where $CO_{2,NAT}$ and $CO_{2,ACC}$ denote the CO_2 concentration under natural exposure conditions

17 and the CO_2 concentration during the accelerated test, respectively, in [%]. The exponent n

18 takes the value of 0.5 [38] but will be evaluated independently for RAC and HVFAC. In this

19 case, concrete samples prior to testing under accelerated carbonation were cured in the same

20 way as in situ concrete structures so the influence of concrete curing conditions can be

21 neglected.

1 Prediction of the carbonation depth under natural exposure conditions was also evaluated
2 using the inverse effective carbonation resistance (R_{ACC}^{-1}) according to the *fib* Model Code
3 2010 [35]:

$$4 \quad x_c(t) = \sqrt{2 \cdot k_e \cdot k_{cur} \cdot (k_t \cdot R_{ACC}^{-1} + \varepsilon_t) \cdot C_s \cdot t \cdot W(t)} \quad (5)$$

5 where,

6 $x_c(t)$ – carbonation depth at the time t [mm],

7 k_e – environmental function [-],

8 k_{cur} – execution transfer parameter [-],

9 k_t – regression parameter [-], average value: 1.25,

10 R_{ACC}^{-1} – inverse effective carbonation resistance of concrete [(mm²/year)/(kg/m³)],

11 ε_t – error term [(mm²/year)/(kg/m³)], average value: 315.5,

12 C_s – CO₂ concentration [kg/m³],

13 $W(t)$ – weather function [-].

14 Equation 5 is a complex version of Eq. (2). However, instead of using a global carbonation
15 rate (k_c) from the literature, the *fib* Model Code 2010 [35] allows the carbonation rate
16 coefficient to be obtained through a formula which takes into account the macro-climate
17 conditions, curing conditions and concrete properties in explicit form. This should allow for a
18 more precise prediction of the carbonation depth over time. However, as with Eq. (4), the
19 application of this model to RAC and HVFAC has not yet been fully evaluated.

20 A database of ordinary Portland cement concrete, RAC and HVFAC carbonation test results
21 was made based on the results available in the literature. This database and own experimental
22 results were used in order to re-evaluate the possible application of previously mentioned
23 carbonation depth models for different concrete types.

24 **4. Experimental procedures**

1 **4.1. Materials and mix proportion**

2 For the purpose of this research, three concrete mixtures were prepared and tested:

3 NAC – reference ordinary Portland cement concrete with NA,

4 RAC – concrete with 100% replacement of coarse NA with RCA,

5 HVFAC – concrete with 50% of class F FA in total cementitious materials mass.

6 NA used in this study was commercially available river aggregate obtained from the Danube

7 River in Serbia divided in three fractions: I (0/4 mm), II (4/8 mm) and III (8/16 mm). It had

8 an oven-dry density of 2550 kg/m³ and water absorption of 1.2% after 24 hours. RCA was

9 obtained from a demolished 40-year old highway bridge in the vicinity of Belgrade, Serbia. It

10 was obtained by crushing the columns and bridge deck in a construction site mobile crusher.

11 Before demolition, structure was clean from impurities as the asphalt had been scraped off the

12 deck. After crushing, RCA was sieved into fractions II (4/8 mm) and III (8/16 mm). Sample

13 cores taken from the demolished structure prior to crushing had a compressive strength of 23

14 MPa in the column and 35 MPa in the bridge deck. The RCA had an oven-dry density of 2370

15 kg/m³ and water absorption of 3.9% after 24 hours. Based on these parameters it can be

16 classified as class B1 which means it can be used for reinforced concrete [44].

17 The commercially available blended Portland cement CEM II/A-M (S-L) 42.5R was used for

18 all types of concrete. This type of cement had additions (grinded slag and limestone) up to 20

19 % of the total mass. It had a specific gravity of 3040 kg/m³. The chemical composition of

20 cement is shown in Table 1.

21 FA used in this study was a by-product from the combustion of coal in thermal power plant

22 "Nikola Tesla B" in Obrenovac, Serbia. The FA was obtained by burning mostly lignite coal

23 and it was collected from the power plant during pneumatic transport before storing in silos.

24 Based on the chemical composition of FA, shown in Table 1, it can be classified as class F FA

1 according to the ASTM C618 classification [45]. The specific gravity of FA was 2075 kg/m³,
 2 and the mean particle size was 8.53 μm.

3 Table 1. Chemical compositions (mass basis) of cement and FA

Oxide	Content in cement [%]	Content in FA [%]
SiO ₂	21.04	58.24
Al ₂ O ₃	5.33	20.23
Fe ₂ O ₃	2.37	5.33
TiO ₂	–	0.45
CaO	60.43	7.62
MgO	2.43	2.01
P ₂ O ₅	–	0.00
SO ₃	3.55	2.21
Na ₂ O	0.22	0.52
K ₂ O	0.70	1.51
MnO	–	0.03
Loss on Ignition	3.53	2.10

4

5 4.2. Casting, curing and testing of specimens

6 The proportioning of the concrete mixtures was based on the absolute volume method.
 7 Concrete mix designs of tested NAC, RAC and HVFAC are given in Table 2. The mixtures
 8 were designed to achieve a compressive strength of 45 MPa (measured on a 100 mm cube)
 9 after 90 days with a slump value in the range of 100–150 mm after mixing. The testing age of
 10 90 days was chosen in order to enable the development of the pozzolanic effect in HVFAC
 11 and in order to give proper time for each concrete to reach its full compressive strength
 12 potential.

13 Table 2. Mixing proportions of tested concretes

Concrete	m _c [kg/m ³]	m _{fa} [kg/m ³]	m _w [kg/m ³]	Natural aggregate			Recycled aggregate	
				m _I [kg/m ³]	m _{II} [kg/m ³]	m _{III} [kg/m ³]	m _{II} [kg/m ³]	m _{III} [kg/m ³]
NAC	285	-	175	815	543	453	-	-
RAC	293	-	175	817	-	-	553	460
HVFAC	200	200	195	810	486	324	-	-

14

1 The objective was to compare NAC with RAC or HVFAC that have similar compressive
 2 strength and workability. The differences in water to binder ratio (w/b) are the expected
 3 consequences of these assumptions. It was decided not to use any water reducing admixtures
 4 because their influence on carbonation is not well known. As reported in the literature,
 5 approximately 3% more cement is needed to achieve the same compressive strength of NAC
 6 and RAC with 100% of coarse RCA [16]. By increasing the cement amount in RAC by 3%
 7 the effective w/b ratio decreased from 0.61 in NAC to 0.60 in RAC. In HVFAC with 50% of
 8 class F fly ash in total cementitious materials mass, the w/b ratio had to be lower in order to
 9 achieve the same compressive strength. It was not possible to make these three types of
 10 concrete with the same w/b ratio and also with the same compressive strength and workability
 11 which was the main goal of the design process.

12 All specimens were cast in steel moulds, and the concrete was compacted using a vibrating
 13 table. For the compressive strength testing at all ages, 100 mm cubic concrete samples were
 14 prepared. Carbonation resistance was tested on 120 x 120 x 360 mm concrete prisms. After
 15 casting, the specimens were covered with wet fabric and stored in the casting room at 20±2°C
 16 with RH 53±10%. They were demoulded after 24 h and the concrete cubes were kept in a
 17 water tank until testing while the concrete prisms were covered with a wet fabric and kept in
 18 the casting room for an additional 7 days. Prism samples were additionally sprayed with water
 19 once a day for an additional 7 days (up to the age of 14 days). Physical and mechanical
 20 properties of tested concretes are shown in Table 3. The values of both mechanical and
 21 durability properties reported in this paper represent mean values of three measurements.

22 Table 3. Mean values of physical and mechanical properties of tested concretes (CoV in %)

Concrete	$\gamma_{c,fresh}$ [kg/m ³]	$\gamma_{c,hardened}$ [kg/m ³]	slump [mm]	$f_{c,14}$ [MPa]	$f_{c,28}$ [MPa]	$f_{c,90}$ [MPa]
NAC	2430 (1.3)	2392 (0.9)	112 (39.3)	38.2 (5.4)	42.7 (2.2)	45.9 (2.2)
RAC	2281 (1.8)	2241 (1.0)	132 (5.8)	34.0 (3.1)	41.6 (3.6)	44.7 (1.3)
HVFAC	2260 (1.1)	2193 (1.9)	103 (25.3)	25.9 (2.4)	32.2 (0.6)	42.3 (1.1)

1 Workability of all tested concretes was in the design range and very similar. It can be seen
2 that the compressive strength increase over time differed between concretes but they all
3 reached the target 90-day compressive strength. However, NAC reached the highest strength
4 that was up to 8% higher compared with the other concrete types.

5 At the age of 90 days, prism samples were divided into two groups: one for the accelerated
6 carbonation tests and the other for the natural carbonation test. Both tests were performed in
7 the Laboratory for Materials at the Faculty of Civil Engineering, University of Belgrade.

8 Accelerated carbonation tests were performed during 28 days at a relative humidity (RH) of
9 $65\pm 5\%$ and a temperature of $20\pm 2^\circ\text{C}$ [35]. Samples were exposed to different CO_2
10 concentrations (1%, 2%, 4% and 16%) in the carbonation chamber Memmert ICH 260C. The
11 samples used for natural carbonation testing were placed in the laboratory under controlled
12 conditions at an RH of 52.2% and a temperature of 24.0°C [46] during 21 for NAC and
13 HVFAC, and 48 months for RAC. An average CO_2 concentration during that period was
14 0.0471% ($0.7677 \cdot 10^3 \text{ kg/m}^3$) with a coefficient of variation of 10.9%. Carbonation depth
15 measurements were performed with a phenolphthalein solution sprayed on the freshly broken
16 concrete surface according to the European standard EN 14630 [47]. The carbonation depth
17 was measured on five points per side, resulting in 20 measurements for each specimen and
18 age.

19 **5. Experimental results and discussions**

20 **5.1. Carbonation resistance at different CO_2 concentrations**

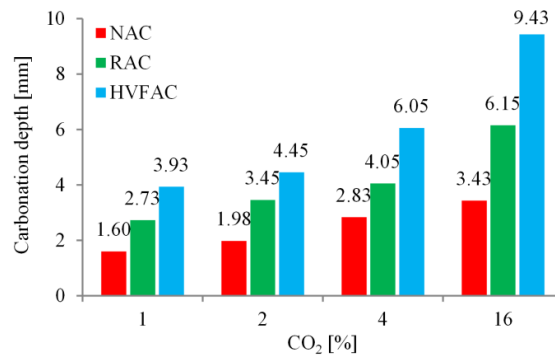
21 Measured carbonation depths, x_c , under natural CO_2 concentration and calculated values of
22 the carbonation coefficient, k_c , (according to Eq. 1) for tested concretes under natural
23 exposure conditions are shown in Table 4. It can be seen that the NAC had 1.25 and 3.36
24 times smaller carbonation coefficients compared with RAC and HVFAC, and thus the highest

1 carbonation resistance. The carbonation coefficient for HVFAC, calculated from the
 2 measured carbonation depth was $6.50 \text{ mm/year}^{0.5}$, which ranked it as a concrete with low
 3 carbonation resistance unlike NAC and RAC [10].

4 Table 4. Measured carbonation depths and calculated values of the carbonation coefficient

Concrete	x_c [mm]	k_c [mm/year ^{0.5}]
NAC	1.70	1.93
RAC	4.81	2.41
HVFAC	8.13	6.50

5 The carbonation coefficient depends on the material properties and environmental conditions,
 6 but also on the CO₂ concentration in the environment. According to Eq. 1 and Eq. 2, k_c under
 7 accelerated tests will be higher compared with k_c under natural exposure conditions
 8 considering that the CO₂ concentration during accelerated tests is drastically higher compared
 9 with concentration under natural exposure conditions. Having this in mind, carbonation
 10 coefficient obtained from accelerated tests cannot be used as an indicator of concrete quality
 11 in terms of resistance to carbonation and as parameter for defining carbonation depth.



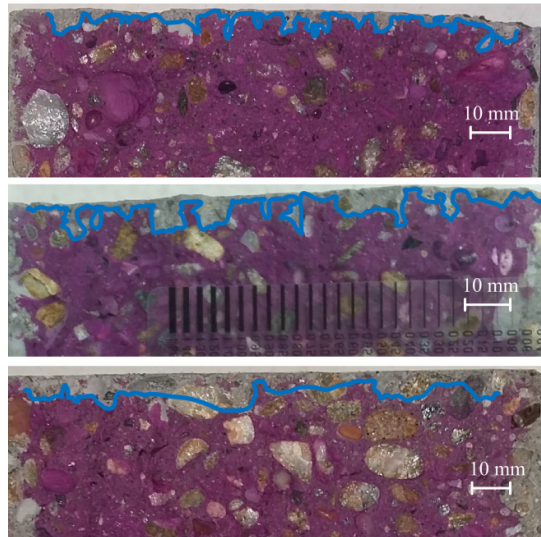
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13 Figure 1. Carbonation depth after 28 days at different CO₂ concentrations

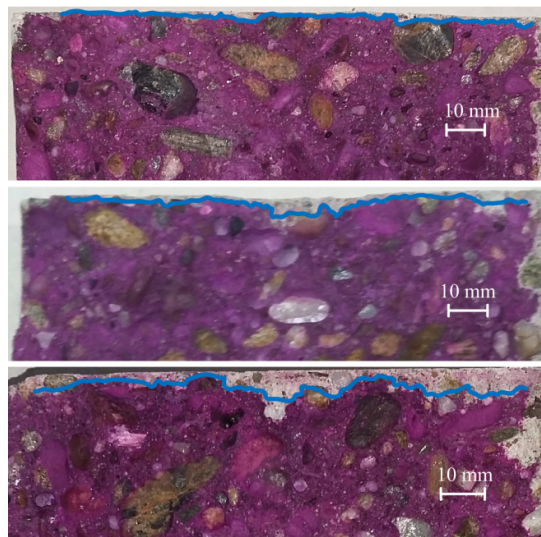
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14 Measured carbonation depths at different CO₂ concentrations after 28 days are shown in
 15 Figure 1. As can be seen, NAC had the smallest carbonation depths at all CO₂ concentration
 16 levels. Although RAC had the same compressive strength as NAC, its carbonation depth was
 17 43% to 73% higher. The higher carbonation depth of RAC was caused by the more porous
 18 structure and the presence of new and old attached mortar [10–12,18]. HVFAC had the

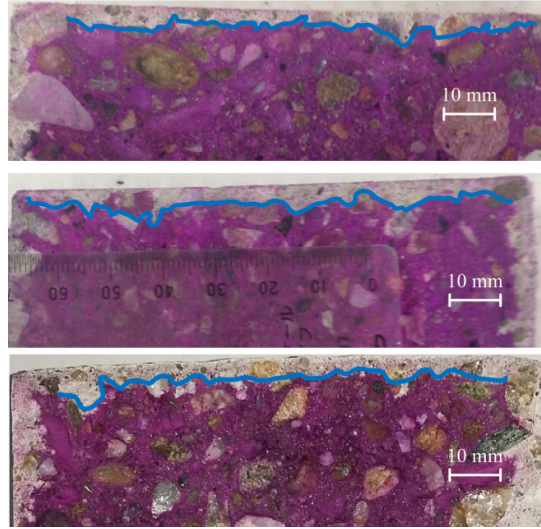
1 highest carbonation depth for all CO₂ concentration rates. Carbonation depth of HVFAC was
2 114% to 175% higher compared with NAC. One of the reasons for this can be the smaller
3 amount of available Ca(OH)₂ in HVFAC compared with NAC or RAC [17,48,49] that led to
4 the faster carbonation of the C-S-H bond [8].



5
6 Figure 2. Carbonation depth measurement with phenolphthalein solution on HVFAC at 4%
7 CO₂ concentration and at the age of 7, 14 and 28 days, respectively



8
9 Figure 3. Carbonation depth measurement with phenolphthalein solution on NAC at 4% CO₂
10 concentration and at the age of 7, 14 and 28 days, respectively



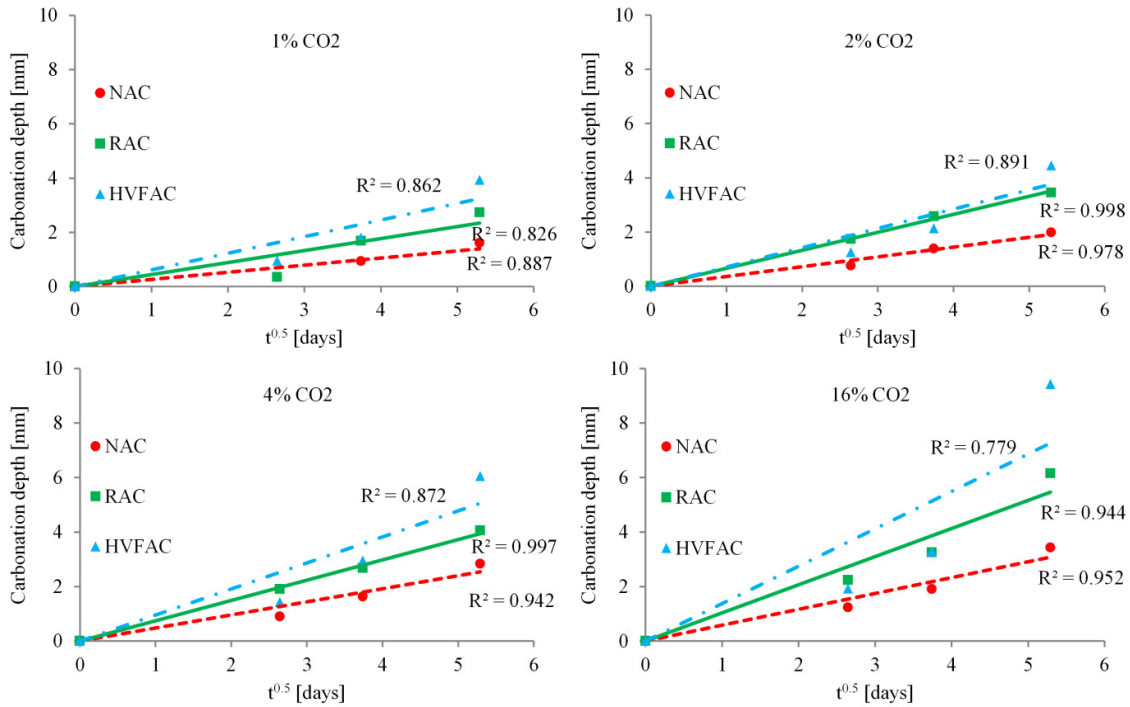
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2 Figure 4. Carbonation depth measurement with phenolphthalein solution on RAC at 4% CO₂
 3 concentration and at the age of 7, 14 and 28 days, respectively

4 Faster carbonation of HVFAC compared with NAC and RAC was also visible in the change
 5 of the carbonated front shape in HVFAC samples over time. Until 14 days, the carbonated
 6 zone was uneven and jagged (Figure 2a,b). The reason may lie in the fact that in HVFAC the
 7 pozzolanic reaction consumes a part of available Ca(OH)₂ most likely to an uneven extent
 8 [50]. This allows the CO₂ to penetrate faster in some parts of the concrete sample where
 9 Ca(OH)₂ is lacking as the part of cement is replaced with FA. As the process evolves over
 10 time, carbonation of the C-S-H bond occurred [8,9,51], leaving a more flat and deep front
 11 (Figure 2c). In NAC and RAC samples the carbonated front was evenly distributed at all ages
 12 (Figure 3, 4).

13 In order to test Eq. (1) and analyse the kinetic of this process, the measured carbonation
 14 depths at all CO₂ concentration levels are shown as a function of the exposure time, Figure 5.
 15 After 7 and 14 days of exposure, HVFAC showed a lower carbonation depth than RAC and
 16 slightly higher than NAC at all CO₂ concentrations. Obviously, there was a slower increase of

- 1 the carbonation depth in HVFAC in the first days of exposure, which was then accelerated
- 2 until 28 days, resulting in a higher depth compared with NAC and RAC.

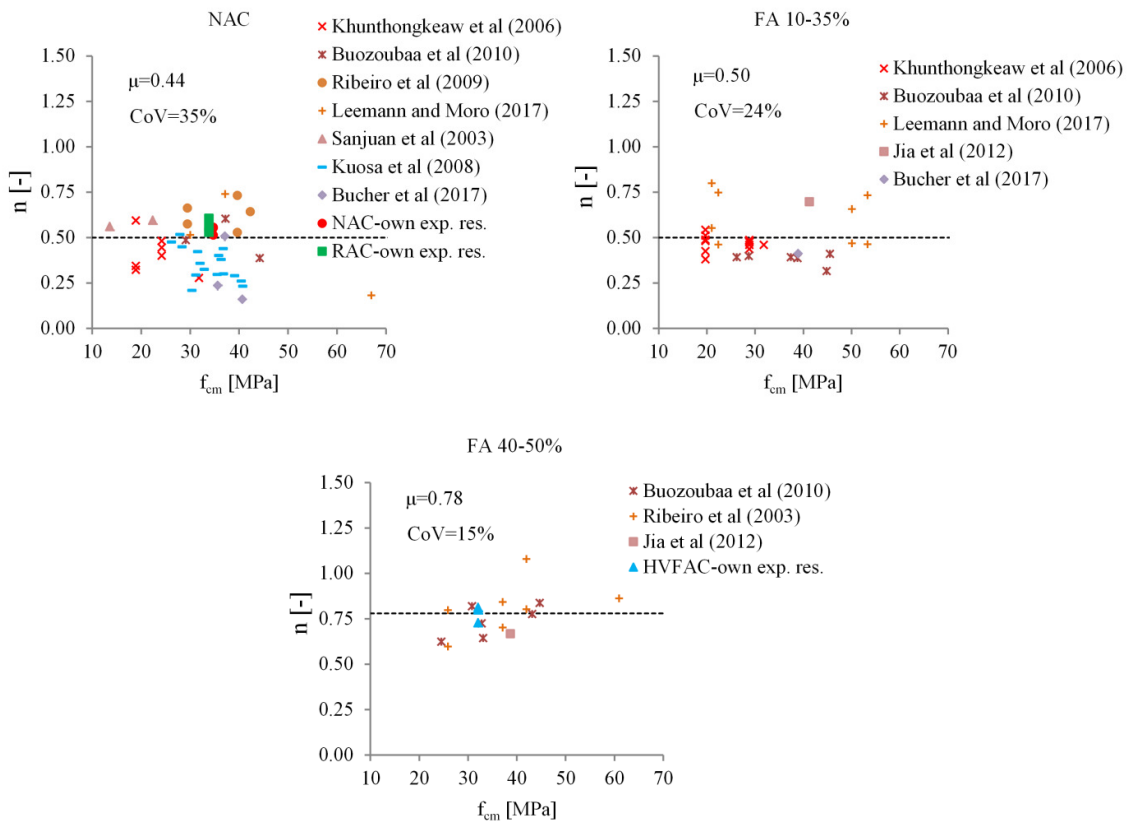


3
4 Figure 5. Carbonation depth at CO₂ concentrations of a) 1%, b) 2%, c) 4% and d) 16% versus
5 square root of time

6 The quality of the linear correlation between the carbonation depth and square root of time
7 (according to Eq. 1) is not similar for all concrete mixes. The coefficient of determination
8 (R^2) ranges from 0.887–0.978, 0.826–0.998 and 0.779–0.891 for NAC, RAC and HVFAC,
9 respectively. It can be assessed as acceptable for NAC and RAC but quite lower for HVFAC
10 which raised the question of the validity and reliability of Eq. (1) for HVFAC.

11 In order to re-evaluate the linear relationship between the carbonation depth and time function
12 $t^{0.5}$, the database of all available results of NAC and FA concrete carbonation test results was
13 made. Studies which provided the data on carbonation depth under natural and accelerated
14 exposure conditions measured on the same concrete were selected. These types of data have
15 been found in seven studies with NAC and seven with FA concrete [28,42,52–58]. In total, 42

1 NAC and 47 FA concrete carbonation depth test results were collected. From all of the
 2 collected FA concrete test results, 17 were obtained on HVFAC mixtures. Unfortunately, no
 3 comparative results for RAC under natural and accelerated exposure conditions were found in
 4 the available literature. In the selected studies, the concrete compressive strength (f_{cm}) ranged
 5 from 13.6 to 67.0 MPa (measured on a standard cylinder), RH ranged from 55% to 83%,
 6 while the CO₂ concentration during the accelerated tests ranged from 1% to 20%. The full
 7 database is given in Appendix A of this paper.



8
 9 Figure 6. Calculated values of exponent n for various concrete mixtures of NAC and FA
 10 concretes

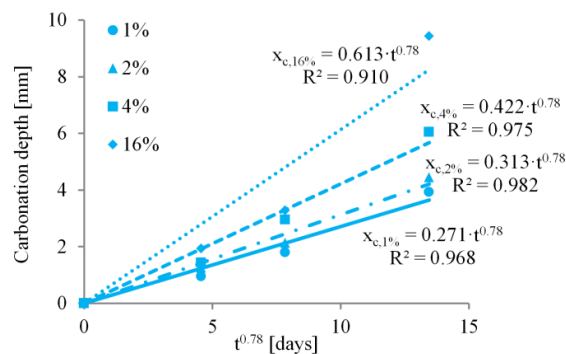
11 Based on the measured carbonation depth for various concrete mixtures of NAC and FA
 12 under natural and accelerated exposure conditions (database) and using Eq. (4), the exponent
 13 n was calculated and shown in Figure 6.

1 For NAC, the exponent n had an average value of 0.44 and a coefficient of variation (CoV) of
 2 35%. For concretes made with relatively small amounts of FA (10% to 35%), the average
 3 value was proved to be 0.50 with a CoV of 24%.
 4 However, if only results obtained on concrete samples with 40% to 50% of FA were taken,
 5 referring thus to HVFAC, the average value of the exponent n was much higher – equal to
 6 0.78 with a CoV of 15%, Figure 6.

7

$$x_{c,HVFAC} = k_c \cdot t^{0.78} \quad (6)$$

8 The linear function between the carbonation depth and new proposed time function $t^{0.78}$ for
 9 HVFAC (Eq. 6) was tested on own experimental results and shown in Figure 7.



10

11 Figure 7. Carbonation depth of HVFAC at CO₂ concentration of 1%, 2%, 4% and 16%

12 As can be seen, the proposed function had a much better correlation with the measured results
 13 compared with the previous function, for all applied CO₂ concentrations. The coefficient of
 14 determination for all CO₂ concentrations ranged from 0.910 to 0.982, similar to those for
 15 NAC and RAC. The relation is based on Fick's first law of diffusion and can be expressed as
 16 follows.

17 The exponent 0.78 does not necessarily mean that the Fick's first law of diffusion is not valid
 18 for HVFAC, but, that different CO₂ binding capacity influence the carbonation process in

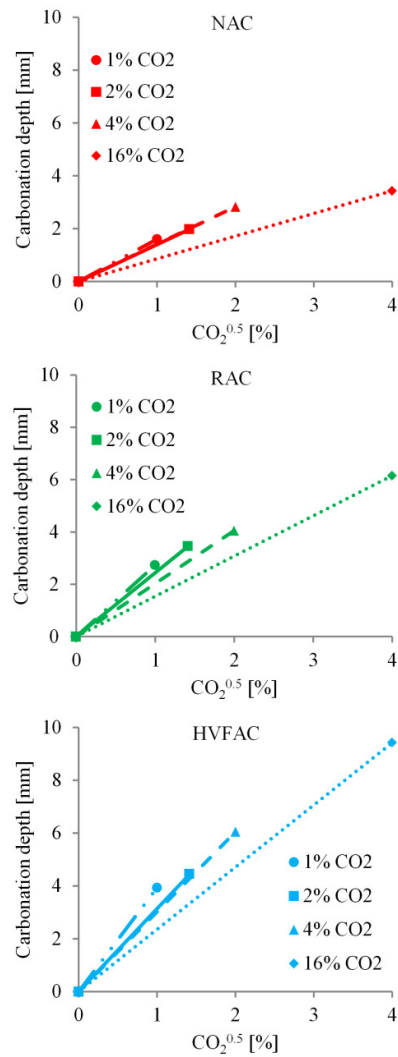
1 HVFAC compared with cement concrete. The exponent value is derived from the statistical
2 analysis as the best fit for set of analysed results.

3 **5.2. Influence of CO₂ concentration on the kinetics of the carbonation process**

4 If the assumption that the coefficient K does not depend on the concentration of the CO₂ to
5 which the sample is exposed is valid (Eq. 2), then the carbonation depth at a certain exposure
6 time can be expressed as a function of the CO₂ concentration. Having that in mind, there
7 should be a unique straight line for a particular material at different CO₂ concentrations, and
8 for the same interval of exposure. The slope of this line will be the coefficient K (Eq. 2).

9 Figure 8 shows the carbonation depth of tested concretes as a function of the CO₂
10 concentration after 28 days of exposure. In order to evaluate the applicability of Eq. (2), the
11 slope of lines plotted at different concentrations was analysed. It can be seen that there is no
12 single line for all concentrations regardless of the type of concrete. The CO₂ concentrations
13 from 1% to 4% did not have a significant impact on the kinetics of the carbonation process,
14 especially for NAC. For RAC and HVFAC, with a concentration increase from 1% to 4%
15 CO₂, a small change in the line slope was noticed. The application of high CO₂ concentrations
16 (16%) led to a noticeable slowing down of the process regardless of the concrete type, which
17 can be seen through the decrease of line slopes, Figure 8.

18 The different line slopes for each particular concrete showed that there was a change in the
19 process kinetics with the increase of the CO₂ concentration. With the increase in CO₂
20 concentration up to 20%, carbonation depth increased, but the process apparently slowed
21 down [59]. Further increase of CO₂ will not lead to additional increase in the carbonation
22 depth, but the porosity of concrete will continue to decrease. This leads to the conclusion that
23 the process itself will change in some way with increasing CO₂ concentration [59].



1

2

Figure 8. Carbonation depth after 28 days as a function of the square root of CO₂

3

concentration

4

The cause of this phenomenon was the increase of concrete internal humidity due to the water

5

produced in the carbonation reaction [60,61]. Humidity is a very important parameter, as the

6

process slows down if the pores are saturated with water. In this case, it was very difficult for

7

CO₂ to react due to the low degree of diffusion in water. On the other hand, if the concrete is

8

too dry, CO₂ cannot be dissolved in a thin layer of water that covers the pore walls and the

9

reaction slows down considerably. The greater the CO₂ concentration, the greater is the

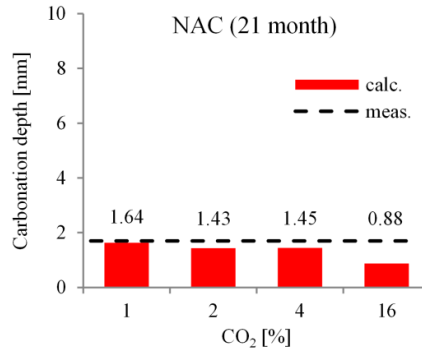
1 amount of produced water that slows down the process. At low CO₂ concentrations, the
2 internal humidity cannot reach a level higher than the external humidity, so the process
3 probably would not change.

4 Another explanation of this phenomenon is given by Castellote et al. [8] and Galan et al. [62].
5 Even if the concrete is fully carbonated as defined by the phenolphthalein test, this does not
6 necessarily mean that it had reached an equilibrium phase state, especially under natural
7 exposure conditions where some Ca(OH)₂ remained unreacted. On the other hand, when
8 carbonating at high CO₂ concentrations Ca(OH)₂ and C-S-H gel completely disappeared.
9 Even at the point when the carbonation process reached an equilibrium phase state, indicated
10 by stabilization in weight, it may continue but at much slower rate [8]. Also, according to
11 Galan et al. [62], at high CO₂ concentrations a layer of Ca(CO)₃ developing on Ca(OH)₂ can
12 significantly protect it against further carbonation.

13 **Prediction of carbonation depth based on accelerated tests and exposure time**

14 Values of the measured carbonation depth for NAC and HVFAC after 21 months and RAC
15 after 48 months of exposure to the natural conditions were compared with the values
16 calculated according to the Eq. (4) (accelerated test measurements at different CO₂
17 concentration levels). The results for NAC and HVFAC are shown in Figures 9 and 10.
18 Figure 9 shows that all calculated carbonation depths for NAC according to Eq. (4) were
19 lower than the measured value under natural exposure conditions ($x_{c,meas.} = 1.70$ mm).
20 Calculated values based on accelerated tests at CO₂ concentrations of 1%, 2% and 4% were
21 3.5%, 16% and 15% lower than measured value, respectively. The estimated depth based on
22 the accelerated test value at a concentration of 16% CO₂ significantly deviates from the
23 measured value under natural conditions – it was 48% lower.

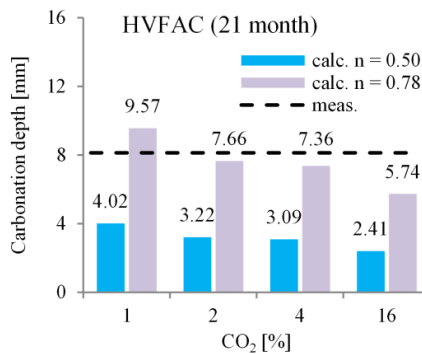
1 There are two possible reasons influencing this phenomenon. First, a change occurs in the
 2 nature of the carbonation process with increasing CO₂ concentration level compared with
 3 natural carbonation process. The second reason may be a slightly higher average temperature
 4 (4°C) during natural exposure conditions in comparison with the accelerated tests which can
 5 accelerate the carbonation process [30,60].



6

7 Figure 9. Calculated and measured carbonation depth of NAC after 21 months of exposure to
 8 natural conditions

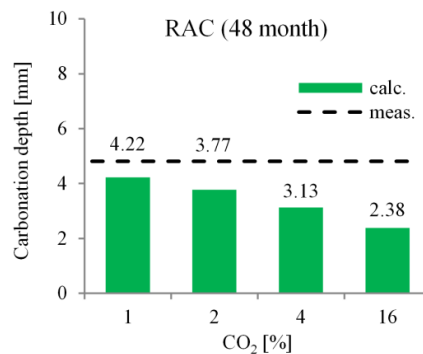
9 Calculated carbonation depths for HVFAC using the exponent $n = 0.5$ and newly proposed n
 10 $= 0.78$ (Eq. 6) are presented in Figure 10. The predictions of carbonation depths using $n = 0.5$
 11 obviously did not represent the carbonation process in reality, being two to three times lower
 12 than the measured value under natural exposure conditions (8.13 mm).



13

14 Figure 10. Calculated and measured carbonation depth of HVFAC after 21 months of
 15 exposure to natural conditions

1 At the same time, calculated carbonation depths using $n = 0.78$ showed better correlation to
 2 the measured value under natural exposure conditions. When the lowest CO₂ concentration of
 3 1% in the accelerated test was applied, the prediction was conservative and calculated depth
 4 was 18% higher than the measured value. Calculated values based on accelerated tests at 2%
 5 and 4% CO₂ were 6% and 9% lower compared with the measured ones, respectively. Again,
 6 the estimated depth that significantly deviates from the measured value is the one calculated
 7 with the concentration of 16% CO₂ and it was 29% lower than the measured value.
 8 Measured carbonation depths of RAC after 48 months of exposure to natural conditions and
 9 calculated depths based on the accelerated test measurements at different concentrations, are
 10 shown in Figure 11. The tested Eq. (4) with $n = 0.5$ backs non-conservative predictions of
 11 carbonation depths for all CO₂ concentrations. A continuous decrease in the calculated depth
 12 with the increase in the CO₂ concentration was noticed. The calculated values, based on the
 13 accelerated tests measurements at CO₂ concentrations of 1%, 2%, 4% and 16% were 12%,
 14 22%, 35% and 50.5% lower than the value measured under natural conditions (4.81 mm),
 15 respectively. As in the case of NAC and HVFAC, the prediction obtained from the test
 16 conducted under a CO₂ concentration of 1% was the most reliable. Modification of Eq. (4) in
 17 terms of using an exponent n different from 0.50 has not been tested for RAC as there is a
 18 limited number of own experimental results and no reliable database for confirmation of
 19 possible findings.



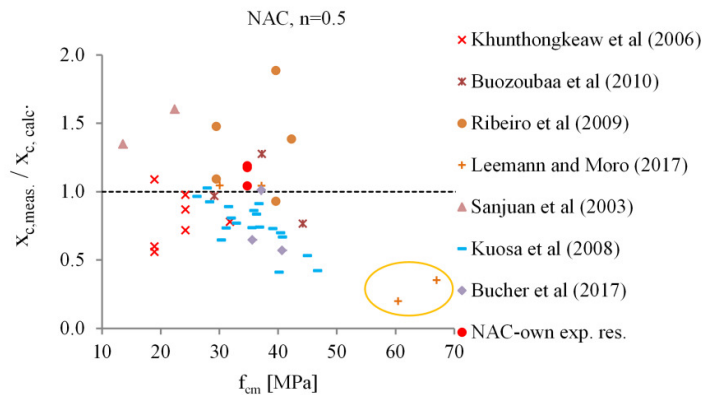
20

1 Figure 11. Calculated and measured carbonation depth of RAC after 48 months of exposure to
2 natural conditions

3 Previous analysis and obtained conclusions were related to only one NAC, RAC and HVFAC
4 designed and used in this study. In order to validate the obtained conclusions, previously
5 collected results from the literature [28,42,52–58] were used.

6 The ratio between the carbonation depths measured under natural exposure conditions ($x_{c, meas.}$,
7 $x_{c, meas.}$) and calculated predictions based on accelerated tests ($x_{c, calc.}$) according to Eq. (4), for
8 various concrete mixtures of NAC and FA are shown in Figures 12–14.

9 The ratio between measured and calculated values of carbonation depths ($x_{c, calc.}/x_{c, meas.}$) for
10 NAC had an average value of 0.87 and a CoV of 38% which means that the predictions are
11 non-conservative. Figure 12 shows that the values of own experimental results for NAC are
12 generally in good agreement with the results found in literature.



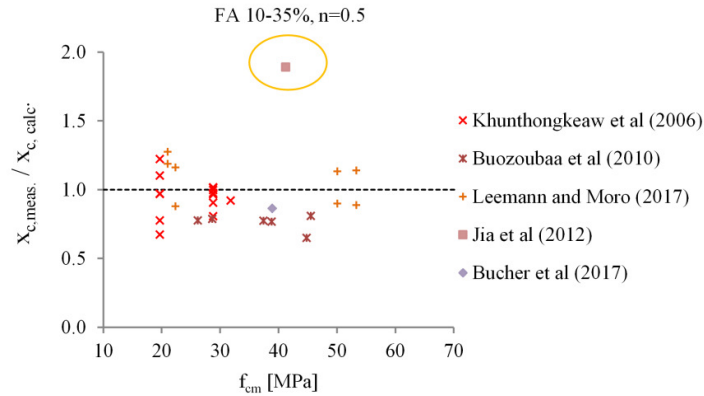
13

14 Figure 12. Ratio of measured and calculated carbonation depth of NAC in the literature

15 The amount of FA in the total mass of cementitious materials in selected studies shown in
16 Figure 13 ranged from 10% to 35%. The ratio between measured and calculated values of the
17 carbonation depths had an average value of 0.98 and a CoV of 24% (with one outlier results).

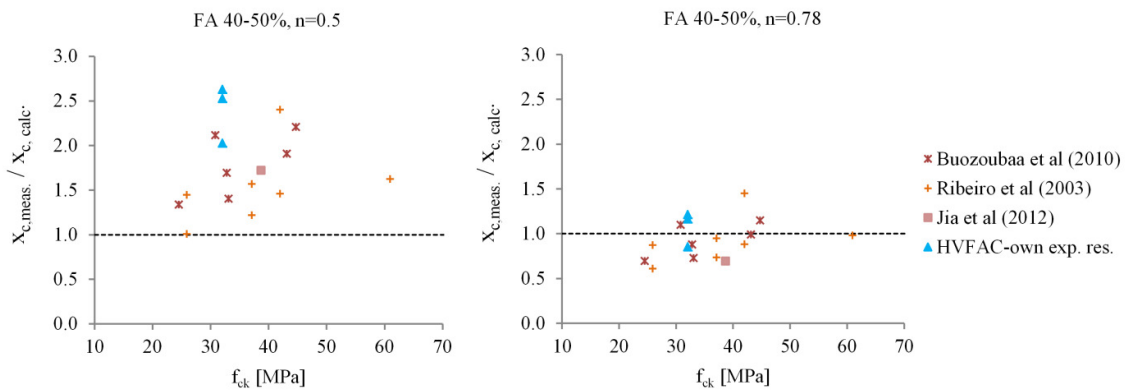
18 The average ratio was higher compared with NAC (0.87). Results from Figure 13 clearly
19 prove that Eq. (4) can be used in its original form (with $n = 0.5$) for the prediction of the

1 carbonation depth of concrete with a FA content up to 35% of the total cementitious materials
 2 mass.



3
 4 Figure 13. Ratio of measured and calculated carbonation depth of concretes made with 10–
 5 35% of FA in the literature

6 Results for concretes with higher amounts of FA (40–50%) in cementitious materials mass are
 7 shown in Figure 14. The ratio between measured and calculated values of the carbonation
 8 depths, for $n = 0.5$ in Eq. (4), had an average value of 1.62 and a CoV of 24%, indicating that
 9 the prediction highly underestimates the real carbonation depth.



10
 11 Figure 14. Ratio of measured and calculated carbonation depth of concretes made with 40–
 12 50% of FA in the literature

1 However, if $n = 0.78$ is used in Eq. (4) to calculate the carbonation depth in concretes with
 2 high FA contents (40% or more), better quality of the results is achieved (Figure 14b). The
 3 ratio between measured and calculated values of the carbonation depths had an average value
 4 of 0.89 and a CoV of 25%, which was very close to the target value of 1.0. This also means
 5 that calculations based on the Eq. (4) using $n = 0.78$ generally give results which are on the
 6 safe side. Figure 14 also shows the ratio for own experimental results for HVFAC that are in
 7 good agreement with the presented results from the literature.

8 **5.3. Prediction of carbonation depth using the *fib* Model Code 2010**

9 In order to determine the inverse effective carbonation resistance of concrete (R_{ACC}^{-1})—a key
 10 parameter in the carbonation model for service life design according to the *fib* Model Code
 11 2010—it is necessary to provide the carbonation depth after 28 days at a CO₂ concentration of
 12 2% (Eq. 7).

$$13 \quad R_{ACC}^{-1} = \left(\frac{x_c}{\tau} \right)^2 \quad (7)$$

14 where,

15 x_c – measured carbonation depth [m],

16 τ – time constant [(s/kg/m³)^{0.5}], for described test conditions: $\tau = 420$.

17 The value x_c can be taken directly from the collected results of the conducted accelerated test
 18 ($x_{c,2\%,meas.}$) or recalculated from the measurements during accelerated tests at other CO₂
 19 concentrations ($x_{c,2\%,calc.}$) using Eq. (4) in the following way:

$$20 \quad x_{c,2\%,calc.}(t=28) = x_{c,meas.ACC} \sqrt{\frac{2\%}{CO_{2,ACC} [\%]}} \cdot \left(\frac{28}{t_{ACC}} \right)^n \quad (8)$$

21 The effects of the environmental actions were taken into account through the adoption of
 22 parameters making it possible to consider the various characteristics of the environment
 23 surrounding the structure.

1 The environmental function k_e considers the influence of RH and is calculated using the
2 following expression:

$$3 \quad k_e = \left(\frac{1 - (RH_{real} / 100)^5}{1 - (65 / 100)^5} \right)^{2.5} \quad (9)$$

4 where,

5 RH_{real} – RH [%], for natural conditions used in experiment (52.2%).

6 In the case of concrete sheltered from rain (as was the case) the value of the weather function
7 defined in Eq. (4) was taken as $W(t) = 1$.

8 The execution transfer parameter k_{cur} considers the influence of curing conditions on the
9 carbonation resistance and it was calculated as

$$10 \quad k_{cur} = \left(\frac{t_c}{7} \right)^{b_c} \quad (10)$$

11 where,

12 t_c – period of curing [days], for the described curing procedure: $t_c=14$ days,

13 b_c – regression exponent [-], according to the *fib* Model Code 2010: $b_c = -0.567$.

14 **5.3.1. Application of the *fib* Model Code 2010 on tested concretes**

15 The possible application of the *fib* Model Code 2010 was tested for the carbonation depth of
16 NAC, RAC and HVFAC measured under natural exposure conditions, Table 5. The
17 difference between the carbonation depths calculated using Eqs. (4) and (5) ($x_{c, fib MC}$) and the
18 measured value ($x_{c, meas.}$) was not significant (up to a 6% difference) for CO₂ concentrations
19 from 1% to 4% for NAC, Table 5. The calculated carbonation depth was 29% lower
20 compared with the measured value for a CO₂ concentration of 16%. However, the *fib* Model
21 Code 2010 gave better predictions of the carbonation depth than the simplified model used in
22 Eq. (4) which even underestimated the carbonation depth after 21 months by 7%.

1 The difference between the carbonation depths calculated using Eq. (5) ($x_{c, \text{fib MC}}$) and the
 2 measured value ($x_{c, \text{meas.}}$) for RAC ranged from 10–31% for CO₂ concentrations from 1% to
 3 4%. Similar to the case of NAC, the greatest difference was obtained for a CO₂ concentration
 4 of 16%. The difference between the carbonation depths of RAC calculated using Eqs. (4) and
 5 (5) was negligible—up to a 3% difference—which confirms the eligibility of these models in
 6 the case of RAC. All these conclusions relate only to the tested RAC (100% replacement). A
 7 lower quantity of class B RCA would probably result in higher prediction model accuracy,
 8 which should be evaluated in future research.

9 Table 5. Values of calculated and measured carbonation depth

Concrete	CO ₂ conc.	$x_{c, \text{meas. ACC}}^*$ [mm]	$x_{c, 2\%, \text{calc.}}$ [mm]	R_{ACC}^{-1} [(m ² /s)/(kg/m ³) · 10 ⁻¹¹]	natural carbonation	
					$x_{c, \text{fib MC}}$ [mm]	$x_{c, \text{meas.}}$ [mm]
NAC ¹⁾	1%	1.60	2.26	2.90	1.81	1.70
	2%	1.98	1.98*	2.22	1.63	
	4%	2.83	2.00	2.27	1.64	
	16%	3.43	1.22	0.83	1.20	
RAC ²⁾	1%	2.73	3.86	8.446	4.32	4.81
	2%	3.45	3.45*	6.747	3.90	
	4%	4.05	2.86	4.637	3.31	
	16%	6.15	2.17	2.669	2.64	
HVFAC ¹⁾	1%	3.93	5.56	17.51	4.02	8.13
	2%	4.45	4.45*	11.23	3.26	
	4%	6.05	4.28	10.38	3.14	
	16%	9.43	3.33	6.30	2.50	

10 * measured values of carbonation depth at different CO₂ concentrations after 28 days

11 ¹⁾ 21 month

12 ²⁾ 48 month

13 When Eq. (5) was applied to HVFAC, the calculated values of the carbonation depth were
 14 more than two times smaller compared with the measured value regardless of the CO₂
 15 concentration level. This supports the fact that the model for NAC cannot be directly applied
 16 to HVFAC and that some adjustments of Eq. (5) in case of HVFAC are needed. The influence
 17 of the concrete quality in terms of the resistance to carbonation is taken in the model through

1 the calculation of the natural inverse effective carbonation resistance of concrete (R^{-1}_{NAT}).
2 Therefore, the analysis of the possible model modifications for HVFAC started from this
3 parameter.

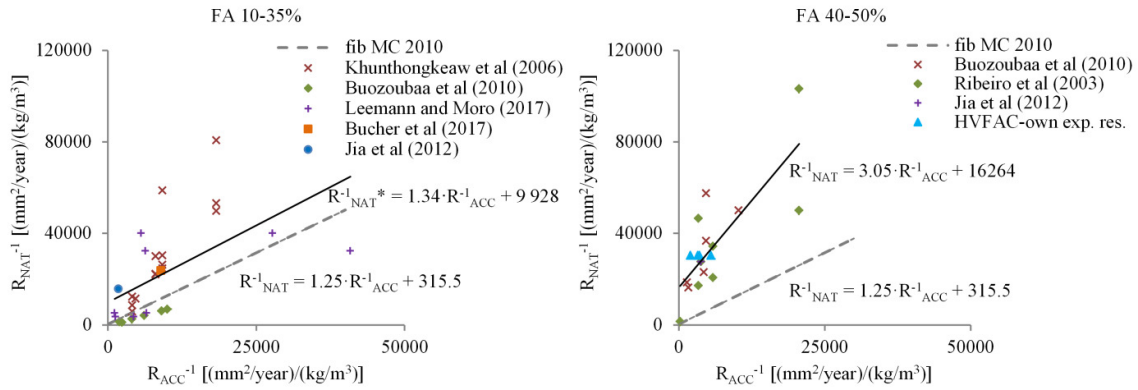
4 **5.3.2. Modification of the proposed model for application in FA concretes**

5 The natural inverse effective carbonation resistance of concrete (R^{-1}_{NAT}) can be obtained
6 directly by measuring the carbonation depth on the existing concrete structure (Eq. 11) or
7 indirectly from the accelerated inverse effective carbonation resistance, R^{-1}_{ACC} , (Eq. 12).

$$8 \quad R^{-1}_{NAT} = \frac{x_c(t)^2}{2 \cdot k_e \cdot k_{cur} \cdot C_s \cdot t \cdot W(t)^2} \quad (11)$$

$$9 \quad R^{-1}_{NAT} = k_t \cdot R^{-1}_{ACC} + \varepsilon_t \quad (12)$$

10 Some reports were selected from the database in order to apply Eq. (11) and calculate R^{-1}_{NAT} .
11 Unfortunately, not all necessary data were provided in these reports. Due to the insufficiency
12 of data regarding the relative humidity under natural conditions, RH = 65% was assumed and
13 only samples in sheltered conditions were observed. The trend line of the obtained
14 relationship between natural and accelerated inverse effective carbonation resistance of
15 various FA concretes is shown in Figure 15 together with the line taken from the *fib* Model
16 Code 2010 [35]. In case of concrete with FA content up to 35% of the total cementitious
17 materials mass, these two lines seem to be parallel or with similar slopes, as the values of k_t
18 which define the slope were similar: 1.34 compared with 1.25 given in the *fib* Model Code
19 2010. The difference was in the line intercept value (9928 compared with 315.5). This value
20 represents the physical meaning of the error term (ε_t) in the transformation between
21 accelerated and natural resistance (from R^{-1}_{ACC} to R^{-1}_{NAT}). In case of HVFAC, there are
22 significant differences both in the slope and in the offset of the trend lines, Figure 15 (right).



1

2

Figure 15. Relationship between natural and accelerated inverse effective carbonation

3

resistance of FA concretes

4

Therefore, a modified *fib* Model Code 2010 relation between R_{ACC}^{-1} and R_{NAT}^{-1} for HVFAC is proposed to be:

5

$$R_{NAT}^{-1*} = 3.05 \cdot R_{ACC}^{-1} + 16264 \quad (13)$$

6

7

In further analyses, when using Eq. (5) for concrete with different amounts of FA, the

8

coefficients k_t and ε_t will be used with the new values summarized in Table 6.

9

Table 6. Values of coefficients k_t and ε_t for concretes with different amounts of FA

FA amount	k_t	ε_t
10-35%	1.34	9928
40-50%	3.05	16264

10

11

The measured to calculated carbonation depth ratios ($x_{c,meas}/x_{c, fib MC*}$) obtained by using the *fib*

12

Model Code 2010 (Eq. 5) and previously described modified parameter R_{NAT}^{-1} for various FA

13

concretes are shown in Figures 16 and 17. For concretes made with relatively small amounts

14

of FA (10–35%), the average value of the ratio ($x_{c,meas}/x_{c, fib MC*}$) changed from 1.35, derived

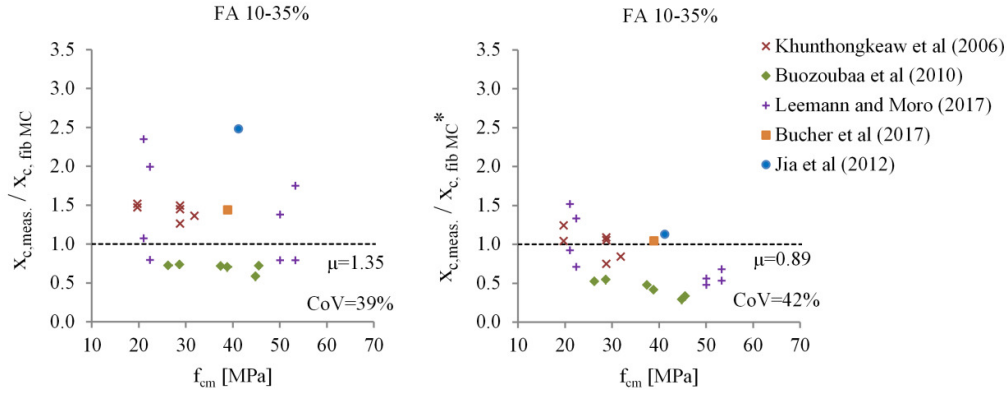
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from original the *fib* Model Code 2010 model (Figure 16-left), to 0.89 when the modified

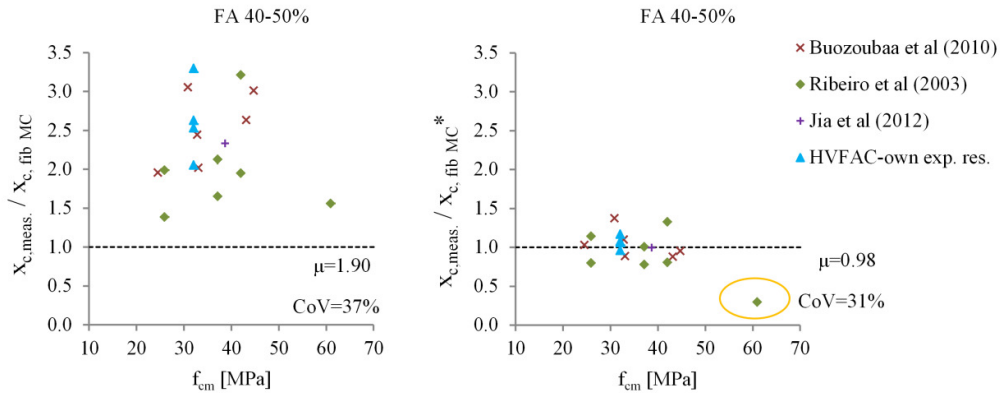
16

model with coefficients from Table 6 was used (Figure 16-right). In the first case, predictions

1 were highly non-conservative while slightly conservative carbonation depths were obtained
 2 using the modified model.



3
 4 Figure 16. Ratio of measured and calculated carbonation depth using the *fib* Model Code
 5 2010 (Eq. 5) with original (left) and modified (right) parameter R^{-1}_{NAT} for concretes made
 6 with 10–35% of FA



7
 8 Figure 17. Ratio of measured and calculated carbonation depth using the *fib* Model Code
 9 2010 (Eq. 5) with original (left) and modified (right) parameter R^{-1}_{NAT} for concretes made
 10 with 40–50% of FA

11 If only studies of HVFAC are included, (with contribution of FA between 40% and 50% in
 12 the total mass of cementitious materials), the changes were even more visible. There was not
 13 even a single result that reached the target average ratio value of 1.0 if the *fib* Model Code

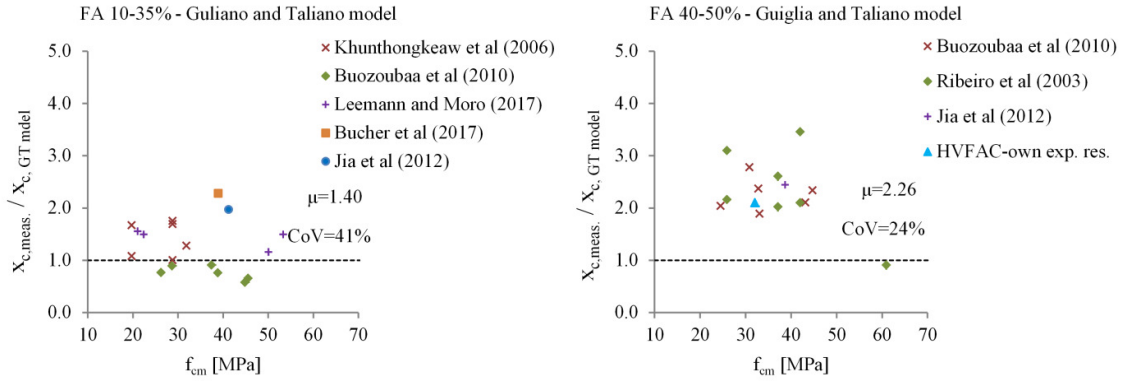
1 2010 was used, Figure 17 (left). Significantly better prediction of the carbonation depth with
2 the average value of the ratio $x_{c,meas.}/x_{c, fib MC*}$ equal to 0.98 was based on the model with the
3 new proposed parameters k_t and ε_t . A relatively high coefficient of variation was mostly
4 affected by the single outlier marked on Figure 17 (right).

5 In the previous analysis, the natural inverse effective carbonation resistance (R^{-1}_{NAT}) was
6 tested and modifications were proposed in case the results of accelerated carbonation tests
7 needed for the calculation of R^{-1}_{ACC} were known. However, the parameter R^{-1}_{NAT} could be
8 also obtained from known compressive strength which is commonly used as a universal
9 indicator of concrete quality. The relationship between these two parameters proposed by
10 Guiglia and Taliano [63] is given as

11
$$R^{-1}_{NAT} = 10^7 \cdot f_{cm}^{-2.1} \tag{14}$$

12 This relation was tested and defined for NAC and no information regarding its possible
13 application to FA concrete was found. The following analysis was conducted in order to
14 evaluate the use of Eq. (14) on the previously described database of FA concretes. The ratio
15 between measured ($x_{c,meas.}$) and calculated ($x_{c,GT model}$) carbonation depths for FA concretes is
16 shown in Figure 18. The carbonation depths were calculated using Eq. (5) and expression for
17 R^{-1}_{NAT} presented in Eq. (14), for given cylinder ($\varnothing 15 \times 30$ cm) compressive strengths. For
18 concretes made with relatively small amounts of FA (10–35%) the average value was 1.40
19 with a relatively high CoV of 41%. The accuracy of this prediction was slightly lower
20 compared with the model in which the parameter R^{-1}_{NAT} was derived from the accelerated test
21 results analysis (the average value was 1.35, Figure 16-left). For concretes with higher
22 amounts of FA (40–50%) the combination of the *fib* Model Code 2010 and Eq. (14) resulted
23 in a significantly less accurate prediction of the carbonation depth compared with the *fib*

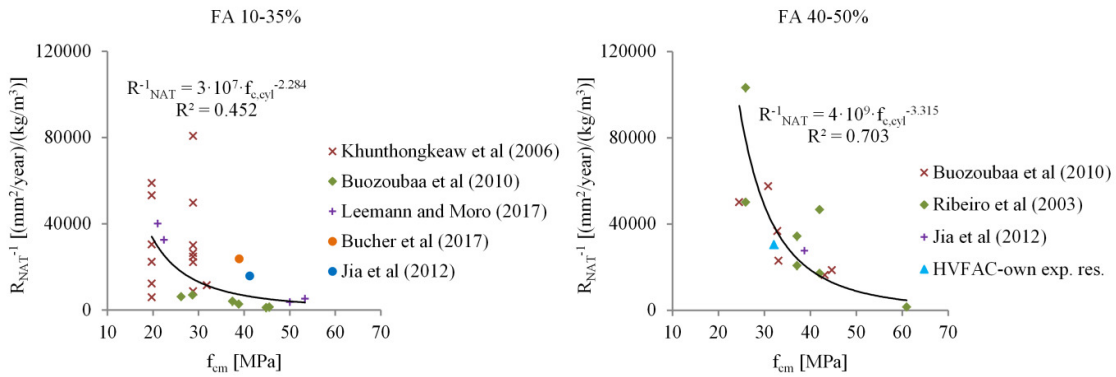
- 1 Model Code 2010 in which the result of the accelerated test was used. The average value
- 2 increased from 1.90 (Figure 16-right) to 2.26 (Figure 18-right).



3
4 Figure 18. Ratio of measured and calculated carbonation depth using the Guiglia & Taliano
5 model [63] based on compressive strength of various FA concretes in the literature
6 It can be seen from Figure 18 that a modification of the proposed model for FA concretes is
7 necessary. The relationship between R^{-1}_{NAT} and compressive strength can be written in the
8 following form:

9

$$R^{-1}_{NAT} = a \cdot f_{cm}^{-b} \tag{15}$$



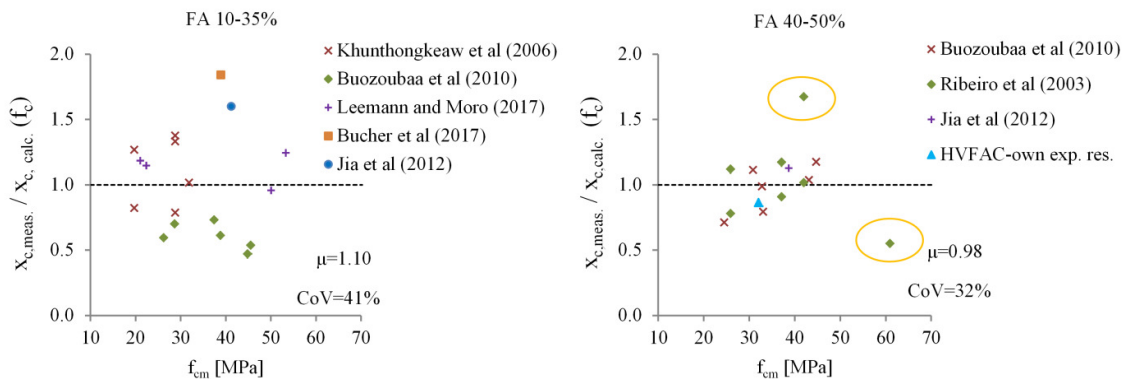
10
11 Figure 19. Relationship between natural effective carbonation resistance and compressive
12 strength for various FA concretes

1 The evaluation of the coefficients a and b from Eq. (15) was conducted on the previously
 2 described database of FA concretes. The inverse effective carbonation resistance under
 3 natural exposure conditions versus the 28-day concrete compressive strength was calculated
 4 and shown in Figure 19.

5 Table 7. Values of coefficients a and b for concretes with different amounts of FA

6 FA amount	7 a	8 b
9 10-35%	$3 \cdot 10^7$	2.284
10 40-50%	$4 \cdot 10^9$	3.315

11 A regression analysis was conducted and the coefficients a and b were determined and
 12 summarized in Table 7. They were used for the calculation of R^{-1}_{NAT} (Eq. 15) and the
 13 carbonation depths ($x_{c,calc.}(f_c)$) based on it according to the *fib* Model Code 2010 (Eq. 5).
 14 The ratio between measured ($x_{c,meas.}$) and calculated ($x_{c,calc.}(f_c)$) carbonation depths for various
 15 FA concretes are shown in Figure 20.



16
 17 Figure 20. Ratio of measured and calculated carbonation depth based on compressive strength
 18 of FA concretes in the literature

19 For concretes made with relatively small amounts of FA (10–35%), the average value was
 20 1.10 with a relatively high CoV of 41%. However, the prediction was better compared with
 21 the model in which R^{-1}_{NAT} was derived from Eq. (12) – the average value was 1.35, Figure 16

1 (left). It can be seen from Figure 20 that in the case of concretes with higher amounts of FA
2 (40–50%), i.e. HVFAC, a new proposed expression for determining R^{-1}_{NAT} which is further
3 used in the *fib* Model Code 2010 resulted in significantly better prediction of the carbonation
4 depth. Moreover, the reliability of predictions for HVFAC obtained in this way was almost
5 the same compared with the modified *fib* Model Code 2010 in which the result of the
6 accelerated test was used (Figure 17) – the average values were 1.02 and 0.98.

7 **6. Conclusions**

8 Based on the conducted measurements of the carbonation depth on NAC, RAC and HVFAC
9 samples and analysis performed using own experimental data and collected results from the
10 prepared database, the following conclusions can be made:

- 11 – The measured carbonation depth of NAC, RAC and HVFAC with similar compressive
12 strengths at different CO₂ concentrations after 28 days showed that RAC and HVFAC had a
13 higher carbonation depth compared with NAC.
- 14 – A linear relationship between the carbonation depth and square root of time ($t^{0.5}$) was
15 appropriate for the concrete in which the content of FA in the total mass of cementitious
16 materials does not exceed 35%. A new proposed function ($t^{0.78}$) enabled better correlation
17 between the calculated and measured results if the amount of FA exceeds 40% of the total
18 cementitious materials mass, i.e. in case of HVFAC.
- 19 – With the increase in CO₂ concentration, the carbonation depth increased, but the
20 carbonation process slowed down.
- 21 – Prediction of the carbonation depth at a certain time and under certain exposure conditions
22 cannot be performed based on the laboratory measurements at high CO₂ concentrations
23 (16%). CO₂ concentrations up to 2% can be used to predict the carbonation depth using Eq.
24 (4) for all tested concretes under sheltered exposure conditions.

1 – Application of the *fib* Model Code 2010 (Eq. 5) for predicting the carbonation depth
2 showed good correlation between measured and calculated values both for tested NAC and
3 RAC. For HVFAC the calculated values of the carbonation depth based on the *fib* Model
4 Code 2010 model were more than two times lower compared with the measured value
5 regardless of the CO₂ concentration level.

6 – A newly proposed relationship between natural and accelerated inverse effective
7 carbonation resistance based on accelerated test results (modified *fib*-Model Code 2010) gave
8 calculated values which were in a good agreement with the measured ones for FA concretes.

9 – The proposed correlation between inverse natural effective carbonation resistance and the
10 compressive strength provided the additional possibility for reliable prediction of the
11 carbonation depth using only one parameter – the compressive strength. However, this
12 approach should be verified by more experimental results on FA concretes.

13 Analysis of experimental results regarding HVFAC carbonation depth under natural and
14 accelerated exposure conditions is one step forward for the evaluation of most commonly
15 used carbonation depth prediction models for these concretes. More experimental results are
16 needed in order to make some general conclusions regarding carbonation depth prediction for
17 RAC. Also it is necessary to determine the accuracy of such predictions as a function of
18 different RCA replacement percentages.

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1 **Appendix A. Supplementary data**

2 Supplementary data associated with this article has been submitted as Mendeley Data.

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